



# WATOC 2017

**11th Triennial Congress of the World Association  
of Theoretical and Computational Chemists**

**27 August – 1 September 2017  
Munich, Germany**



**BOOK OF ABSTRACTS  
WITH SCIENTIFIC PROGRAM**



LUDWIG-  
MAXIMILIANS-  
UNIVERSITÄT  
MÜNCHEN

[www.watoc2017.com](http://www.watoc2017.com)



## Scientific Chair / Local Scientific Committee / PCO

---

### Scientific Chair

Prof. Dr. Christian Ochsenfeld  
Department of Chemistry  
Ludwig-Maximilians-Universität (LMU) München  
Butenandtstr. 7  
81377 Munich, Germany

### Local Scientific Committee (University of Munich, LMU, Germany)

Dr. Asbjörn M. Burow  
Dr. Thomas-Christian Jagau  
Professor Regina de Vivie-Riedle  
Professor Hubert Ebert  
Professor Hendrik Zipse  
Professor Christian Ochsenfeld

### Hosting Society

WATOC  
World Association of Theoretical and Computational Chemists  
[www.watoc.net](http://www.watoc.net)  
[www.watoc2017.com](http://www.watoc2017.com)

### Organizer & Congress Office

INTERPLAN Congress, Meeting & Event Management AG  
Landsberger Str. 155  
80687 Munich, Germany  
[www.interplan.de](http://www.interplan.de)

### Project Management

Jana Bylitza  
Phone: +49 (0) 89 548234-806  
Email: [j.bylitza@interplan.de](mailto:j.bylitza@interplan.de)

### Sponsoring

Katharina Krines  
Email: [k.krines@interplan.de](mailto:k.krines@interplan.de)

### Exhibition

Oliver Heinke  
Email: [o.heinke@interplan.de](mailto:o.heinke@interplan.de)

Photos: © [muenchen.de/muenchen tourismus](http://muenchen.de/muenchen_tourismus) © Jürgen Fälchle – [fotolia.de](http://fotolia.de)  
Status: August 2017. All information is subject to change.





# SCIENTIFIC PROGRAM



Time	Foyer	
12:00 – 15:00	REGISTRATION	
Time	Philharmonic Hall	
	<b>OPENING CEREMONY</b> <i>Chair: Christian Ochsenfeld</i>	
15:00 – 15:50	<b>Opening Schedule:</b> <i>Christian Ochsenfeld</i> (Chair of WATOC2017) <i>Walter Thiel</i> (WATOC President) <i>Barbara Conradt</i> (Vice President of the University of Munich (LMU)) <i>Helmut Schwarz</i> (President of Humboldt Foundation (AvH)) Music Intermezzo by <i>Ville Kaila</i> (violin), <i>Lika Bibileishvili</i> (piano)	
15:50 – 17:10	Plenary Session A <i>Chair: Peter Gill</i>	
15:50 – 16:30	PL-1	<i>Todd Martinez</i> Ground and excited state dynamics on graphical processing units
16:30 – 17:10	PL-2	<i>Benedetta Mennucci</i> Present and future of multiscale approaches combining quantum chemistry and classical models: a personal overview
17:10 – 17:40	COFFEE BREAK	
17:40 – 19:00	Plenary Session B <i>Chair: Leo Radom</i>	
17:40 – 18:20	PL-3	<i>Trygve Helgaker</i> Quantum chemistry in magnetic fields
18:20 – 19:00	PL-4	<i>Helmut Schwarz</i> Mechanistic variants of metal-oxide mediated C-H bond activation: experiment and theory in concert
Time	Foyer	
19:00 – 22:00	WELCOME RECEPTION – supported by BASF	

Time	Philharmonic Hall		Carl-Orff Hall		Black Box		Small Concert Hall		Carl-Amery Hall		Multipurpose Room	
09:00 09:40	PL-5	Plenary Session C <i>Chair: Kenneth Ruud</i> Edward Valeev Reduced scaling and controlled precision: extending the reach of many-body electronic structure										
09:40 10:10		COFFEE BREAK										
10:10 12:15	Invited Session 1 <i>Chair: Thomas Jagau</i>		Invited Session 2 <i>Chair: Tim Clark</i>		Invited Session 3 <i>Chair: Tomasz Wesolowski</i>		Invited Session 4 <i>Chair: Hans Jørgen Aagaard Jensen</i>		Invited Session 5 <i>Chair: Manabu Sugimoto</i>		Invited Session 6 <i>Chair: Henry Rzepa</i>	
10:10	I-011	<i>Peter Gill</i> Strong correlation in electron gases	I-021	Peter Schwerdtfeger From graphene to graphyne, fullerenes, fulleroids, gaudienes and their golden duals	I-031	Lucas Visscher Subsystem and approximate DFT approaches for electronically excited states of complex molecular systems	I-041	Kenneth Ruud 4-component relativistic calculations with periodic boundary conditions	I-051	<i>Hiromi Nakai</i> Chemical reaction simulations on CO2 chemical absorption process	I-061	<i>Odile Eisenstein</i> Can carbon-13 NMR chemical shifts inform on reactivity in organometallic chemistry?
10:35	I-012	<i>Garnet Chan</i> Notes on the complexity of electronic structure theory	I-022	Kwang Soo Kim Graphene nanoribbon based electronics and spintronics	I-032	Neepa Maitra Confronting memory-dependence in time-dependent density functional theory	I-042	<i>Pekka Pyykkö</i> Recent results on compounds of heavy, and heaviest elements	I-052	<i>Nuria Lopez</i> New aspects in the simulations of heterogeneous catalysis	I-062	<i>Michael Buehl</i> Exploring NMR properties of paramagnetic Cu phenolic oxime complexes
11:00	I-013	<i>Jürgen Gauss</i> Beyond standard coupled-cluster theory and towards full configuration interaction	I-023	Jean-Luc Bredas Polymer/fullerene solar cells: characterization of the intermolecular interactions and interfacial charge-transfer states	I-033	Sharon Hammes-Schiffer Multicomponent density functional theory: integrating electronic and nuclear quantum effects	I-043	<i>Wenjian Liu</i> New Scenarios for Strongly Correlated Electrons	I-053	<i>Tore Brinck</i> $\sigma$ -hole Bonding in the Catalysis of Nanostructured Metals: Surface Properties as Guides to Local Reactivity	I-063	<i>Gustavo Aucar</i> NMR spectroscopic paramaters of HB containing molecules and aggregates of DNA base pairs
11:25	I-014	<i>Poul Jørgensen</i> Cluster perturbation theory for energies and molecular properties	I-024	Marco Bernardi Advances in computing charge carrier dynamics from first principles	I-034	Eberhard Gross Potential-energy surfaces and Berry phases beyond the born-oppenheimer approximation: a new perspective on non-adiabatic dynamics	I-044	<i>Trond Saue</i> Variational perturbation theory in geochemistry	I-054	<i>Stuart Macgregor</i> Modelling alkane $\sigma$ -Complexes in the solid state	I-064	<i>Ibon Alkorta</i> Anion-anion and cation-cation halogen and hydrogen bonded complexes
11:50	I-015	<i>Martin Head-Gordon</i> Some recent advances in variational energy decomposition analysis of electronic structure calculations	I-025	Jochen Blumberger Simulation of electron transfer on the nanoscale: from molecules to biomolecules to materials	I-035	Katarzyna Pernal Adiabatic connection approach toward including dynamic correlation for multireference wavefunctions	I-045	<i>Marcel Swart</i> Characterization of reactive high-valent transition-metal complexes	I-055	<i>Michelle Coote</i> Directionality and the role of polarization in electrostatic catalysis	I-065	<i>Sotiris Xantheas</i> Modeling of the spectroscopic signatures of water in different environments
12:15 13:45	LUNCH BREAK											

Time	Philharmonic Hall		Carl-Orff Hall		Black Box		Small Concert Hall		Carl-Amery Hall		Multipurpose Room	
13:45 – 15:50	Invited Session 7 <i>Chair: Henrik Zipse</i>		Invited Session 8 <i>Chair: Martin Head-Gordon</i>		Invited Session 9 <i>Chair: Hiromi Nakai</i>		Invited Session 10 <i>Chair: H. Bernhard Schlegel</i>		Invited Session 11 <i>Chair: Oliver Kühn</i>		Invited Session 12 <i>Chair: Stefan Knippenberg</i>	
13:45	I-071	<i>Jeremy Harvey</i> Modelling reaction mechanisms and kinetics in homogeneous catalysis: challenges and progress	I-081	Gustavo Scuseria Symmetry projected coupled cluster theory	I-091	Weitao Yang Localized orbital scaling correction for systematic elimination of delocalization error in density functional approximations	I-101	Kurt Kremer Open systems simulations of macromolecular solutes through adaptive resolutions simulations (AdResS)	I-111	David Clary Quantum dynamical and semi-classical calculations on chemical reactions with application to decomposition of nerve agents	I-121	Benjamin Fingerhut Numerical exact MACGIC-QUAPI simulations of electron transfer dynamics in Drosophila cryptochrome (dCRY)
14:10	I-072	<i>Peter Richard Schreiner</i> London dispersion effects in molecular chemistry – reconsidering steric effects[1]	I-082	Hans-Joachim Werner Accurate treatment of long-range correlation effects in large molecules using explicitly correlated local coupled-cluster methods	I-092	Peter Pulay Ultrafast quantum/molecular mechanics: thermodynamic integration and van der Waals parameters	I-102	Florian Müller-Plathe Multiscale molecular modelling of soft materials: the challenge of dynamics	I-112	Irene Burghardt High-dimensional quantum dynamics of functional organic polymer materials: Coherence, localization, and (dis)order	I-122	Christel Marian TADF efficiencies in coinage-metal coordination complexes and metal-free donor-acceptor systems
14:35	I-073	<i>Leo Radom</i> Impact of hydrogen bonding on the susceptibility of peptides to oxidation	I-083	Örs Legeza Tensor product methods and entanglement measures for strongly correlated molecular systems	I-093	Henry F. Schaefer Fast construction of the exchange operator in an atom-centered basis with concentric atomic density fitting	I-103	Christoph Dellago Exploring the mechanism and kinetics of nucleation processes: from crystallization to cavitation	I-113	Roland Mitric Light-induced nonadiabatic dynamics: from isolated molecules to molecular assemblies and light-harvesting nanostructures	I-123	Ilaria Ciofini New tools for the description of excited states of molecular systems in complex environmen
15:00	I-074	<i>Yitzhak Apeloig</i> Isomerization mechanisms around E=E' (E,E'=C,Si) bonds. Experiment and theory	I-084	Jeppe Olsen Wave functions with several sets of optimized orbitals	I-094	Dage Sundholm Numerical electronic structure theory methods for massively parallel computations on molecules	I-104	Christine Peter A multiscale simulation perspective on mineralization processes	I-114	Ivano Tavernelli New strategies for non-adiabatic dynamics with trajectories	I-124	Satoshi Maeda Artificial force induced reaction (AFIR) method for automated search of adiabatic and non-adiabatic pathways
15:25	I-075	<i>Kendall Houk</i> Dynamics of pericyclic reactions	I-085	John Stanton Active thermochemical tables: what they are, why I care about them, and why you should	I-095	Petr Čársky Fourier transform of 1/r on graphical processing units – promising tool for applications in nanolithography	I-105	Alexander Nemukhin Computational modeling of molecular processes in proteins	I-115	Graham Worth Quantum dynamics simulations of photo-excited molecules using the MCTDH method	I-125	Henrik Koch The curious case of conical intersections in coupled cluster theory
15:50 – 16:20	COFFEE BREAK											



Time	Philharmonic Hall		Carl-Orff Hall		Black Box		Small Concert Hall		Carl-Amery Hall		Multipurpose Room	
16:20 – 18:25	Contributed Session 1 <i>Chair: David Tozer</i>		Contributed Session 2 <i>Chair: Sotiris Xantheas</i>		Contributed Session 3 <i>Chair: Jörn Manz</i>		Contributed Session 4 <i>Chair: William Hase</i>		Contributed Session 5 <i>Chair: Kaori Fukuzawa</i>		Contributed Session 6 <i>Chair: Henk Eshuis</i>	
16:20	C-011	<i>Georg Schreckenbach</i> Modeling of two-dimensional (2D) materials: influence of chemical modifications	C-021	<i>Thomas Kühne</i> The name is bond - hydrogen bond	C-031	<i>Shirin Faraji</i> Utilizing light for repair of light-induced DNA damages: clever mode of action of DNA photolyases	C-041	<i>Manabu Sugimoto</i> First-principles molecular dynamics simulations on ammonia synthesis and decomposition	C-051	<i>Andreas Hauser</i> Carbon nanotubes immersed in superfluid helium: An incomplete flooding due to quantum effects	C-061	<i>Mercedes Alonso</i> Conductance switching in expanded porphyrins through aromaticity and topology changes
16:35	C-012	<i>Lorenzo Maschio</i> Local correlation for crystalline solids: dual basis sets by projection in the reciprocal space	C-022	<i>Tristan Bereau</i> High-throughput screening of drug-membrane thermodynamics	C-032	<i>Oliver Kühn</i> Ultrafast spin-flip dynamics in transition metal complexes triggered by soft X-ray light	C-042	<i>Tetsuya Taketsugu</i> Reaction-path bifurcation analyses based on Valley-Ridge transition and global reaction route mapping	C-052	<i>Raul Alvarez-Idaboy</i> The role of acid-base equilibria in formal hydrogen transfer reactions: uric acid with tryptophanyl radical	C-062	<i>Daniel Aravena</i> Spin-dependent transport and magnetoresistance in metalloporphyrin-based supramolecular wires at room temperature
16:50	C-013	<i>Marek Sierka</i> Density functional theory for periodic systems using density fitting and continuous fast multipole method	C-023	<i>Ragnar Björnsson</i> New insights into nitrogenase: QM/MM broken-symmetry DFT studies of FeMoco and the P-cluster	C-033	<i>Debashree Ghosh</i> Photoprotection mechanism in eumelanin	C-043	<i>Mark Waller</i> Retrosynthesis and reaction prediction with deep neural networks	C-053	<i>Albeiro Restrepo</i> Thermodynamics of the partition of Ibuprofen in a lipid bilayer	C-063	<i>Alexandre Magalhães</i> Catalyzing chemical reactions inside carbon nanotubes
17:05	C-014	<i>Joao B. L. Martins</i> Adsorption of glycerol and dihydroxyacetone on CaO and MgO surfaces	C-024	<i>Alister Page</i> Quantum chemical insights into polymer solvation and Hofmeister effects in aqueous and non-aqueous environments	C-034	<i>Daniel Roca-Sanjuán</i> Chemically-induced excited-state chemistry	C-044	<i>Seiji Mori</i> Graph theory approach in exploration of reaction path networks: Rh(I)BINAP-catalyzed isomerization of allylic amine	C-054	<i>Alessandro Contini</i> Automatization of the NwAT-MMGBSA method to rescore docking results in medium-throughput virtual screening applications	C-064	<i>Michal Straka</i> Theoretical calculations of endohedral fullerenes: from chemical bonding to single-molecule switches
17:20	C-015	<i>Wolfgang Hieringer</i> Electronic structure of molecules at metal surfaces: recent results on organic molecules and coordination compounds	C-025	<i>Olaf Wiest</i> The past, present, and future of Q2MM	C-035	<i>Bo Durbbeej</i> Exploiting excited-state aromaticity for the design of efficient light-driven rotary molecular motors	C-045	<i>Woo Youn Kim</i> Automated searching method for reaction paths using molecular graphs and chemical reaction network	C-055	<i>Przemyslaw Dopieralski</i> Stressed disulfide bonds in alkaline solution	C-065	<i>Matthias Lein</i> Structural and electronic properties of carbon nano-onions
17:35	C-016	<i>Ralf Tonner</i> Explaining organic chemistry at surfaces with energy decomposition analysis	C-026	<i>Dmitry Nerukh</i> Hybrid molecular dynamics - hydrodynamics modelling of liquid solutions: whole virus at atomistic resolution	C-036	<i>László Turi</i> Electronic excited state lifetimes of anionic water clusters: a quantized time correlation function approach	C-046	<i>Anoop Ayyappan</i> Exploring chemical evolution using tabu-search based automated reaction finding algorithm	C-056	<i>Joonkyung Jang</i> Wetting behavior of a surface decorated with periodic pillars	C-066	<i>Juan F. Espinal</i> Nickel effect on the spacing of 002 plane in a graphite-like structure
17:50	C-017	<i>Antti Karttunen</i> Crystal structure prediction of inorganic-organic coordination polymers	C-027	<i>Laurence Leherste</i> Reduced point charge models of proteins - influence of protein-solvent interactions	C-037	<i>Luca De Vico</i> How to control the absorption wavelength of light harvesting complexes	C-047	<i>Wolfgang Quapp</i> Patterns of moving saddle points in catalysis and mechanochemistry	C-057	<i>Petra Imhof</i> Communication in proteins and protein-substrate complexes	C-067	<i>Oscar Lung Wa Chung</i> Mechanistic insights on Ni-catalyzed selective C-O activation & Cu-catalyzed reductive CO <sub>2</sub> coupling to form oxalate
18:05	C-018	<i>Jon M. Matxain</i> Transition metal doped magnetic Zn12S12 nanoparticles	C-028	<i>Xabier Lopez</i> Insights into the structural toxicity of aluminum with biomolecules, using a computational approach	C-038	<i>Valérie Brenner</i> Excited states deactivation in model proteins chains: Nonadiabatic dynamics simulations and ab initio methods	C-048	<i>Michael Springborg</i> On the theoretical optimization of properties	C-058	<i>Wieslaw Nowak</i> Camphore's and Huperzine's adventures in proteinland	C-068	<i>Amalia I. Poblador Bahamonde</i> Mechanistic investigation on the Pd-catalyzed hydrogenation of 1,6-enynes: a DFT approach
18:20 – 20:00	DINNER BREAK											
20:00 – 22:00	Poster Session 1 – supported by ACS Energy Letters											

Time	Philharmonic Hall		Carl-Orff Hall		Black Box		Small Concert Hall		Carl-Amery Hall		Multipurpose Room	
09:00 – 09:40	PL-6	Plenary Session D <i>Chair: Josef Michl</i> <i>Giulia Galli</i> Electrochemistry meets condensed matter physics: first principles simulations of photo-catalytic materials										
09:40 – 10:10		COFFEE BREAK										
10:10 – 12:15	Invited Session 13 <i>Chair: Teresa Head-Gordon</i>		Invited Session 14 <i>Chair: Arne Lüchow</i>		Invited Session 15 <i>Chair: Regina de Vivie-Riedle</i>		Invited Session 16 <i>Chair: Attila Császár</i>		Invited Session 17 <i>Chair: Roland Mitric</i>		Invited Session 18 <i>Chair: Christine Peter</i>	
10:10	I-131	<i>Walter Thiel</i> Semiempirical quantum chemistry: methodology and excited-state dynamics	I-141	<i>Ali Alavi</i> Recent developments and applications of full configuration interaction quantum Monte Carlo	I-151	Leticia González Photostability and photodamage in DNA building blocks	I-161	<i>Joel Bowman</i> Many-body potentials for water and protonated water clusters and VSCF/VCI calculations of IR spectra	I-171	<i>Fernando Martin</i> Attochemistry: imaging and controlling electron dynamics in molecules	I-181	<i>Zexing Cao</i> Global simulation of cyanohydrin cleavage by hydroxynitrile lyases
10:35	I-132	<i>Stefan Grimme</i> Applications of the extended tight binding method (GFN-xTB)	I-142	<i>Seiichiro Ten-no</i> Multi-state effective Hamiltonian and size-consistency corrections for stochastic configuration interactions	I-152	Roland Lindh Non-adiabatic chemiluminescent dynamics of the methyl-substituted 1,2-dioxetanes	I-162	<i>Robert Berger</i> What molecules can reveal about fundamental interactions	I-172	<i>Shaul Mukamel</i> Novel multidimensional spectroscopy of conical intersections with X-ray pulses and quantum light	I-182	<i>Tim Clark</i> Metadynamics simulations of G-protein coupled receptors
11:00	I-133	<i>Frank Jensen</i> Developing improved force fields	I-143	<i>Roi Baer</i> Stochastic orbitals for electronic structure and quantum chemistry	I-153	<i>Chantal Daniel</i> Simulation of ultrafast excited state dynamics in transition metal complexes	I-163	<i>R. Benny Gerber</i> Computational vibrational spectroscopy: anharmonic algorithms and determination of 3D structures of biomolecular conformers	I-173	<i>H. Bernhard Schlegel</i> Angular dependence of ionization by short, intense pulses of linear and circularly polarized light	I-183	<i>Markus Meuwly</i> Quantitative atomistic simulations for chemical and biological applications
11:25	I-134	<i>Siewert-Jan Marrink</i> Computational microscopy of (bio) molecular processes	I-144	<i>David Tanner</i> New formulation of quantum mechanics using complex trajectories: application to nonadiabatic transitions and optical excitation	I-154	<i>George Schatz</i> Theories of SERS, TERS, electrochemistry and plasmon-enhanced energy transfer	I-164	<i>Lorenz S. Cederbaum</i> On systems with and without excess energy in environment ICD and other interatomic mechanisms	I-174	<i>Peter Saalfrank</i> Light-driven processes in molecular systems: from photophysics to photochemistry	I-184	<i>Sereina Riniker</i> Replica-exchange enveloping distribution sampling (RE-EDS) to calculate relative binding free energies
11:50	I-135	<i>Jan H. Jensen</i> Using semiempirical methods for fast and automated predictions	I-145	<i>Mark Gordon</i> Dispersion in intermolecular interactions	I-155	<i>Joseph Subotnik</i> Electrochemistry and non-adiabatic dynamics at metal surfaces: the importance of electron-electron correlation	I-165	<i>Sergey Yurchenko</i> Theoretical molecular line lists for atmospheric characterizations of exoplanets	I-175	<i>Peter Knowles</i> On the perturbative computation of ionization energies	I-185	<i>Xuhui Huang</i> Kinetics-controlled molecular self-assembly processes elucidated by kinetic network models
12:15 – 13:45	LUNCH BREAK											

Time	Philharmonic Hall		Carl-Orff Hall		Black Box		Small Concert Hall		Carl-Amery Hall		Multipurpose Room	
13:45 15:50	Invited Session 19 <i>Chair: Johan Åqvist</i>		Invited Session 20 <i>Chair: Trygve Helgaker</i>		Industry Session 1 - <i>supported by BASF</i> <i>Chair: Ansgar Schäfer</i>		Invited Session 21 <i>Chair: Markus Meuwly</i>		Invited Session 22 <i>Chair: Odile Eisenstein</i>		Invited Session 23 <i>Chair: Gregory Beran</i>	
13:45	I-191	<i>Teresa Head-Gordon</i> New methods and models for condensed phase simulation	I-201	<i>Don Truhlar</i> Recent progress in density functional theories	IN-1	<i>Peter Deglmann</i> The challenge of chemical thermodynamics and kinetics for real world	I-211	<i>Michele Parrinello</i> Enhanced sampling for chemistry	I-221	<i>Elfi Kraka</i> A comprehensive view on the Claisen rearrangement of chorismate via a new quantum chemical toolbox	I-231	<i>Takeshi Yanai</i> Projector augmented wave method incorporated into Gauss-type atomic orbital based density functional theory
14:10	I-192	<i>Jiali Gao</i> Methods and applications of multistate density functional theory (MSDFT)	I-202	<i>Carlo Adamo</i> Non-empirical double-hybrid functionals: more theoretical constrains, better performances?	IN-2	<i>Christoph Taeschler</i> Mechanistic aspects of high temperature reactions of acetonitrile	I-212	<i>Ulf Ryde</i> Comparison of quantum-mechanical approaches to calculate ligand-binding affinities with free-energy perturbation	I-222	<i>Gabriel Merino</i> Massive search of planar hyper-coordinate carbon atoms	I-232	<i>Claudia Draxl</i> From evaluation of methodology to error bars in computational materials science
14:35	I-193	<i>Modesto Orozco</i> DNA. A fascinating multiscale problem	I-203	<i>Kieron Burke</i> Reliable DFT results for spin-crossover complexes	IN-3	<i>Michael Edmund Beck</i> Digging deep into binding modes in protein-Ligand-complexes by quantum chemistry	I-213	<i>Zhipan Liu</i> Automated reaction pathway sampling using stochastic surface walking method for predicting chemical reactions	I-223	<i>Raghavan B. Sunoj</i> Non-covalent interactions in asymmetric catalysis: a mechanistic voyage from rationalizations to predictions	I-233	<i>Beate Paulus</i> The method of increments applied to weakly bound systems
15:00	I-194	<i>Shina Caroline Lynn Kamerlin</i> Dynamics, flexibility, cooperativity and the evolution of enzyme function	I-204	<i>G Narahari Sastry</i> Cooperativity of non-covalent interactions	IN-4	<i>Marcel Verdonk</i> The use of scoring functions for structure-based drug discovery	I-214	<i>GuanHua Chen</i> Time-dependent density-functional theory for open system and its applications	I-224	<i>Gopalan Rajaraman</i> Are single molecule magnets predictable? Learning from Ab-initio calculations on lanthanide and transition metal molecular-magnets	I-234	<i>Krzysztof Szalewicz</i> Physics-based intermolecular potentials for material design
15:25	I-195	<i>Helmut Grubmüller</i> Towards a mechanistic understanding of ribosomal function	I-205	<i>David Sherrill</i> Large datasets for benchmarking noncovalent interactions	IN-5	<i>Thomas Fox</i> Free energy calculations in drug design	I-215	<i>Michele Pavanello</i> Real and imaginary-time electron dynamics of open quantum subsystems	I-225	<i>Laura Gagliardi</i> Computationally guided discovery of metal-decorated metal-organic frameworks active for catalysis	I-235	<i>WanZhen Liang</i> Analytic energy gradient and hessian of TD-DFT/MM excited-state: implementation and applications
15:50 16:20	COFFEE BREAK											

Time	Philharmonic Hall		Carl-Orff Hall		Black Box		Small Concert Hall		Carl-Amery Hall		Multipurpose Room	
16:20 – 18:20	Contributed Session 7 <i>Chair: Kieron Burke</i>		Contributed Session 8 <i>Chair: Max Holthausen</i>		Industry Session 2 - <i>supported by BASF</i> <i>Chair: Robert Franke</i>		Contributed Session 9 <i>Chair: Daniel Escudero</i>		Contributed Session 10 <i>Chair: Woo Youn Kim</i>		Contributed Session 11 <i>Chair: Iris Antes</i>	
16:20	C-071	Mario Piris NOF-MP2: a global method for the electron correlation	C-081	Andrey Rogachev Trianionic corannulene: tuning stability of supramolecular aggregates with alkali metal size	IN-6	Glenn Jones Industrial applications of first-principles modelling to obtain quality measures for screening of catalyst materials	C-091	Masayoshi Nakano Quantum master equation approach to singlet fission dynamics in molecular aggregates	C-101	Mercè Deumal Unraveling the magnetic transition temperature from changes in spin correlation	C-111	Ferran Feixas Accelerating metal-directed protein folding and molecular recognition with enhanced sampling techniques
16:35	C-072	Heather Kulik Recovering the flat plane condition in electronic structure theory at semi-local density functional theory cost	C-082	Carsten Baldauf About underappreciated, yet active conformations of thiourea organocatalysts			C-092	Carmen Herrmann Pathways in molecular conductance and spin coupling	C-102	Nathalie Guihery The magnetic couplings sensitivity to Fock exchange in DFT is not due to spin over-delocalization	C-112	Snezana Zaric Role of aromatic, aliphatic and backbone interactions in the stability of amyloids
16:50	C-073	Pierre-François Loos Dressing the CI matrix with explicit correlation	C-083	Brian Yates A new mechanism for gold catalysis	IN-7	Hanne Falsig A complete reaction mechanism for standard and fast SCR of NOx on VOx/TiO2(001) catalysts	C-093	Takatoshi Fujita Exciton dynamics in organic optoelectronic materials	C-103	Annika Bande Quantum dot inter-Coulombic decay governed by the quantum size effect	C-113	Vladimir Palyulin Design of AMPA receptor positive allosteric modulators: QSAR studies, virtual screening, and molecular dynamics simulations
17:05	C-074	Henk Eshuis Performance of the random phase approximation for first-row transition metal catalysis	C-084	Hélène Bolvin Magnetic coupling between F magnetic centers			C-094	Paula Homem-de-Mello Photophysical properties of macrocycles: a computational and experimental study	C-104	Martin Rahm Ternary dot hydrides: a new class of stable and potentially superconducting compounds	C-114	José Pedro Cerón-Carrasco AQUILES web server: open the eyes to blind docking
17:20	C-075	Jiri Klimes Highly accurate binding energies from the random phase approximation with singles corrections	C-085	Masato Kobayashi Study on metal nanocluster catalysts based on quantum chemical calculation and informatics	IN-8	Martin Letz Investigations on SiO2 glasses to answer the question: “What is a ‘good’ glass structure?”	C-095	Tangui Le Bahers Modeling the photochromism of sulphur-doped sodalites using DFT, TD-DFT and SAC-CI methods	C-105	Ian Mackinnon Density functional theory as a predictive tool for superconductivity	C-115	Niels Hansen Thermodynamics of self-assembly of perylene derivatives
17:35	C-076	Eduard Matito Separation of dynamic and nondynamic correlation	C-086	Lubomír Rulíšek Calibrating aurophilic interactions in weakly bound [L–Au–X]... [L’–Au–X] dimers by experiment and theory			IN-9	Matthias Bremer Increasing the polarity of liquid crystals - synthesis and computations	C-096	Basile F.E. Curchod Shedding light on the approximations underlying Ab initio multiple spawning	C-106	Fernando Ruipérez Design of new disulfide-based organic compounds for the improvement of self-healing materials
17:50	C-077	Jan Řezáč Describing non-covalent interactions in semiempirical QM methods: state of the art and future	C-087	Zahra Jamshidi Surface-enhanced Raman spectroscopy due to charge-transfer chemical mechanism: effect of surface and electric field	IN-10	Thomas Eckl Automated high-throughput DFT simulations for the development of enhanced energy storage and energy conversion materials			C-097	William Glover Polarizable QM/MM for excited-state dynamics	C-107	Toyokazu Ishida Computational modeling of thermal energy storage materials
18:05	C-078	Ekaterina Pas A new spin ratio scaled MP2 (SRS-MP2) method for the prediction of intermolecular interactions	C-088	Jean Christophe Tremblay Irreversible tautomerization in porphycene on Cu(111) induced by scanning tunnelling microscopy			C-098	Matthias Stein Hydrogen conversion in [NiFe]-enzymes and bio-inspired complexes	C-108	Eliseo Ruiz Spin crossover complexes: a challenge from theory to single-molecule devices	C-118	Ole Swang Towards reliable computed thermodynamic data for aqueous metal ions: the case of cadmium
18:20 – 20:00	DINNER BREAK											
20:00 – 22:00	Poster Session 2— <i>supported by The Journal of Physical Chemistry</i>											



Time	Philharmonic Hall		Carl-Orff Hall		Black Box		Small Concert Hall		Carl-Amery Hall		Multipurpose Room	
09:00 09:40	PL-7	Plenary Session E <i>Chair: Peter Richard Schreiner</i> Pavel Hobza Noncovalent interactions: theory and applications										
09:40 10:10		COFFEE BREAK										
10:10 12:15	Invited Session 24 <i>Chair: Mark Gordon</i>		Invited Session 25 <i>Chair: Gernot Frenking</i>		Invited Session 26 <i>Chair: Guan Hua Chen</i>		Invited Session 27 <i>Chair: Martin Kaupp</i>		Invited Session 28 <i>Chair: Qiang Cui</i>		Invited Session 29 <i>Chair: Dominika Zgid</i>	
10:10	I-241	<i>Alán Aspuru-Guzik</i> Quantum computation for quantum chemistry	I-251	Sason Shaik Oriented electric fields as future smart reagents in chemistry	I-261	Karsten Reuter Refining first-principles photo-electrocatalysis	I-271	<i>David Tozer</i> Exchange-correlation functionals from density scaling	I-281	<i>Marcus Elstner</i> Multi-scale methods for electron and exciton transfer in biological and organic materials	I-291	<i>Bogumil Jeziorski</i> Theoretical determination of properties of helium for new temperature and pressure standards
10:35	I-242	<i>Michele Ceriotti</i> Machine-learning unifies the modelling of materials and molecules	I-252	Clémence Corminboeuf Bringing volcano plots as a tool to understand and predict homogenous catalysts	I-262	Fabrizia Negri Challenges in modeling electronic structure, optical and transport properties of conjugated molecular materials	I-272	<i>Hannes Jonsson</i> Self-interaction corrected energy functional applied to molecules and solids	I-282	<i>Elena Laura Coitiño Izaguirre</i> Sulfenic acid or sulfenate? A matter of protein environment and water access in oxidized Cysteine sites of physiological relevance	I-292	<i>Manuel Yáñez</i> Spontaneous generation of radicals and design of anion sponges through Beryllium bonds
11:00	I-243	<i>Markus Reiher</i> Interactive and automated exploration of reaction mechanisms	I-253	Julia Rice Nucleobases: from the prebiotic world to self-healing polymers	I-263	<i>Mariachiara Pastore</i> From dye-sensitized TiO2 to dye-Sensitized NiO heterointerfaces: a new challenge for theory	I-273	<i>Julien Toulouse</i> Combining density-functional theory and many-body methods	I-283	<i>Matthias Heyden</i> Solvation and solvent-mediated driving forces: Spatially resolved information from detailed atomistic trajectories	I-293	<i>Johannes Kästner</i> Improvements of instanton theory to simulate atom tunneling in astrochemical reactions
11:25	I-244	<i>Matthias Scheffler</i> Big data of the chemical physics of materials: discovering interpretable patterns, correlations and causality	I-254	<i>Matthias Bickelhaupt</i> Rational design of chemical reactions	I-264	<i>Biswarup Pathak</i> Atomistic modeling of nanocluster based electrodes for fuel cell applications	I-274	<i>Erin R. Johnson</i> Dispersion interactions from the exchange-hole dipole moment	I-284	<i>Ville Kaila</i> Deciphering molecular mechanisms of energy-converting proteins from simulations across scales	I-294	<i>Eluvathingal D. Jemmis</i> Borophenes, borospherenes, boranes, 3D-boron allotropes and boron-rich solids
11:50	I-245	<i>Gregory Voth</i> Ultra-coarse-graining and its applications	I-255	William Hase Development and applications of direct Dynamics simulations	I-265	<i>Zhigang Shuai</i> Understanding intramolecular singlet fission process in D-A polymer from correlated wave-function perspective	I-275	<i>Matthias Ernzerhof</i> Factorizations of the exchange-correlation hole	I-285	<i>Holger Gohlke</i> Efficient approximation of configurational entropy changes upon binding to biomolecules	I-295	<i>Péter G. Szalay</i> On the accuracy of coupled-cluster-type methods describing excited states
12:15 13:00	LUNCH BREAK											
13:00 20:00	EXCURSIONS											
20:00 22:00	Löwenbräukeller (Address: Nymphenburger Str. 2)											
	CONGRESS DINNER											

Time	Philharmonic Hall		Carl-Orff Hall		Black Box		Small Concert Hall		Carl-Amery Hall		Multipurpose Room	
09:00 – 09:40	PL-8	Plenary Session F <i>Chair: So Hirata</i> <i>Hiroshi Nakatsuji</i> Exact general theory for solving Schrödinger equations of atoms and molecules: Free-complement theory and applications										
09:40 – 10:10		COFFEE BREAK										
10:10 – 12:15	Invited Session 30 <i>Chair: Asbjörn Buraw</i>		Invited Session 31 <i>Chair: Manuel Yáñez</i>		Invited Session 32 <i>Chair: Luca Frediani</i>		Invited Session 33 <i>Chair: Christof Hättig</i>		Invited Session 34 <i>Chair: Bogumil Jeziorski</i>		Invited Session 35 <i>Chair: Zexing Cao</i>	
10:10	I-301	<i>Filipp Furche</i> Recent developments in random phase approximation methods	I-311	<i>Josef Michl</i> Oligosilanes: intuitive understanding of $\sigma$ delocalization in loose and localization in tight helical conformations	I-321	<i>Chiara Cappelli</i> A fully polarizable embedding model for molecular spectroscopy of aqueous solutions	I-331	<i>Anna Krylov</i> Visualizing the contributions of virtual states to two-photon absorption cross-sections	I-341	<i>Rodney J. Bartlett</i> Quantitative molecular orbital theory	I-351	<i>Pedro Fernandes</i> Nanosecond-timescale conformational dynamics of enzymes, and its impact on reaction rates
10:35	I-302	<i>Axel Becke</i> Vertical excitation energies from the adiabatic connection	I-312	<i>Gernot Frenking</i> Aspects of chemical bonding	I-322	<i>Jacob Kongsted</i> Excited states in complex systems through polarizable (density) embedding	I-332	<i>Xiaosong Li</i> Two-component non-collinear time-dependent spin density functional theory for electronic dynamics and excited state calculations	I-342	<i>Andreas Köhn</i> Applications of interenally contracted multireference coupled-cluster theory	I-352	<i>Yiqin Gao</i> Computer simulations of chemical reactions in solution
11:00	I-303	<i>Eunji Sim</i> Reliable DFT results with density correction	I-313	<i>Marco Nascimento</i> Are one-electron bonds any different from standard two-electrons covalent bonds?	I-323	<i>Lyudmila Slipchenko</i> Polarizable embedding and beyond: modeling photoactive proteins with the effective fragment potential method	I-333	<i>Andreas Dreuw</i> Algebraic diagrammatic construction - a versatile approach to excited states, ionization potentials and electron affinities	I-343	<i>Shuhua Li</i> Advances in Electronic Structure Methods for Strongly Correlated Systems and Condensed Phase Systems	I-353	<i>Young Min Rhee</i> Simulating photo-excited dynamics of biological complexes: overcoming present challenges with interpolated potentials
11:25	I-304	<i>Andreas Görling</i> Density-functional methods with the accuracy and wide applicability of high-level multi-reference approaches	I-314	<i>Julia Contreras-García</i> A new model for reference densities - really getting rid of interactions	I-324	<i>Fred Manby</i> Multiscale embedding methods for accurate quantum chemistry of complex systems	I-334	<i>Spiridoula Matsika</i> Theoretical studies of the interaction of uracil with low energy electrons	I-344	<i>Jiri Pittner</i> DMRG-externally-corrected local pair natural orbital based coupled cluster method	I-354	<i>Carmay Lim</i> How native and alien metal cations bind ATP
11:50	I-305	<i>Paul Ayers</i> Variational principle for partitioning molecules into atomic contributions	I-315	<i>Russell J. Boyd</i> Insight into hydrogen-bonded clusters and noncovalent interactions from changes in atomic energies	I-325	<i>Kurt V. Mikkelsen</i> Exploitation of solar energy	I-335	<i>John Herbert</i> First-principles exciton models, with application to singlet fission	I-345	<i>Ove Christiansen</i> Tensor decomposition and coupled cluster theory	I-355	<i>David Smith</i> A multiscale computational investigation of SILPcatalysis: the water-gas shift reaction
12:15 – 13:45	LUNCH BREAK											

Time	Philharmonic Hall		Carl-Orff Hall		Black Box		Small Concert Hall		Carl-Amery Hall		Multipurpose Room	
13:45 15:50	Invited Session 36 <i>Chair: Jiali Gao</i>		Invited Session 37 <i>Chair: Filipp Furche</i>		Invited Session 38 <i>Chair: Julien Toulouse</i>		Invited Session 39 <i>Chair: Francesco Aquilante</i>		Invited Session 40 <i>Chair: Andreas Dreuw</i>		Invited Session 41 <i>Chair: Brian Yates</i>	
13:45	I-361	<i>Richard Henchman</i> Theory for the entropy of liquid mixtures of flexible molecules	I-371	<i>Marcel Nooijen</i> Towards a local coupled cluster theory for solids	I-381	<i>So Hirata</i> Many-body Green’s function theory: algebraic recursions, linked- and irreducible-diagram theorems, and general-order algorithms	I-391	<i>Toru Shiozaki</i> On-the-fly CASPT2 surface hopping dynamics	I-401	<i>Patrick Norman</i> Response theory techniques to address X-ray spectroscopies	I-411	<i>Igor Alabugin</i> Reinventing cycloaromatization reactions: the diradical /zwitterion dichotomy
14:10	I-362	<i>Johan Åqvist</i> Entropy and enzyme catalysis	I-372	<i>Georg Kresse</i> The relation between the random phase approximation and GW and analytic forces for the RPA	I-382	<i>Dominika Zgid</i> Green’s function embedding methods	I-392	<i>David Tew</i> Quantum dynamics on accurate electronic potentials	I-402	<i>Daniel Crawford</i> Streamlining coupled cluster response theory	I-412	<i>Miroslav Urban</i> DFT study of the Au-C bond formation in gold implanted polyethylene
14:35	I-363	<i>Qiang Cui</i> Understanding metalloenzyme catalysis with QM/MM free energy simulations	I-373	<i>Silke Biermann</i> Electronic structure calculations for correlated electron materials: a dynamical mean field perspective	I-383	<i>Denis Jacquemin</i> Is BSE/GW an effective method for modeling optical spectra of molecules?	I-393	<i>Yuki Kurashige</i> Ab initio modeling of inter-molecular electronic transition processes in molecular aggregates	I-403	<i>Benoît Champagne</i> Towards investigating the optical properties of molecular and ionic crystals using multi-scale approaches	I-413	<i>Attila Császár</i> Astructural molecules
15:00	I-364	<i>Pavel Jungwirth</i> Cell penetration and membrane fusion: two sides of the same coin	I-374	<i>Volker Blum</i> Affordable high numerical accuracy for large molecules and materials from numeric atom-centered basis functions	I-384	<i>Lucia Reining</i> Quasi-particles and satellites from a direct approach to the calculation of many-body Green’s functions	I-394	<i>Hans Jørgen Aagaard Jensen</i> Open-shell MC-srDFT - a new way to describe high-spin, low-spin, intermediate spin states and more	I-404	<i>Sonia Coriani</i> Developing theoretical “beam-lines” for modern experiments	I-414	<i>Annia Galano</i> The role of acid-base equilibria in the antioxidant and pro-oxidant activity of phenolic compounds
15:25	I-365	<i>Gerhard Hummer</i> Molecular simulations of lipid membrane sensing and remodeling dynamics	I-375	<i>Gregory Beran</i> Ab initio molecular crystallography: Aiding and abetting experiment	I-385	<i>Wim Klopper</i> Using the GW and Bethe-Salpeter methods in molecular quantum chemistry	I-395	<i>Piotr Piecuch</i> Stochastic CC(P;Q) theory: converging high-level coupled-cluster energetics by Monte Carlo sampling and moment expansions	I-405	<i>Antonio Rizzo</i> Electronic nonlinear spectroscopies: recent contributions of theory and computational science	I-415	<i>Munir Skaf</i> Thermodynamic forces between plant cell wall constituents
15:50 16:20	COFFEE BREAK											

Time	Philharmonic Hall	Carl-Orff Hall	Black Box	Small Concert Hall	Carl-Amery Hall	Multipurpose Room
<b>16:20</b> <b>18:20</b>	Contributed Session 12 <i>Chair: David Tew</i>	Contributed Session 13 <i>Chair: Wolfgang Domcke</i>	Contributed Session 14 <i>Chair: Andy Teale</i>	Contributed Session 15 <i>Chair: Reinhold Fink</i>	Contributed Session 16 <i>Chair: Tanya K. Todorova</i>	Contributed Session 17 <i>Chair: Marco Nascimento</i>
16:20	C-121 <i>Jan M.L. Martin</i> Explicitly correlated benchmark study on water clusters: The right answer for the right reason?	C-131 <i>Nick Mayhall</i> Multiexcitons and strong correlation via single-excitation wavefunctions: applications and future directions	C-141 <i>Stella Stopkowicz</i> Accurate treatment for ground and excited states of atoms and molecules in strong magnetic fields	C-151 <i>Martin Kaupp</i> Mixed valency and local hybrid functionals	C-161 <i>Mark Iron</i> Computational insights into sulphur isotopic fractionation in carbonate-associated sulphate	C-171 <i>José Enrique Barquera-Lozada</i> Aromaticity from the point of view of the vorticity of the current density tensor
16:35	C-122 <i>Ricardo Mata</i> GoBench: a joint initiative for experimental benchmarking of quantum chemical methods	C-132 <i>Remco Havenith</i> The computation of dielectric constants	C-142 <i>Sandra Lubert</i> Recent advances in theoretical spectroscopy from ab initio molecular dynamics	C-152 <i>Lars Goerigk</i> Double-hybrid density functionals: is there anything new to tell?	C-162 <i>Silvia Simon</i> Tailoring resonance assisted hydrogen bonds	C-172 <i>Fabio Pichierri</i> Cesium cation- $\pi$ interactions: DFT and QAIM studies
16:50	C-123 <i>Peter Nagy</i> Approaching CCSD(T)/CBS energies for large molecules with the linear-scaling local natural orbital CCSD(T) method	C-133 <i>Andrzej L. Sobolewski</i> Organic photovoltaics with p-f-n junctions: computational study of ferroelectric columnar molecular clusters	C-143 <i>Malgorzata Biczysko</i> Anharmonic effects on vibrational spectra intensities: infrared, Raman, vibrational circular dichroism, and Raman optical activity	C-153 <i>Sergei Vyboishchikov</i> Exchange-Correlation Potentials and Energy Densities in Spherically Confined Atoms	C-163 <i>Ulrike Salzner</i> Effect of biradical character of organic molecules on Opto electronic properties	C-173 <i>András Stirling</i> Hypervalency and reactivity from Wannier orbitals
17:05	C-124 <i>Graham Fletcher</i> Large-scale valence bond applications: excitons and transition metal complexes	C-134 <i>Thomas Koerzdoerfer</i> Accurate ionization potentials, electron affinities, and photoelectron spectra of molecules from first principles	C-144 <i>Takeshi Iwasa</i> Infrared absorption spectroscopy beyond the dipole approximation based on the multipolar Hamiltonian: Theory and application	C-154 <i>Arindam Chakraborty</i> Linked-cluster formulation of screened electron-hole interaction from explicitly-correlated geminal functions without using unoccupied states	C-164 <i>Hong-Xing Zhang</i> Computationally driven design of efficient photosensitizer for dye-sensitized solar cell applications	C-174 <i>Leonardo Belpassi</i> Charge-displacement analysis: a simple tool to reveal charge transfer effects throughout the whole periodic table
17:20	C-125 <i>Jean-Philip Piquemal</i> Scalable polarizable molecular dynamics using Tinker-HP: millions of atoms on thousands of cores	C-135 <i>Emanuele Coccia</i> Dissipation and dephasing for molecules close to plasmonic nanoparticles: an ab initio approach	C-145 <i>Franco Egidi</i> Toward the accurate simulation of vibrationally-resolved spectra for spin-forbidden transitions	C-155 <i>István Mayer</i> Local spins	C-165 <i>Martial Boggio-Pasqua</i> Computational studies of the photoswitching mechanisms in photochromic ruthenium complexes	C-175 <i>Apostolos Kalamos</i> The nature of the chemical bond in Be containing molecules: Be $2^{+}$ , $0^{-}$ , Be $3$ , Be $00^{-}$ , Be $0Be^{+}$ , $0^{-}$
17:35	C-126 <i>Joonsuk Huh</i> Vibronic boson sampling	C-136 <i>Robert Góra</i> Microhydration induces qualitative changes in the photochemistry of biomolecular building blocks	C-146 <i>Sergei Ivanov</i> Nuclear correlation effects in X-ray spectroscopy from a time-domain perspective	C-156 <i>Fan Wang</i> Spin-orbit coupling effects of open-shell systems with coupled-cluster theory	C-166 <i>Aurélien Perrier</i> Photosensitizing properties of functionalized thiolate-protected gold nanoclusters: insights from theory	C-176 <i>David Wilson</i> Theoretical investigation of a strong cis-effect in an imidazole-imidazolium substituted alkene
17:50	C-127 <i>Luca Frediani</i> PCMSolver: a modern, modular approach to include solvation in any quantum chemistry code	C-137 <i>Isabelle Navizet</i> Role of the environment in bioluminescence emission: QM/MM study	C-147 <i>Stepan Sklenak</i> DFT calculations of NMR parameters of framework and extra-framework atoms in silicon-rich zeolites	C-157 <i>Mikael P. Johansson</i> Can spin-state energetics of transition metal complexes be accurate at single reference level?	C-167 <i>David Henry</i> Modifying the reactivity of gallium nanoclusters with ligands	C-177 <i>Ignacy Cukrowski</i> Fragment attributed molecular system energy change (FAMSEC) in the study of interactions and molecular stability
18:05	C-128 <i>Sebastian Höfener</i> Combining frozen-density embedding with the conductor-like screening model using Lagrangian techniques	C-138 <i>Stefan Knippenberg</i> Investigation of optical probes for membrane phase recognition	C-148 <i>Alfonso Hernández-Laguna</i> Elastic behavior of White Micas solid solutions as a function of the pressure	C-158 <i>Ran Friedman</i> Specific ion interactions with biomolecules: molecular dynamics simulations and energy decomposition analysis	C-168 <i>Thibaud Étienne</i> Orbital relaxation and electronic transitions - what is the nature of Handy's Z-vector?	C-178 <i>Hugo Gattuso</i> Efficiently modeling the electronic circular dichroism of amino and nucleic acids ensembles
<b>18:20</b> <b>20:00</b>	DINNER BREAK					
<b>20:00</b> <b>22:00</b>	Poster Session 3 – supported by ACS Publications					



Time	Philharmonic Hall	
09:00 10:20	Plenary Session G <i>Chair: David Sherrill</i>	
09:00 09:40	PL-9	<i>Francesco Evangelista</i> Multireference coupled cluster theory, infinities and renormalization
09:40 10:20	PL-10	<i>Johannes Neugebauer</i> Subsystem density-functional theory for properties and spectra of complex chemical systems
10:20 10:50	COFFEE BREAK	
10:50 12:10	Plenary Session H <i>Chair: Walter Thiel</i>	
10:50 11:30	PL-11	<i>Ursula Roethlisberger</i> Next generation first-principles based multiscale simulations: computational chemistry meets artificial intelligence
11:30 12:10	PL-12	<i>Frank Neese</i> Wavefunction based correlation methods for large molecules: recent developments, applications and limitations
12:10 12:50	CLOSING CEREMONY AND POSTER AWARDS	



# PLENARY TALKS



## Ground and Excited State Dynamics on Graphical Processing Units

**Todd J. Martínez<sup>1</sup>**

*<sup>1</sup>Department of Chemistry and The PULSE Institute, Stanford University, Stanford, CA  
94305*

The development and numerous applications of ab initio multiple spawning (AIMS) have shown that ab initio nonadiabatic dynamics was both possible and predictively accurate. However, a major bottleneck remained in the solution of the electronic structure problem. Here, we discuss recent advances that have enabled large scale ground and excited state ab initio molecular dynamics for molecules with hundreds of even thousands of atoms for as long as nanoseconds. These recent advances exploit graphical processing units (GPUs) and new algorithms adapted for these architectures. We discuss the ab initio exciton model which further introduces significant parallelism through coarse-graining of the electronic structure problem in the context of the Forster exciton model for excited states. We show that the ab initio exciton model can be implemented with not only locally excited states, but also charge transfer and triplet-triplet states. First applications for photosynthetic proteins and singlet fission are discussed. If time permits, we also discuss new applications in the context of fluorescent proteins.

## **Present and future of multiscale approaches combining quantum chemistry and classical models: a personal overview**

**Benedetta Mennucci**

*Dipartimento di Chimica e Chimica Industriale, University of Pisa, via G. Moruzzi 13,  
56124 Pisa, Italy*

In the last decades, quantum chemistry has enormously extended the boundaries of its applicability towards systems of increasing dimension and processes of increasing complexity. A large part of this progress is due to the integration of quantum chemical methods with classical models. Different strategies have been proposed depending on the characteristics of the system/process to be investigated. For example, continuum models have dominated the field of solvated molecules [1] while atomistic approaches based on Molecular Mechanics force fields have been largely used for simulating biological systems [2]. Integrations of the two different classical models have also been proposed.

Here, a personal overview of the main achievements obtained so far and the future challenges will be given with particular reference to the simulation of photoinduced processes [3].

[1] J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **105**, 2999 (2005).

[2] H. M. Senn, W. Thiel, *Angew. Chem. Int. Ed.* **48**, 1198 (2009).

[3] C. Curutchet, B. Mennucci, *Chem. Rev.* **117**, 294 (2017).



## Quantum Chemistry in Magnetic Fields

**Trygve Helgaker<sup>1</sup>, Alex Borgoo<sup>1</sup>, James Furness<sup>2</sup>, Jürgen Gauss<sup>3</sup>, Kai Lange<sup>1</sup>, Sarah Reimann<sup>1</sup>, Stella Stopkowicz<sup>3</sup>, Andy Teale<sup>1,2</sup>, Erik Tellgren<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, University of Oslo, Box 1033 Blindern, N-0315 Oslo, Norway*

<sup>2</sup>*School of Chemistry, University Park Nottingham, NG7 2RD, UK*

<sup>3</sup>*Institute für Physikalische Chemie, Universität Mainz, D-55099 Mainz, Germany*

In strong magnetic fields, chemistry changes: electronic states change their character, atoms and molecules change their shape, and their interactions with radiation are affected, often in a dramatic manner. Such magnetic-field induced changes are not only fascinating as a contrast to the chemistry observed on the earth, they are also relevant to astrophysics, where molecules in stellar atmospheres are subject to strong magnetic fields. Our calculations on molecular systems in strong magnetic fields have revealed and highlighted many interesting phenomena such as the transition to diamagnetism of paramagnetic molecules at a critical field strength [1,2]. Perhaps most interestingly, antibonding orbitals are stabilized in a magnetic field, leading to bound triplet H<sub>2</sub> at field strengths of about 10<sup>5</sup> Tesla, appropriate for some white-dwarf atmospheres [3].

In this talk, we review the theory and application of quantum-chemical electronic-structure methods for molecules in magnetic fields — including coupled-cluster theory [4] but with special emphasis on density-functional theory (DFT). We demonstrate that Kohn–Sham current-density functional theory (CDGT) with meta-GGA exchange–correlation functionals provide a good description of molecules in magnetic fields, at a reasonable cost [5].

- [1] E. I. Tellgren, A. Soncini, and T. Helgaker, *J. Chem. Phys.* **129**, 154114 (2008).
- [2] E. I. Tellgren, T. Helgaker, and A. Soncini, *Phys. Chem. Chem. Phys.* **11**, 5489 (2009).
- [3] K. K. Lange, E. I. Tellgren, M. R. Hoffmann, and T. Helgaker, *Science* **337**, 327 (2012).
- [4] S. Stopkowicz, J. Gauss, K. K. Lange, E. I. Tellgren, and Trygve Helgaker, *J. Chem. Phys.* **143**, 074110 (2015).
- [5] J. W. Furness, J. Verbeke, E. I. Tellgren, S. Stopkowicz, U. Ekström, T. Helgaker, and A. Teale. *J. Chem. Theory Comput.* **11**, 4169 (2015)

## Mechanistic Variants of Metal-oxide Mediated C–H bond Activation: Experiment and Theory in Concert

H. Schwarz<sup>1</sup>, N. Dietl<sup>1</sup>, C. Geng<sup>1</sup>, J. Li<sup>1</sup>, M. Schlangen<sup>1</sup>, S. Shaik<sup>2</sup>, S. Zhou<sup>1</sup>, T. Weiske<sup>1</sup>

<sup>1</sup>*Institut für Chemie der Technischen Universität Berlin and UniCat Berlin,  
Straße des 17. Juni 135, 10623 Berlin, Germany*

<sup>2</sup>*The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

Hydrogen-atom transfer (HAT) constitutes a key process in a broad range of chemical transformations as it covers heterogeneous, homogeneous, and enzymatic reactions [1]. While open-shell metal oxo species [MO]• are no longer regarded as being involved in the industrially relevant heterogeneously catalyzed oxidative coupling of methane ( $2\text{CH}_4 + \langle\text{O}\rangle \rightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{O}$ ), these reagents are rather versatile in bringing about (gas-phase) hydrogen-atom transfer, even from methane at ambient conditions. In this lecture, various mechanistic scenarios e.g., homo- as well as heterolytic C–H bond cleavage involving proton-coupled electron transfer will be presented, and it will be demonstrated how these are affected by the composition of the metal-oxide cluster ions [2]. Examples will be discussed, how ‘doping’ the clusters permits the control of the charge and spin situation at the active site and, thus, the course of the reaction. Also, the interplay between supposedly inert support material and the active site – the so-called ‘aristocratic atoms’ – of the gas-phase catalyst will be addressed, and gas-phase HAT from methane will be analyzed in the broader context of thermal activation of inert C–H bonds by metal-oxo species and it will be shown that the investigation of ‘doped’ metal oxide clusters as mimics for catalytic processes is about to enter into widely uncharted territory of chemistry, a field in which “each atom counts” [3].

Finally, novel coupling processes of a single “activated” carbon atom with methane to deliver  $\text{C}_2\text{H}_4$  will be reported. Here, an unprecedented, mechanistically unique  $\text{Cu}^+$ -mediated (or charge-induced) insertion of a carbon atom into two C–H bonds of  $\text{CH}_4$  takes place in a synchronous, barrier-free process [4].

Most importantly, it is the interplay of state-of-the art experiments with electronic structure calculations that has enormously enriched our mechanistic understanding of seemingly simple bond-activation reactions [5].

- [1] Schwarz, H. *Chem. Phys. Lett.* **629**, 91 (2015).
- [2] Schwarz, H.; González Navarrete, P.; Li, J.; Schlangen, M.; Sun, X.; Weiske, T.; Zhou, S. *Organometallics* DOI: 10.1021/acs.organomet.6b00372 (2016).
- [3] Schwarz, H. *Angew. Chem. Int. Ed* **54**, 10090 (2015).
- [4] Geng, C.; Li, J.; Weiske, T.; Schlangen, M.; Shaik, S.; Schwarz, H. submitted for publication.
- [5] Schwarz, H. *Isr. J. Chem.* **54**, 1413 (2014).

## Reduced scaling and controlled precision: extending the reach of many-body electronic structure

Edward F Valeev<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Virginia Tech, Blacksburg, VA 24014, USA*

Recent work on reduced-scaling explicitly correlated many-body methods, such as coupled-cluster singles and doubles, has demonstrated computation of energies of large molecular assemblies (with hundreds of atoms) with near-linear complexity and with precision sufficient for chemical accuracy in most scenarios.[1] Nevertheless it is desirable to free many-body electronic structure methods from the fundamental numerical limitations of the LCAO technology to extend their reach to new frontiers such as high-density solids. Here we revisit non-LCAO numerical formulations of the many-body methods[2] and consider how to exploit the successful low-rank structures of the correlated wave functions suggested by the LCAO reduced-scaling methodology.

[1] F. Pavošević, C. Peng, P. Pinski, C. Riplinger, F. Neese, E. F. Valeev, *J. Chem. Phys.* **146**, 174108 (2017).

[2] F. A. Bischoff, E. F. Valeev, *J. Chem. Phys.* **139**, 114106 (2013).

**Electrochemistry meets condensed matter physics: first principles simulations of photo-catalytic materials**

Giulia Galli  
Institute for Molecular Engineering  
University of Chicago  
[gagall@uchicago.edu](mailto:gagall@uchicago.edu)  
<http://galligroup.uchicago.edu/>

We discuss the results of first principles simulations of heterogeneous photo-catalytic materials, in particular of interfaces between photo-absorbers, catalysts and water in photo-electrochemical cells. We focus on the identification of descriptors for the optimization of photo-conversion properties, and on the role of complex morphologies.

## Noncovalent Interactions: Theory and Applications

Pavel Hobza

*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Prague 16610, Czech Republic*

Noncovalent interactions play an important role in chemistry, physics and biology. Reliable characteristics like stabilization energy, structure and vibrational frequencies are obtained only at very high theoretical level covering significant portion of correlation/dispersion energy. The benchmark values are usually obtained using composite coupled cluster (CC) schemes which offer the possibility of improving the accuracy of results obtained by adding excitation operators of increasing order. It was shown that already CCSD(T)/CBS method yields an accurate and reliable description of noncovalent interactions, yet is only applicable to systems with several tens of atoms.[1] The method is used not only to solve specific chemical and biological problems but mainly for the verification and/or parametrization of more approximate methods applicable to extended molecular clusters with several hundred or thousands of atoms. Here the databases of accurate stabilization energies and geometries developed in our laboratory (S22, S66, X40 and L7) play an indispensable role.[1]

Systematically attractive dispersion energy forms frequently a dominant part of overall attraction and its computation represents an important test case for various computational schemes. We were among first who recognized that DFT techniques do not cover it [2] and as early as in 2001 added empirical dispersion to DF-TB scheme what considerably improve the efficiency of the method.[3] In a similar way we corrected also other semiempirical QM methods and the PM6-D3H4X scheme available in the MOPAC suite represents one of the most efficient and accurate semiempirical QM schemes used in the field of noncovalent interactions.[4] Dispersion energy which can be compared with gravitation determines the structure and dynamics of biomolecules. We demonstrated it in the case of DNA and proteins where its neglect completely deteriorated the structure and thus also the function of these biomacromolecules.[5]

Applicability of procedures described is demonstrated for evaluation of binding free energies of several extended systems like host – guest [6], protein – ligand [7] and surface – admolecule [8] ones.

- [1] J. Rezac, P. Hobza, *Chem. Rev.* **116**, 5038 (2016).
- [2] P. Hobza, J. Sponer, T. Reschel, *J. Comp. Chem.* **16**, 1315 (1995).
- [3] M. Elstner, P. Hobza, T. Frauenheim, S. Suhai, E. Kaxiras, *J. Chem. Phys.* **114**, 5149 (2001).
- [4] J. Rezac, P. Hobza, *J. Chem. Theory Comput.* **8**, 141 (2012).
- [5] M. Kolar, T. Kubar, P. Hobza, *J. Phys. Chem. B* **114**, 13446 (2010); J. Cerny, M. Kabelac, P. Hobza, *J. Am. Chem. Soc.* **130**, 16055 (2008).
- [6] J. Hostas *et al*, *Chem. Eur. J.* **22**, 17226 (2016); D. Sigwalt *et al*, *J. Am. Chem. Soc.* **139**, 3249 (2017).
- [7] A. Pecina *et al*, *J. Chem. Inf. Model.* **57**, 127 (2017).
- [8] R. Zboril, P. Jelinek, P. Hobza, *in preparation*.



## Exact general theory for solving Schrödinger equations of atoms and molecules: Free-complement theory and applications

Hiroshi Nakatsuji

*Quantum Chemistry Research Institute, 16 Kyoto Technoscience Center,  
14 Yoshida Kawaramachi, Sakyo-ku, Kyoto 606-8305 Japan*

Chemistry is a science of complex matters that occupy this universe and biological world that are composed of atoms and molecules. The essence is diversity. However, surprisingly, whole of this science is governed by a simple quantum principle represented by the Schrödinger and Dirac equations. Therefore, if we can find an accurate useful general method of solving these equations under the fermionic and/or bosonic constraints, we can replace somewhat empirical methodologies of this science with purely quantum theoretical and computational logics. This is a purpose of our series of studies - called “exact theory” in our laboratory. Free complement (FC) theory is an exact general theory for solving the Schrödinger equation. After a series of studies to realize exact structure in the wave function under study, we could overcome the divergence difficulty caused by the singularity of the Coulomb potential included in the Hamiltonian [1]. High accuracy and easy implementations of the theory were demonstrated with several applications [2]. Similar theory was shown valid also for the Dirac equation [3]. More recently, we have formulated the FC theory in local and transferable mathematical structures that are common to the chemical formulas used daily in chemistry [4]. Combining with the inter exchange (*i*Exg) theory for antisymmetrization [5], we could formulate an order-N exact theory that can cover not only small atoms and molecules, but also large and even giant molecular systems. Combining further with the efficient sampling methodologies, we could develop a stable local Schrödinger equation (LSE) method [6] that leads to the solution of the Schrödinger equation in chemical accuracy (within kcal/mol in absolute energy). In this lecture, an overview of the theoretical background and the results of applications will be given. The computations were done mostly with the super-parallel computers at Okazaki IMS Computer Center, whom we acknowledge for their supports.

- [1] H. Nakatsuji, *J. Chem. Phys.* **113**, 2949 (2000); **115**, 2000 (2001); *Phys. Rev. A* **65**, 052122 (2002); *Phys. Rev. Lett.* **93**, 030403 (2004); *Acc. Chem. Res.* **45**, 1480 (2012).
- [2] *PRA*, **72**, 062502 (2005); *JCP*, **117**, 9, (2002); **127**, 224104 (2007); **139**, 074105 (2013).
- [3] H. Nakatsuji and H. Nakashima, *Phys. Rev. Lett.* **95**, 050407 (2005).
- [4] H. Nakatsuji et al. *TSUBAME e-Science J.* **11**, 8, 24 (2014); ISTCP, North Dakota, (2016).
- [5] H. Nakatsuji and H. Nakashima, *J. Chem. Phys.* **142**, 194101 (2015).
- [6] H. Nakatsuji, et al. *Phys. Rev. Lett.* **99**, 240402 (2007); *J. Chem. Phys.* **142**, 084117 (2015).

## Multireference Coupled Cluster Theory, Infinities, and Renormalization

Francesco A. Evangelista<sup>1</sup>, Chenyang Li<sup>1</sup>, Kevin P. Hannon<sup>1</sup>

<sup>1</sup>*Department of Chemistry and Cherry Emerson Center for Scientific Computation, Emory University, 1515 Dickey Dr., Atlanta, Georgia (USA)*

Despite the enormous progress made in the description of molecules with closed-shell ground states, a general, robust, and systematically-improvable multireference method to treat near-degenerate electronic states is still lacking. The framework of coupled cluster theory is a natural candidate for creating hierarchies of multireference approaches that can be made arbitrarily accurate. However, efforts to develop genuine multireference coupled cluster methods have often resulted in computational schemes that suffer from numerical instabilities or that can target only a limited number of active orbitals. To address these issues, we have recently developed a novel approach to multireference theories inspired by renormalization group methods. Our work is based on the similarity renormalization group (SRG)—a many-body formalism to diagonalize operators using a series of infinitesimal transformations. [1,2] Because of its renormalization group structure, the SRG naturally avoids divergences that arise from small energy denominators. Starting from the SRG, we have recently proposed a multireference *driven* SRG (MR-DSRG) scheme for Quantum Chemistry applications. [3,4] The MR-DSRG provides a convenient framework to derive numerically-robust multireference theories with electron correlation treated perturbatively or at a level comparable to that of coupled cluster methods. This talk will give an overview of recent developments, including novel schemes to treat near-degenerate ground and excited states and conical intersections.

- [1] S. D. Głazek, K. G. Wilson, *Phys. Rev. D* **49**, 4214 (1994).
- [2] F. Wegner, *Ann. Phys. Rev.* **506**, 77 (1994).
- [3] F. A. Evangelista, *J. Chem. Phys.* **141**, 054109 (2014).
- [4] C. Li, F. A. Evangelista, *J. Chem. Theory Comput.* **11**, 2097 (2015).
- [5] C. Li, F. A. Evangelista, *J. Chem. Phys.* **144**, 164114 (2016).

## Subsystem Density-Functional Theory for Properties and Spectra of Complex Chemical Systems

**Johannes Neugebauer**

*Theoretische Organische Chemie, Organisch-Chemisches Institut and  
Center for Multiscale Theory and Computation, Westfälische Wilhelms-Universität Münster  
Corrensstraße 40, 48149 Münster, Germany; email: j.neugebauer@uni-muenster.de*

Subsystem Density Functional Theory (subsystem DFT, sDFT) and density-based embedding methods have become increasingly popular over the past years (for reviews, see Refs. [1, 2]). Important new developments concern the combination of correlated wavefunction methods with DFT-based embedding techniques and the use of accurate (sometimes called “exact”) embedding strategies. Here, our recent and ongoing efforts to utilize such developments for the calculation of molecular properties and spectra, in particular for excited states of embedded molecules [3, 4], will be presented. A particular focus will be on the construction of protein electron densities and the inclusion of protein effects in excitation-energy calculations [5]. Additionally, our recent generalized energy and analytical gradient implementation [6] gives access to vibrational spectra and other properties, for which preliminary results will be presented.

- [1] C.R. Jacob and J. Neugebauer, *WIREs Comput. Mol. Sci.* **4**, 325 (2014).
- [2] T.A. Wesolowski, S. Shedge, and X. Zhou, *Chem. Rev.* **115**, 5891 (2015).
- [3] D.G. Artiukhin, C.R. Jacob, and J. Neugebauer, *J. Chem. Phys.* **142**, 234101 (2015).
- [4] T. Dresselhaus and J. Neugebauer, *Theor. Chem. Acc.* **134**, 97 (2015).
- [5] A. Goez and J. Neugebauer, *Mol. Phys.* **115**, 526 (2017).
- [6] D. Schlüns, M. Franchini, A.W. Götz, J. Neugebauer, C.R. Jacob, L. Visscher, *J. Comput. Chem.* **38**, 238 (2017).

## Next Generation First-Principles Based Multiscale Simulations: Computational Chemistry Meets Artificial Intelligence

**Martin Bircher, Esra Bozkurt, Nicholas Browning<sup>1</sup>, Marta Da Silva Perez<sup>1</sup>,  
Elisa Liberatore<sup>1</sup>, and Ursula Rothlisberger<sup>1</sup>**

*<sup>1</sup>Institute of Chemical Sciences and Engineering ISIC; Laboratory of Computational Chemistry and Biochemistry, EPFL, Avenue Forel 15, 1015 Lausanne, Switzerland*

First-principles and mixed quantum mechanical/molecular mechanical (QM/MM) molecular dynamics (MD) simulations have become powerful tools for the investigation of a broad range of dynamical phenomena in electronic ground and excited states. However, for some applications, it can still be difficult to find a workable compromise to solve the combined challenge of high accuracy, large system size and long time scales.

In this talk, we will present some of our ongoing work to push the current limits of first-principles based molecular dynamics simulations further. We are currently developing a new general multiscale interface to the first-principles molecular dynamics code CPMD which allows flexible combinations of different electronic structure and force field methods in QM/MM, QM/QM or QM/QM/MM multiscale simulations.

In addition, applying multiple-time step techniques, on-the-fly force matching and machine learning, it is possible to perform first-principles simulations for extended spatial and temporal scales for a fraction of the cost.

The combination of methods from computational chemistry (CC) with approaches from artificial intelligence (AI) not only opens new avenues for the analysis of high-dimensional simulation data, it also enables the efficient exploration of chemical space for compound design and the machine learning of forces/energies during MD simulations.

In this talk, we will present some illustrative examples for the application of CC/AI approaches in the simulation of biological systems, the design of biomimetic compounds and the investigation of photovoltaic materials.

## Wavefunction based correlation methods for large molecules: Recent developments, applications and limitations

Frank Neese<sup>1</sup>

<sup>1</sup> Max Planck Institut für Chemische Energiekonversion, Stiftstr. 34-36, D-45470 Mülheim an der Ruhr, Germany, Frank.Neese@cec.mpg.de

Local correlation methods that capitalize on the short-range nature of inter-electronic correlations to bring down the computational cost down, have a long history in quantum chemistry. However, it has been proven difficult to maintain sufficient accuracy in solving the equations associated with the various single- or multi-reference correlation methods. Unfortunately, the required accuracy amounts to 99.9% or better of the canonical correlation energy obtained with the same method. Together with our collaborators, our group has developed a family of domain-based local pair natural orbital (DLPNO) methods that realize linear scaling, a low pre-factor and robust performance. In recent years, our efforts have concentrated on making various single- and multi-reference correlation methods (DLPNO-MP2,<sup>[1]</sup> DLPNO-CCSD(T),<sup>[2]</sup> DLPNO-NEVPT2,<sup>[3]</sup> DLPNO-MkMRCC<sup>[4]</sup>) applicable to routine computational chemistry investigations. This requires the applicability to closed-<sup>[2b-d]</sup> and open-shell<sup>[2a, 5]</sup> states, excited states,<sup>[6]</sup> molecular properties,<sup>[7]</sup> and explicitly correlation.<sup>[1, 8]</sup> Tools were developed that allow for a chemically intuitive interpretation of the results (local energy decomposition,<sup>[9]</sup> ab initio ligand field theory<sup>[10]</sup>). These methods now find widespread application in computational chemistry. The talk will discuss recent developments, real-life applications and will close by discussing the prospects and limitations of the methodology.

- [1] P. Pinski, C. Riplinger, E. F. Valeev, F. Neese, *J. Chem. Phys.* **2015**, 143.
- [2] a) M. Saitow, U. Becker, C. Riplinger, E. Valeev, F. Neese, *J. Chem. Phys.* **2017**, 146, 164105; b) C. Riplinger, P. Pinski, U. Becker, E. F. Valeev, F. Neese, *J. Chem. Phys.* **2016**, 144; c) C. Riplinger, B. Sandhöfer, A. Hansen, F. Neese, *J. Chem. Phys.* **2013**, 139; d) C. Riplinger, F. Neese, *J. Chem. Phys.* **2013**, 138.
- [3] Y. Guo, K. Sivalingam, E. F. Valeev, F. Neese, *J. Chem. Phys.* **2016**, 144.
- [4] O. Demel, J. Pittner, F. Neese, *J. Theo. Comp. Chem.* **2015**, 11, 3104-3114.
- [5] A. Hansen, D. G. Liakos, F. Neese, *J. Chem. Phys.* **2011**, 135.
- [6] a) A. K. Dutta, M. Nooijen, F. Neese, R. Izsak, *J. Chem. Phys.* **2017**, 146, 11; b) A. K. Dutta, F. Neese, R. Izsak, *J. Chem. Phys.* **2016**, 145.
- [7] D. Datta, S. Kossmann, F. Neese, *J. Chem. Phys.* **2016**, 145.
- [8] a) F. Pavošević, C. Peng, P. Pinski, C. Riplinger, F. Neese, E. Valeev, *J. Chem. Phys.* **2017**, 146, 174108; b) F. Pavosevic, P. Pinski, C. Riplinger, F. Neese, E. F. Valeev, *J. Chem. Phys.* **2016**, 144; c) F. Pavosevic, F. Neese, E. F. Valeev, *J. Chem. Phys.* **2014**, 141.
- [9] W. B. Schneider, G. Bistoni, M. Sparta, M. Saitow, C. Riplinger, A. A. Auer, F. Neese, *J. Theo. Comp. Chem.* **2016**, 12, 4778-4792.
- [10] M. Atanasov, D. Ganyushin, K. Sivalingam, F. Neese, in *Molecular Electronic Structures of Transition Metal Complexes II, Vol. 143* (Eds.: D. M. P. Mingos, P. Day, J. P. Dahl), **2012**, pp. 149-220.



# INVITED TALKS



## Strong correlation in electron gases.

**Marat Sibaeu, Peter M. W. Gill**

*Research School of Chemistry, Australian National University, Canberra ACT 2601, Australia*

The problem of “strong correlation” is one of the most pressing in modern theoretical chemistry. In systems that exhibit this phenomenon, the electrons are poorly described by models based on the traditional one-electron orbital picture and many of the most popular methods (e.g. Hartree-Fock and DFT) in the computational chemist’s repertoire are therefore ruled out. This is particularly unfortunate because such systems often possess highly desirable electronic and magnetic properties [1].

In its extreme form, strong correlation causes electrons to become so coupled that they localize onto the lattice sites of a “Wigner crystal” [2] and this curious state of matter has been investigated by various workers over the years [3, 4, 5, 6, 7].

In this lecture, I will describe our recent studies of strong correlation within the uniform gases formed by electrons confined to the surface of a sphere [8, 9, 10, 11, 12, 13]. In particular, I will highlight a simple wavefunction ansatz that yields surprisingly accurate energies.

- [1] J. Quintanilla, C. Hooley, *Physics World*, **22**, 32 (2009).
- [2] E. Wigner, *Phys. Rev.* **46**, 1002 (1934).
- [3] E. Wigner, *Trans. Faraday Soc.* **34**, 678 (1938).
- [4] R. A. Coldwell-Horsfall, A. A. Maradudin, *J. Math. Phys.* **1**, 395 (1960).
- [5] W. J. Carr, *Phys. Rev.* **122**, 1437 (1961).
- [6] D. M. Ceperley, B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- [7] N. D. Drummond, Z. Radnai, J. R. Trail, M. D. Towler, R. J. Needs, *Phys. Rev. B* **69**, 085116 (2004).
- [8] P. F. Loos, P. M. W. Gill, *Phys. Rev. Lett.* **103**, 123008 (2009).
- [9] P. F. Loos, P. M. W. Gill, *J. Chem. Phys.* **135**, 214111 (2011).
- [10] P. M. W. Gill, P. F. Loos, *Theor. Chem. Acc.* **131**, 1069 (2012).
- [11] P. F. Loos, P. M. W. Gill, *Phys. Rev. Lett.* **108**, 083002 (2012).
- [12] P. M. W. Gill, P. F. Loos, D. Agboola, *J. Chem. Phys.* **141**, 244102 (2014).
- [13] D. Agboola, A. L. Knol, P. M. W. Gill, P. F. Loos, *J. Chem. Phys.* **143**, 084114 (2015).



**Notes on the complexity of electronic structure theory**

**Narbe Mardirossian<sup>1</sup>, James McClain<sup>1</sup>, Garnet Kin-Lic Chan<sup>1</sup>**

*<sup>1</sup>Division of Chemistry and Chemical Engineering, Pasadena, CA 91125, USA*

I will discuss the exact complexity of common quantum chemistry methods.

## **Beyond Standard Coupled-Cluster Theory and Towards Full Configuration Interaction**

**Jürgen Gauss**

*Institut für Physikalische Chemie, Johannes Gutenberg-Universität Mainz,  
Duesbergweg 10-14, 55128 Mainz, Germany*

While single-reference coupled-cluster (CC) theory has evolved in recent years to a standard tool for high-accuracy quantum-chemical calculations, the CC treatment of so-called multireference cases still poses a challenge. We analyze in this presentation the suitability of both equation-of-motion CC theory as well as state-of-the-art multireference CC schemes for the treatment of these difficult cases. In addition, some entirely new ideas for treating the electron-correlation problem are presented based on a many-body expansion for the correlation energy, thereby aiming at a sufficiently accurate solution of the full configuration-interaction problem and providing at the same time a scheme well suited for massively parallel computing.

## Cluster perturbation theory for energies and molecular properties

**Poul Jørgensen<sup>1</sup>, Filip Pawłowski<sup>1, 2</sup>, Jeppe Olsen<sup>1</sup>**

<sup>1</sup>*qLEAP Center for Theoretical Chemistry, Department of Chemistry, Aarhus University,  
Langelandsgade 140, DK-8000 Aarhus C, Denmark*

<sup>2</sup>*Department of Chemistry and Biochemistry, Auburn University, Auburn, Alabama  
36849-5312, United States*

We introduce a new class of perturbation models—the cluster perturbation (CP) models—where the major drawbacks of Møller-Plesset perturbation theory (MPPT) and coupled cluster perturbation theory (CCPT) have been overcome. In CP theory, we consider a target excitation space relative to the Hartree-Fock state and partition the target excitation space into a parent and an auxiliary excitation space. The zeroth-order state is a coupled cluster (CC) state in the parent excitation space and the target state is the CC state in the target excitation space. The perturbation series in CP theory is determined in orders in the fluctuation potential for the energy and for molecular properties with the zeroth-order contribution in the series being the energy or the molecular property for the CC parent state and with the series formally converging to the energy or the molecular property for the CC target state. The applicability of CP theory to both the energy and molecular properties and the numerical results for the CP energy and molecular property series have demonstrated the superiority of CP theory compared to previous perturbation models and low-order corrections in the CP perturbation series may be expected soon to become a state-of-the-art electronic structure models for determination of energies and molecular properties of target state quality for single-configuration dominated molecular systems.

## **Some Recent Advances in Variational Energy Decomposition Analysis of Electronic Structure Calculations**

Martin Head-Gordon  
Department of Chemistry  
University of California, Berkeley  
Berkeley CA, USA

Intermolecular interactions are central to the formation of clusters, supramolecular interactions, and many aspects of the behavior of molecules in condensed phases. The relevant forces are well understood: permanent and induced electrostatics, Pauli repulsions, attractive dispersive interactions, and charge-transfer interactions. However, they are only uniquely defined at long range. Similar issues arise in understanding the chemical bond, where the components and net interaction are even larger. The purpose of this talk is to discuss several key issues associated with making a well-defined variational EDA based on modern electronic structure theory calculations, first for non-bonded interactions, and then for bonded interactions. The relevant theory will be discussed with an emphasis on new advances that appear to resolve many of the main formal issues. After that, a range of applications to non-bonded complexes, and a representative set of chemical bonds will be presented.

.

## From Graphene to Graphyne, Fullerenes, Fulleroids, Gaudienes and their Golden Duals.

**Peter Schwerdtfeger<sup>1</sup>, Lukas Trombach<sup>1</sup>, Dage Sundholm<sup>2</sup>,  
Andreas Hauser<sup>3</sup>, Lukas Wirz<sup>4</sup>, and James Avery<sup>5</sup>**

<sup>1</sup>*The New Zealand Institute for Advanced Study and the Institute for Natural and  
Mathematical Sciences, Massey University, Auckland, New Zealand*

<sup>2</sup>*University of Helsinki, Department of Chemistry, Helsinki, Finland.*

<sup>3</sup>*Institut für Experimentalphysik, TU Graz, Graz, Austria*

<sup>4</sup>*CTCC, Department of Chemistry, University of Oslo, Oslo, Norway*

<sup>5</sup>*Computer Science Department, Copenhagen University, Copenhagen, Denmark*

Graphene is a material with many potential applications. For example, we can introduce nano-holes into graphene membranes for the design of efficient molecular sieves [1]. Our research group has recently succeeded to efficiently separate He-3 from He-4 by quantum tunneling [2]. Graphene can also be wrapped around a sphere to form fullerene structures. 12 pentagons have to be however introduced to satisfy Euler's polyhedral formula [3]. Graphene can also be modified to graphyne by vertex insertions. From this one obtains new fullerene structures called gaudienes [4]. Such structures can be explained using topology and graph theory which form the basis of our general-purpose computer program *Fullerene* that creates accurate 3D structures for any fullerene isomer. It also creates dual structures corresponding to a triangulation of a sphere. Such a dual structure has recently been found experimentally in Lai-Shang Wang's group at Brown University, and consists of 16 gold atoms on a sphere. These unique triangulations of a sphere related to fullerene duals have exactly 12 vertices of degree five. The icosahedral hollow gold cages previously postulated are related to halma transforms of C<sub>20</sub> [5]. This dual mapping also relates the (chiral) gold nanowires observed to the (chiral) carbon nanotubes. In fact, the Mackay icosahedra well known in gold cluster chemistry are related to the dual halma transforms of the smallest possible fullerene C<sub>20</sub>.

[1] A. Hauser, P. Schwerdtfeger, *Phys. Chem. Chem. Phys.* **14**, 13292 (2012).

[2] A. Hauser, P. Schwerdtfeger, *J. Phys. Chem. Lett.* **3**, 209 (2012).

[3] P. Schwerdtfeger, L. Wirz, J. Avery, *Wiley Interdisciplinary Reviews (WIRE): Computational Molecular Science* **5**, 96 (2015).

[4] D. Sundholm, L. N. Wirz, P. Schwerdtfeger, *Nanoscale* **7**, 15886 (2015).

[5] L. Trombach, S. Rampino, L.-S. Wang, P. Schwerdtfeger, *Chem. Europ. J.* **22**, 8823 (2016).

## Graphene nanoribbon based electronics and spintronics

Kwang S. Kim<sup>1</sup>

<sup>1</sup>*Center for Superfunctional Materials, Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Korea*

Modulation of orbitals in molecules or bands in materials is useful to tune the electron/spin transport in molecular/materials systems. Here, I discuss electron/spin transport and molecular fingerprinting using graphene nanoribbon (GNR) with density functional theory coupled to non-equilibrium Green function theory. By utilizing Fano-resonance driven 2-dimensional molecular electronics spectroscopy, the hyper-sensitive quantum conductance spectra of a GNR placed across a fluidic nanochannel can lead to fast DNA sequencing including cancerous methylated nucleobases detection [1, 2]. There was a difficulty in studying transport phenomena using the bottom-gate control of zigzag GNR (zGNR), because the chemical equilibrium between electrons in zGNR and electrodes requires electron reservoir. It is now possible to study the top/back-gate effects in field effect transistor (FET) under external potential using the iso-chemical potential approach [3]. It is also interesting to study graphene edges which show intriguing spin states [4]. By utilizing magnetic field control, a GNR spin-valve device shows the super magneto-resistance behavior as a spin filter which transmits near perfect spin-polarized current [5]. Such an intriguing behavior can also be obtained for chemically edge functionalized zGNRs under transverse electric field without magnetic field control [6]. Since on-site Coulomb repulsion governs spin splitting under electron accumulation/depletion, the current-voltage characteristics of the edge-modified zGNR under in-plane transverse electric field show the perfect spin filtering as a chemical spintronic device. Alteration of magnetic properties of zGNR by tuning the transverse electric field would be a promising method to construct magnetic/nonmagnetic switches.

- [1] S. K. Min, W. Y. Kim, Y. Cho, K. S. Kim, *Nat. Nanotechnol.* **6**, 162 (2011).
- [2] A. C. Rajan, M. R. Rezapour, J. Yun, Y. Cho, W. J. Cho, S. K. Min, G. Lee, K. S. Kim, *ACS Nano* **8**, 1827 (2014).
- [3] J. Yun, G. Lee, K. S. Kim, *J. Phys. Chem. Lett.* **7**, 2478 (2016).
- [4] C. Hyun, J. Yun, W. J. Cho, C. W. Myung, J. Park, G. Lee, Z. Lee, K. Kim, and K. S. Kim, *ACS Nano* **9**, 4669 (2015).
- [5] W. Y. Kim, K. S. Kim, *Nat. Nanotechnol.* **3**, 408 (2008).
- [6] M. R. Rezapour, J. Yun, G. Lee, K. S. Kim, *J. Phys. Chem. Lett.* **7**, 5049 (2016).

**Polymer/fullerene solar cells: Characterization of the intermolecular interactions and interfacial charge-transfer states**

**Jean-Luc Bredas**

*School of Chemistry and Biochemistry and  
Center for Organic Photonics and Electronics  
Georgia Institute of Technology  
Atlanta, Georgia 30332-0400*

In this presentation, we will first introduce the working principles of organic solar cells and rationalize the need for the presence of both an electron-donor component (usually a conjugated polymer or oligomer) and an electron-acceptor component (often a fullerene derivative).

We will then discuss the impact that inter-molecular arrangements and interactions at the polymer/fullerene interfaces have on the performance of bulk-heterojunction solar cells. We will describe the results of combined electronic-structure calculations and molecular-dynamics simulations. In particular, we will examine:

- (i) the propensity of the fullerene molecules to dock preferentially on top of the electron-poor moiety or electron-rich moiety of the polymer, as a function of the nature and location of the polymer side chains; and
- (ii) the impact that the packing arrangements have on the energetic distribution of the charge-transfer interfacial electronic states and their localization/delocalization characteristics.

This work is supported by ONR (Award N00014-14-1-0580 for the Center for Advanced Organic Photovoltaics and Award N00014-17-1-2208).



## Advances in Computing Charge Carrier Dynamics from First Principles

**Marco Bernardi<sup>1</sup>**

<sup>1</sup>*Department of Applied Physics and Materials Science, California Institute of Technology,  
1200 E California Blvd, Pasadena, United States*

Calculations of charge transport and ultrafast dynamics have relied on heuristic approaches for the past several decades. Recent progress in combining density functional theory and related methods with kinetic equations, such as the Boltzmann transport equation (BTE), are enabling spectacular advances in computing carrier dynamics in materials from first principles. A special role is played by the interaction between charge carriers and lattice vibrations, also known as the electron-phonon (e-ph) interaction, which dominates carrier dynamics at room temperature and for carrier energies within a few eV of the band edges.

We will discuss our recently developed methods to compute and interpolate e-ph scattering processes on ultra-fine Brillouin zone grids, and then show how these developments enable new computations of charge transport and ultrafast dynamics, including:

- 1) Accurate ab initio calculations of the carrier mobility in polar semiconductors [1] and oxides, including new methods to treat complex materials with structural phase transitions (e.g., perovskites).
- 2) The ultrafast dynamics and detailed scattering mechanisms of excited carriers, achieved using a new parallel algorithm to propagate in time the BTE [2]. Its application to gallium nitride sheds light on a key open problem in light emission technologies.
- 3) Dynamical processes of relevance in valleytronics, including valley lifetimes and inter-valley scattering as a function of temperature. We compute timescales ranging from fs to ms, which push the accuracy of our methods and provide a microscopic understanding of recent diamond valleytronics experiments.

We conclude by outlining code development efforts, open problems and future directions.

[1] J.-J. Zhou and M. Bernardi *Phys. Rev. B (Rapid Commun.)* **94**, 201201 (2016).

[2] V. Jhalani, J.-J. Zhou and M. Bernardi *Nano Letters* (2017); Accepted. Preprint available at arXiv:1703.07880 [cond-mat.mtrl-sci]

## Simulation of electron transfer on the nanoscale: from molecules to biomolecules to materials

Jochen Blumberger<sup>1</sup>

<sup>1</sup>*Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK*

Electron transfer (ET) and transport processes are of outstanding importance both in Nature (photosynthesis, respiration) and the renewable energy industry (photovoltaics, solar fuels). While a hierarchy of theoretical descriptions for ET exist, ranging from Marcus-type rate theories to non-adiabatic dynamics with classical and quantum nuclei, virtually all approaches require reasonably accurate estimates of electronic coupling matrix elements between electron donor and acceptor, denoted  $H_{ab}$ . In my presentation I will describe our recent efforts in establishing high-level ab-initio databases for electronic coupling matrix elements between pi-conjugated organic molecules (denoted HAB11[1] and HAB7[2]) and discuss the performance of computationally more efficient DFT approaches and of an ultrafast descriptor based method[3]. I will then present applications of the validated DFT approaches to the calculation of rates for hole tunneling between F-centre defects in metal oxides[4] and to calculation of charge transport rates in biological nanowires composed of multi-heme proteins[5]. While in these systems the charge carrier is spatially localized hopping from one site to the next, we show that this picture is no longer valid for charge transport in textbook single-crystalline organic semiconducting materials such as rubrene, pentacene or C<sub>60</sub>. Here I will present results obtained from explicit propagation of the electron and nuclear dynamics as obtained from an efficient site-basis implementation of Tully's fewest switches surface hopping with ultrafast estimation of electronic coupling matrix elements as one of the main features[6].

- [1] A. Kubas, F. Hoffmann, A. Heck, H. Oberhofer, M. Elstner, and J. Blumberger, *J. Chem. Phys.* **140**, 104105 (2014).
- [2] A. Kubas, F. Gajdos, A. Heck, H. Oberhofer, M. Elstner, and J. Blumberger, *Phys. Chem. Chem. Phys.* **17**, 14342 (2015).
- [3] F. Gajdos, S. Valner, F. Hoffmann, J. Spencer, M. Breuer, A. Kubas, M. Dupuis, and J. Blumberger, *J. Chem. Theory Comput.* **10**, 4653 (2014).
- [4] K. McKenna and J. Blumberger, *Phys. Rev. B* **86**, 245110 (2012).
- [5] M. Breuer, K. M. Rosso, and J. Blumberger, *Proc. Nat. Acad. Sci. USA* **111**, 611 (2014).
- [6] J. Spencer, F. Gajdos, and J. Blumberger, *J. Chem. Phys.* **145**, 64102 (2016).

## Subsystem and approximate DFT approaches for electronically excited states of complex molecular systems

**Pablo Lopez-Tarifa<sup>1</sup>, Robert Rüger<sup>1,2</sup>, Lucas Visscher<sup>1</sup>**

<sup>1</sup>*Section Theoretical Chemistry, Department of Chemistry and Pharmaceutical Sciences, Vrije Universiteit Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands*

<sup>2</sup>*Scientific Computing & Modelling NV, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands*

In this talk I will discuss the calculation of electronically excited states using subsystem density functional theory and tight-binding approaches. These techniques are sufficiently fast to allow for extensive conformational sampling of complex molecular systems and can therefore be combined with classical molecular dynamics simulations. I will briefly discuss the workflow automatization tools that we have developed for this purpose, but will largely focus on electronic structure aspects of these techniques.

As an example of our use of subsystem methods, I will discuss the calculation of the chromophore excitations and their couplings in natural light-harvesting systems [1]. While these techniques can combine DFT with wave function techniques [2], I will in this talk focus on the possibilities to include in this approach also the very efficient TD-DFTB [3,4] method.

- [1] P. López-Tarifa, N. Liguori, N. van den Heuvel, R. Croce, and L. Visscher, *submitted*
- [2] S. Hoefener, A.S.P. Gomes, L. Visscher, J. Chem. Phys. **136** 044104 (2012).
- [3] R. Rüger, E. van Lenthe, T. Heine, L. Visscher, J Chem Phys. **144**, 184103. (2016).
- [4] R. Rüger, T. Niehaus, E. van Lenthe, T. Heine, L. Visscher, J Chem Phys. **145** 184102 (2016).

## **Confronting Memory-Dependence in Time-Dependent Density Functional Theory**

**Neepa T. Maitra<sup>1</sup>**

*<sup>1</sup>Department of Physics and Astronomy, Hunter College and the Graduate Center Physics Program City University of New York, 695 Park Avenue, New York, NY 10065, USA*

The exchange-correlation potential of time-dependent density functional theory depends on the history of the density, the initial wave function, and the initial choice of Kohn-Sham wave function. This memory-dependence plays an important role in non-perturbative electron dynamics, yet is missing in all approximations being used today. We investigate a number of orbital-dependent functional approximations that we derive from a decomposition of the exact time-dependent exchange-correlation potential into kinetic and interaction components, and analyse the root of the errors on a series of model systems. The performance of each approximation depends critically on the choice of initial Kohn-Sham wave function. This work paves the way for practical non-adiabatic functional approximations that should improve the accuracy and reliability of TDDFT for applications far from the ground state.

## Multicomponent Density Functional Theory: Integrating Electronic and Nuclear Quantum Effects

Sharon Hammes-Schiffer

*Department of Chemistry, University of Illinois at Urbana-Champaign, 600 South Mathews Avenue, Urbana, Illinois, 61801 USA*

Nuclear quantum effects such as zero point energy, nuclear delocalization, and tunneling play an important role in a wide range of chemical processes. Typically density functional theory (DFT) calculations invoke the Born-Oppenheimer approximation and include nuclear quantum effects as corrections following geometry optimizations. The nuclear-electronic orbital (NEO) multicomponent DFT method treats select nuclei, typically protons, quantum mechanically on the same level as the electrons [1-3]. A major challenge has been the design of electron-proton correlation functionals that produce even qualitatively accurate proton densities. Recently an electron-proton correlation functional, epc17, was derived analogously to the Colle-Salvetti formulation for electron correlation and was implemented within the self-consistent-field procedure of multicomponent DFT to treat electrons and protons in a consistent manner [4]. This NEO-DFT/epc17 method produces accurate proton densities and proton affinities for molecular systems with a computational expense similar to that of standard electronic DFT. This approach includes the nuclear quantum effects of protons during geometry optimizations and accurately describes the impact of proton delocalization and zero point energy on optimized geometries. NEO-DFT/epc17 is a promising approach for the inclusion of nuclear quantum effects and non-Born-Oppenheimer effects in calculations of proton affinities,  $pK_a$ 's, optimized geometries, minimum energy paths, reaction dynamics, tunneling splittings, and vibronic couplings for a wide range of chemical applications.

- [1] A. Chakraborty, M. V. Pak, S. Hammes-Schiffer, *Phys. Rev. Lett.* **101**, 153001 (2008).
- [2] A. Chakraborty, M. V. Pak, S. Hammes-Schiffer, *J. Chem. Phys.* **131**, 124115 (2009).
- [3] T. Culpitt, K. R. Brorsen, M. V. Pak, S. Hammes-Schiffer, *J. Chem. Phys.* **145**, 044106 (2016).
- [4] Y. Yang, K. R. Brorsen, T. Culpitt, M. V. Pak, S. Hammes-Schiffer, submitted.

## Potential Energy Surfaces and Berry Phases Beyond the Born-Oppenheimer Approximation: A New Perspective on Non-Adiabatic Dynamics

E.K.U. Gross

*Max Planck Institute of Microstructure Physic, Weinberg 2, Halle (Saale), Germany*

Some of the most fascinating phenomena in Chemistry and Physics, such as the process of vision, exciton dynamics in photovoltaic systems, as well as phonon-driven superconductivity occur in the regime where the non-adiabatic coupling of electronic and nuclear motion is essential. To tackle such situations one has to face the full Hamiltonian of the complete system of electrons and nuclei. We deduce an exact factorization [1] of the full electron-nuclear wavefunction into a purely nuclear part and a many-electron wavefunction which parametrically depends on the nuclear configuration and which has the meaning of a conditional probability amplitude. The equations of motion for these wavefunctions lead to a unique definition of *exact* potential energy surfaces as well as *exact* geometric phases, both in the time-dependent and in the static case. We discuss a case where the exact Berry phase vanishes although there is a non-trivial Berry phase for the same system in Born-Oppenheimer approximation [2], implying that in this particular case the Born-Oppenheimer Berry phase is an artifact. In the time-domain, whenever there is a splitting of the nuclear wavepacket in the vicinity of an avoided crossing, the exact time-dependent surface shows a nearly discontinuous step [3]. This makes the classical force on the nuclei jump from one to another adiabatic surface, reminiscent of Tully surface hopping algorithms. Based on this observation, we propose novel mixed-quantum-classical algorithms which provide a rather accurate, much improved (over surface hopping) description of decoherence [4]. This is demonstrated for the photo-induced ring-opening of oxirane [5]. We present a multi-component density functional theory [6] that provides an avenue to make the fully coupled electron-nuclear system tractable for large systems. Finally, we apply the concept of exact factorization to a purely electronic wave function, thereby separating, in a formally exact way, fast degrees of freedom (the core electrons) from slow degrees of freedom (electrons that ionize or produce harmonics). This allows us to deduce, in a controlled way, the so-called single-active-electron approximation and systematic improvements thereof [7].

- [1] A. Abedi, N.T. Maitra, E.K.U. Gross, Phys. Rev. Lett. 105, 123002 (2010).
- [2] S.K. Min, A. Abedi, K.S. Kim, E.K.U. Gross, Phys. Rev. Lett. 113, 263004 (2014).
- [3] A. Abedi, F. Agostini, Y. Suzuki, E.K.U. Gross, Phys. Rev. Lett. 110, 263001 (2013).
- [4] S.K. Min, F. Agostini, E.K.U. Gross, Phys. Rev. Lett. 115, 073001 (2015).
- [5] F. Agostini, S.K. Min, I. Tavernelli, E.K.U. Gros, J. Phys. Chem. Letters (2017).
- [6] R. Requist, E.K.U. Gross, Phys. Rev. Lett. 117, 193001 (2016).
- [7] A. Schild, E.K.U. Gross, Phys. Rev. Lett. 118, 163202 (2017).

## Adiabatic connection approach toward including dynamic correlation for multireference wavefunctions

*Katarzyna Pernal*

*Institute of Physics, Lodz University of Technology  
ul. Wolczanska 219, 90-924 Lodz, Poland*

It is already well understood that including dynamic correlation in multireference approaches is necessary to obtain quantitative results in description of electronic structures of molecules. It remains a problem, however, how to account or the missing part of electron correlation in efficient, stable, and size-consistent manner. One of the most common methods - the truncated configuration interaction (CI) expansion - breaks size-consistency and may lead to factorial scaling. Perturbation methods, on the other hand, are problematic due to ambiguities in choosing zeroth-order effective Hamiltonian, difficulties with preserving size-extensivity and possible erratic behaviour resulting from intruder state problem.

Recently, we have successfully proposed to employ adiabatic connection (AC) formalism to account for electron correlation in a wide family of multireference wavefunctions that can be recast as antisymmetrized product of strongly orthogonal group product functions [1]. The AC formalism, used in connection with the Extended Random Phase Approximation [2], provides an efficient and stable method for computing correlation energy. The nearly linear behaviour of the AC integrand affords for simple interpolation schemes simplifying the AC correlation energy expression even further. We have shown that the AC construction employed for the GVB (generalized valence bond) reference wavefunction leads to obtaining excellent description of molecules in both weak and strong correlation regimes.

### References

- [1] K. Pernal, *submitted*, (2017).
- [2] K. Chatterjee, K. Pernal *J. Chem. Phys.* **2012**, 137, 204109.



## 4-component relativistic calculations with periodic boundary conditions

**Kenneth Ruud<sup>1</sup>, Marius Kadek<sup>1</sup>, Michal Repisky<sup>1</sup>, Stanislav Komorovsky<sup>2</sup>**

<sup>1</sup>*Centre for Theoretical and Computational Chemistry, Department of Chemistry, University of Tromsø — The Arctic University of Norway, 9037 Tromsø, Norway*

<sup>2</sup>*Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dubravská cesta 9, 84536 Bratislava 45, Slovak Republic*

Relativistic effects are known to be important for the electronic structure and properties of compounds containing heavy elements. [1] Methods for calculating relativistic effects at the four-component level of theory are now well developed, allowing fairly large molecules of experimental interest to be studied using four-component methodology. [2]

However, the majority of the four-component studies consider only molecules in the gas phase. However, many compounds containing heavy elements exist as (molecular) solids, and there are to date no published methodology that allows four-component calculations to be calculated including the effects of periodic boundary conditions.

I will in this talk present the theoretical framework for four-component relativistic density-functional theory and Hartree–Fock calculations including periodic boundary conditions. The approach uses Gaussian atomic basis functions building on the pioneering work of Pisani and Dovesi in the non-relativistic domain, [3] allowing for an all-electron description of the solid material. This will allow us to study molecular properties that depend on the electron density close to the nucleus, where relativistic effects are the largest, such as for instance electric field gradients or core-electron excitations observed in X-ray spectroscopy.

A key element to ensure computational efficiency is the use of Clifford algebra to accelerate the relativistic molecular electronic structure calculations based on the four-component Dirac–Coulomb Hamiltonian. [4] The properties of the algebra can be used to significantly reduce the floating point operations and memory requirements associated with the integral evaluation and the construction of Fock matrices.

In the talk, I will outline the basic features of the approach and present the first relativistic four-component calculations of molecular systems with periodic boundary conditions applied.

[1] P. Pyykkö, *Ann. Rev. Phys. Chem.* **63**, 45 (2012).

[2] J. Vicha, J. Novotny, M. Straka, M. Repiský, K. Ruud, S. Komorovsky and R. Marek, *Phys. Chem. Chem. Phys.* **17**, 24944 (2015).

[3] C. Pisani and R. Dovesi, *Int. J. Quantum Chem.* **17**, 501 (1980).

[4] M. Repisky, S. Komorovsky, K. Ruud, *in preparation*.

## Recent Results on Compounds of Heavy, and Heaviest Elements

**Pekka PYYKKÖ<sup>a</sup>**

<sup>a</sup>*Department of Chemistry, University of Helsinki, POB 55 (A.I. Virtasen aukio 1), 00014 Helsinki, Finland;*

*e-mail: [Pekka.Pyykko@helsinki.fi](mailto:Pekka.Pyykko@helsinki.fi)*

### Abstract

Three points will be made:

1) Although the atomic ground state of Element 103, Lr, or lawrencium differs from that of Lu (Element 71, or lutetium) in being  $(p_{1/2})^1$  instead of  $d^1$ , the electronic structures of a number of *molecules* of the two elements remain very similar [1]. The Periodic Table is about chemistry.

2) In the suggested short-row Periodic Table for the Elements 1-172, the Elements 121-138 were nominally assigned to a 5g series [2]. In a study of their hexafluorides, it was indeed found that the 5g populations increase linearly from E125 to E129 or Group 7 to Group 11 [3]. Notice that an oxidation state of +6 and an octahedral structure were then imposed. Fully relativistic four-component density functional methods were used in the DIRAC software.

3) In an estimate of the nuclear stopping power of antiprotons ( $p^-$ ) in matter [4], the nuclei are not particularly heavy, but one of the 'electrons', namely the antiproton, is. Actually the dynamics of the  $p^-$  is treated using molecular dynamics, in a potential obtained for the rest from quantum chemistry. Note that the low-lying, s-states of the antiproton would lead to annihilation of a  $p$  and the  $p^-$ , but the high-angular-momentum states are not annihilated. This stopping power is important in the production of antimatter (combining  $p^-$  with  $e^+$ ). The conclusion is that the 'nuclear' term in the stopping power is considerably larger for the antiproton than for the proton. Although we deal with scattering rather than bound states of the (anti)proton, this could be termed *antiproton chemistry*.

References:

- [1] W-H. Xu, P. Pyykkö, Phys. Chem. Chem. Phys. **18** (2016) 17351.
- [2] P. Pyykkö, Phys. Chem. Chem. Phys. **13** (2011) 161.
- [3] J-P. Dognon, P. Pyykkö, Angew. Chem. Int. Ed. **56** (2017). DOI: 10.1002/anie.201701609.
- [4] K. Nordlund, D. Sundholm, P. Pyykkö, D. Martinez Zambrano, F. Djurabekova, Phys. Rev. A (submitted).

## New Scenarios for Strongly Correlated Electrons

Wenjian Liu<sup>a</sup> and Mark R. Hoffmann<sup>b</sup>

<sup>a</sup>College of Chemistry and Molecular Engineering, Peking University, Beijing, China

<sup>b</sup>University of North Dakota, Grand Forks, USA

**Keywords:** strong correlation; static-dynamic-static; iterative configuration interaction

**Abstract:** According to when the static and dynamic components of electron correlation are treated, the available correlated wave function methods can be classified into three families, viz., "static-then-dynamic", "dynamic-then-static", and "static-dynamic-static (SDS)" [1]. In this lecture, I will discuss two novel approaches: (1) nonorthogonal state interaction (NOSI) [2,3] of the "dynamic-then-static" family. Here, dynamic correlation (at any level of methodology) is first built into each individually optimized non-Aufbau model functions before the diagonalization in the space of nonorthogonal, dynamically correlated states is performed for static correlation; (2) *restricted* SDS[4], which employs *the same number* ( $N_p$ ) of primary, secondary and external states for describing the static, dynamic, and again static components of correlation. That is, the secular equation to be diagonalized is of dimension  $3N_p$ , irrespective of the numbers of correlated electrons and orbitals. Even the lowest-order realization of this seemingly *restricted* SDS framework, i.e., SDSPT2, is already very accurate for classic test problems of variable degeneracies [4,5], whereas a high-order realization, i.e., iCI (iterative Configuration Interaction), can converge monotonically and quickly to full CI from above, even when a rather poor reference is taken as the start [1]. Time permitting, I will also highlight fundamental problems pertinent to relativistic explicitly correlated wave function methods [6,7].

1. W. Liu and M. R. Hoffmann, iCI: iterative CI toward full CI, J. Chem. Theory Comput. 2016, 12, 1169; (E) 2016, 12, 3000.
2. W. Liu, Ideas of relativistic quantum chemistry, Mol. Phys. 2010, 108, 1679.
3. C. Huang and W. Liu, A generic nonorthogonal state interaction approach for strongly correlated electrons (unpublished).
4. W. Liu and M. R. Hoffmann, SDS: the 'static-dynamic-static' framework for strongly correlated electrons, Theor. Chem. Acc. 2014, 133, 1481.
5. Y. Lei, W. Liu, and M. R. Hoffmann, Further development of SDSPT2 for strongly correlated electrons, Mol. Phys. (DOI: 10.1080/00268976.2017.1308029).
6. Z. Li, S. Shao, and W. Liu, Relativistic explicit correlation: Coalescence conditions and practical suggestions, J. Chem. Phys. 2012, 136, 144117.
7. W. Liu, S. Shao, and Z. Li, Relativistic explicit correlation: problems and solutions, in *Handbook of Relativistic Quantum Chemistry*, ed. W. Liu (Springer, 2016).

## Variational perturbation theory in geochemistry

Trond Saue

*Laboratoire de Chimie et Physique Quantiques,  
UMR 5626 CNRS — Université Toulouse III-Paul Sabatier, 118 route de Narbonne,  
F-31062 Toulouse, France*



In my presentation I will discuss the following questions

1. Can the effect of nuclear size be observed in rovibrational spectroscopy ?
2. What is the possible impact on geochemistry ?
3. What is the identity of the two gentlemen in the photograph and their connection ?

[1] S. Knecht and T. Saue, *Chem. Phys.* **401**, 10 (2012).

[2] A. Almoukhalalati, A. Shee and T. Saue, *PCCP* **18**, 15406 (2016).

## Characterization of reactive high-valent transition-metal complexes

**Marcel Swart<sup>1,2</sup>, Wesley R. Browne<sup>3</sup>, Aidan R. McDonald<sup>4</sup>, A. S. Borovik<sup>5</sup>**

<sup>1</sup>ICREA, Pg. Lluís Companys 23, 08010 Barcelona Spain

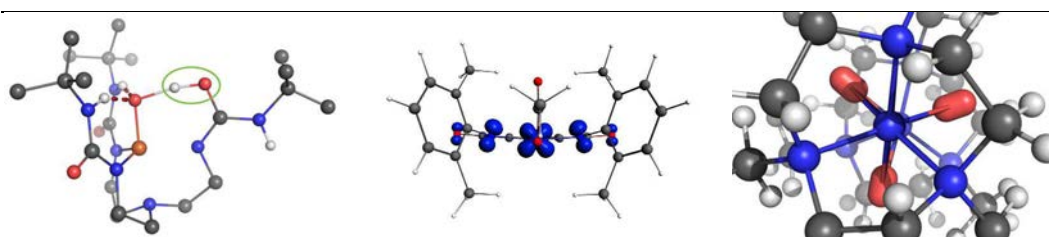
<sup>2</sup>IQCC & Dept. Chem., Univ. Girona, Campus Montilivi (Ciències), 17003 Girona, Spain

<sup>3</sup>Univ. Groningen, Stratingh Institute, Nijenborgh 4, 9747 AG Groningen, Netherlands

<sup>4</sup>Trinity College Dublin, School of Chemistry, College Green, Dublin, Ireland

<sup>5</sup>Univ. California Irvine, Dept. Chemistry, California 92697, United States

Oxidation processes of hydrocarbons in a selective, efficient and environment-friendly manner remains one of the major challenges at present today.[1] The majority of these studies is based on experiment, and computational chemistry plays sometimes an important role,[2-3] in giving a description of e.g. spectroscopy or transition state structures to lead to a deeper understanding of what is going on. This is in particular true for the influence of the spin state on reactivity.[3] The oxidation reactions on hydrocarbons usually involve high-valent metal-hydroxo ( $\text{Fe}^{\text{IV}}\text{-OH}$ ,  $\text{Ni}^{\text{III}}\text{-OH}$ )[4-5] or metal-oxo ( $\text{Fe}^{\text{IV}}\text{=O}$ ,  $\text{Ni}^{\text{IV}}\text{=O}$ )[6] species. Here I will give an overview of the spin-state consistent tools needed[2] and how these can be used for determining oxidation states,[5-7] where the proton goes in a high-valent iron(IV)-hydroxo complex,[4] based on a consistent and accurate computational description of IR, Raman, UV-Vis, and Mössbauer spectroscopy.



Financial support from COST (H2020), GenCat and MINECO is greatly acknowledged.

### References

- [1] S.T. Kleespies, W.N. Oloo, A. Mukherjee, L. Que, *Inorg. Chem.* **2015**, *54*, 5053.
- [2] M. Swart, M. Gruden, *Acc. Chem. Res.* **2016**, *49*, 2690.
- [3] M. Swart, M. Costas, *Spin states in Biochemistry and inorganic chemistry: Influence on Structure and Reactivity*. Wiley, Chichester, **2015**, ISBN 978-1-118-89831-4.
- [4] E.A. Hill, A.C. Weitz, E. Onderko, A. Romero-Rivera, Y. Guo, M. Swart, E.L. Bominaar, M.T. Green, M.P. Hendrich, D.C. Lacy, A.S. Borovik, *J. Am. Chem. Soc.* **2016**, *138*, 13143.
- [5] P. Pirovano, E. Farquhar, M. Swart, A.R. McDonald, *J. Am. Chem. Soc.* **2016**, *138*, 14362.
- [6] S.K. Padamati, D. Angelone, A. Draksharapu, G. Primi, D.J. Martin, M. Tromp, M. Swart, W.R. Browne, *J. Am. Chem. Soc.* **2017**, *ASAP*, DOI 10.1021/jacs.7b04158.
- [7] M. Swart, *Chem. Commun.* **2013**, *49*, 6650.

## Chemical Reaction Simulations on CO<sub>2</sub> Chemical Absorption Process

Hiromi Nakai<sup>1,2,3,4</sup>

<sup>1</sup>*Department of Chemistry and Biochemistry, School of Advanced Science and Engineering,  
Waseda University, Tokyo 169-8555, Japan*

<sup>2</sup>*Research Institute for Science and Engineering, Waseda University, Tokyo 169-8555,  
Japan*

<sup>3</sup>*CREST, Japan Science and Technology Agency, Tokyo 102-0075, Japan*

<sup>4</sup>*ESICB, Kyoto University, Kyoto 615-8520, Japan*

Global warming, which is caused by increasing greenhouse gases such as CO<sub>2</sub>, is a big environmental issue now. The CO<sub>2</sub> capture and storage (CCS) techniques separate CO<sub>2</sub> from exhaust gas of fossil fuel power plants, and then store it underground. Among several CCS techniques, the CO<sub>2</sub> chemical absorption process using amine solution attracts attention as the most practical method. The overall chemical reactions occurring in the absorption and regeneration towers are the same except for the directions of the reactions, which are controlled by temperature: namely, ~40 and ~120 degrees Celsius, respectively. The present study analyzed the CO<sub>2</sub> chemical absorption process using amine solution from the dynamic point of view [1]. The reaction dynamics was examined by our massive parallel computational code, i.e., DC-DFTB-K [2], which combined the linear-scaling divide-and-conquer (DC) technique with the density functional based tight binding (DFTB) method as being useful for the K computer.

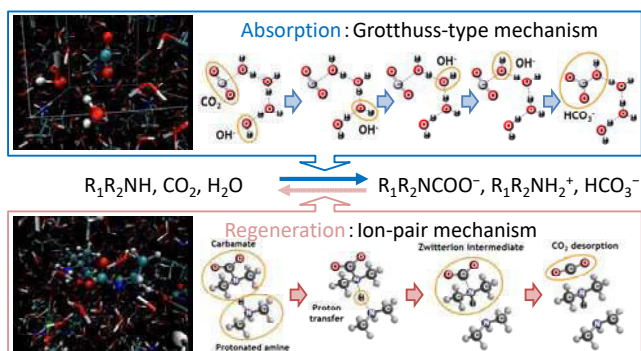


Fig. 1. Reaction mechanisms for CO<sub>2</sub> absorption and regeneration processes proposed by the DC-DFTB-MD simulations.

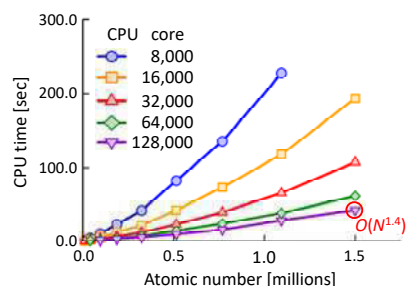


Fig. 2. CPU times for DC-DFTB energy calculations of water clusters.

[1] H. Nakai, Y. Nishimura, T. Kaiho, T. Kubota, H. Sato, *Chem. Phys. Lett.* **647**, 127 (2016).

[2] H. Nishizawa, Y. Nishimura, M. Kobayashi, S. Irle, H. Nakai, *J. Comput. Chem.* **37**, 1983 (2016).

## **New Aspects in the Simulations of Heterogeneous Catalysis**

**N. Lopez<sup>1</sup>**

*<sup>1</sup>Institute of Chemical Research of Catalonia, Av. Països Catalans, 16, 43007 Tarragona  
Spain*

In the present talk I will describe the progress in different areas of the modeling in heterogeneous catalysis. I will address novel problems related to the properties of oxides and a new set of descriptors that we have developed for these materials. In an alternative direction I will describe the novel properties of decorated nanoparticles that open a complete new area of research for which suitable structure-activity relationships have not been developed yet.

## **$\sigma$ -hole Bonding in the Catalysis of Nanostructured Metals: Surface Properties as Guides to Local Reactivity**

**Joakim Halldin Stenlid and Tore Brinck**

<sup>1</sup> *Applied Physical Chemistry, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden. [tore@kth.se](mailto:tore@kth.se)*

Nanostructured metals often exhibit vastly different catalytic properties than crystalline surfaces. The most prominent example is gold, which is chemically inert in crystalline form, whereas gold nanoparticles are excellent catalysts for many reactions. The nanostructural effects depend on low-coordinated atoms with high binding affinity for the reactants, typically Lewis-bases. However, the physical basis behind the correlation between coordination number and binding strength has not been fully resolved.

The molecular electrostatic potential [ $V(\mathbf{r})$ ] has been used extensively to analyze chemical reactivity and intermolecular interactions. Brinck et al. demonstrated already in 1992 that the interactions of halogens with Lewis bases, i.e. halogen bonding, can be explained by the presence of surface maxima in  $V(\mathbf{r})$  at the end of the halogen atom along the extension of the bond [1]. Clark et al. later introduced the  $\sigma$ -hole as a denotation of the positive end-region [2]. Murray and Politzer extended  $\sigma$ -hole bonding to compounds of group IV-VII elements [3]. Here we show that the catalytically active sites of nanostructured metals can be identified as  $\sigma$ -holes. Low-coordinated metal atoms typically have associated areas of positive surface  $V(\mathbf{r})$  and the surface maxima at these sites correlate with the catalytic activity. This is apparent from the surface  $V(\mathbf{r})$  of gold and platinum clusters; surface maxima are found at low-coordinated atomic sites, and their magnitudes increase in the order surfaces, edges and corners in agreement with the increasing catalytic activity. For smaller metal clusters, we have found good quantitative correlations between surface maxima and binding energies of Lewis bases.

Our studies indicate that electrostatics plays a key role in the binding events leading to catalysis, but that the interactions also have significant contributions from charge transfer and polarization. To account for these effects, we have defined the local electron attachment energy as complement to  $V(\mathbf{r})$  [4]. We will show that it provides similar site selectivity maps as  $V(\mathbf{r})$ , but generally gives better correlations for the binding energies of Lewis bases to metal nanoparticles, in particular for the binding of soft bases.

[1] T. Brinck, J. Murray, and P. Politzer, *Int. J. Quant. Chem.* **57** (1992)

[2] T. Clark, M. Hennemann, J.S. Murray, and P. Politzer, *J. Mol. Mod.* **13**, 291 (2007).

[3] J.S. Murray, P. Lane, and P. Politzer, *J. Mol. Mod.* **15**, 723 (2009).

[4] T. Brinck, P. Carlqvist, and J.H. Stenlid, *J. Phys. Chem. A* **120**, 10023 (2016).

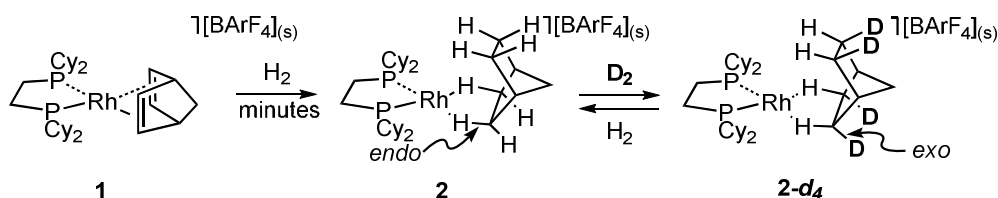


## Modelling Alkane $\sigma$ -Complexes in the Solid State

Tobias Krämer and Stuart A. Macgregor

*Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK*

$\sigma$ -alkane complexes have long been postulated as intermediates on the reaction pathway for C-H activation.[1] Such species are, however, notoriously unstable, making the direct observation of their reactivity extremely challenging. A step change in this area has come from the use of gas-solid reactivity developed by the Weller group as a means to prepare stable  $\sigma$ -alkane complexes.[2] Thus exposure of the alkene precursor  $[(\text{Cy}_2\text{P}(\text{CH}_2)_2\text{PCy}_2)\text{Rh}(\text{NBD})]\text{BAr}^{\text{F}}_4$ , **1** (NBD = norbornadiene,  $\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$ ), to  $\text{H}_2$  gas effects a crystal-to-crystal transformation to give the corresponding  $\sigma$ -alkane  $[(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2)\text{Rh}(\text{NBA})]\text{BAr}^{\text{F}}_4$ , **2** (NBA = norbornane). **2** proves to be stable for months allowing for its detailed spectroscopic characterization and reactivity studies.



This contribution will detail our use of periodic DFT calculations to model the formation, structure and reactivity of **2**. In particular the observation of reversible H/D exchange in **2** links a  $\sigma$ -alkane complex directly to a C-H bond activation event. Intriguingly, however, this occurs at the *exo*-positions implying significant rearrangement of the NBA ligand within the crystal lattice. The modelling of these process will be described along with parallel experimental studies that elucidate the details of these processes.[3]

[1] C. Hall, R. N. Perutz, *Chem. Rev.* **96**, 3125 (1996)

[2] S. D. Pike, A. L. Thompson, A. G. Algarra, D. C. Apperley, S. A. Macgregor, A. S. Weller, *Science* **337**, 1648 (2012)

[3] F. M. Chadwick, T. Krämer, T. Gutmann, N. H. Rees, A. L. Thompson, A. J. Edwards, G. Buntkowsky, S. A. Macgregor, A. S. Weller, *J. Am. Chem. Soc.* **138**, 13369 (2016)

## Directionality and the Role of Polarization in Electrostatic Catalysis

**Michelle L. Coote<sup>1</sup>, Ganna Gryn'ova<sup>1,2</sup>**

<sup>1</sup> *ARC Centre of Excellence for Electromaterials Science, Research School of Chemistry, Australian National University, Canberra ACT 2601 Australia*

<sup>2</sup> *Institut des Sciences et Ingénierie Chimiques, École polytechnique fédérale de Lausanne, CH-1015 Lausanne, Switzerland*

It is well known that the rate of redox reactions can be manipulated by means of an electrical potential gradient. However, as elegantly demonstrated by Shaik and co-workers, external electric fields should also be able to catalyse non-redox processes by electrostatically stabilizing the dipoles associated with charge-separated valence bond contributors of transition states, thereby enhancing resonance and lowering the barrier [1]. However, since these effects are directional in nature, implementing electrostatic catalysis in practice has been a challenge. Recently we have addressed this problem, and experimentally demonstrated practical electrostatic catalysis using two complementary approaches. First, we have used charged functional groups on the substrate, auxiliary or catalyst to deliver a localized oriented electric field that can be modulated by simple pH changes [2-3]. Second, with collaborators, we have used various surface chemistry techniques to control the orientation of reagents in an external electric field [4-5]. Interestingly, our own theoretical studies of some of these systems indicate that, due to polarization, electrostatic effects on reaction barriers and enthalpies actually have a significant non-directional component [6-7]. This suggests we may one day be able to design reactions where alignment in an electric field is not necessary for catalysis, thus broadening its scope. This presentation will briefly outline our progress toward practical electrostatic catalysis, but with a focus on the role of polarization in determining the strength of these effects.

[1] S. Shaik, D. Mandal, R. Ramanan, *Nat. Chem.* **2016**, 8, 1091-1098

[2] G. Gryn'ova, D.L. Marshall, S.J. Blanksby, M. L. Coote *Nat. Chem.* **2013**, 5, 474-481.

[3] M. Klinska, L. M. Smith, G. Gryn'ova, M.G. Banwell, M.L. Coote, *Chem. Sci.* **2015**, 6, 5623–5627.

[4] A.C. Aragonès, N.L. Haworth, N. Darwish, S. Ciampi, N.J. Bloomfield, G.G. Wallace, I. Diez-Perez and M.L. Coote, *Nature* **2016** 531, 88-91.

[5] L. Zhang; Y.B. Vogel, B.B. Noble, V.R. Gonçalves, N. Darwish, A.P. Le Brun, J.J. Gooding, G.G. Wallace, M.L. Coote, S. Ciampi, *J. Am. Chem. Soc.* **2016**, 38, 9611–9619.

[6] G. Gryn'ova, M.L. Coote *J. Am. Chem. Soc.* **2013**, 135, 15392-15403.

[7] Gryn'ova, G.; Coote, M.L. *Aust. J. Chem.* **2016**, 70, 367-372.

## Can carbon-13 NMR chemical shifts inform on reactivity in organometallic chemistry?

Odile Eisenstein<sup>1,2</sup>, Christophe Raynaud<sup>1</sup>, Christophe Copéret<sup>3</sup>

<sup>1</sup>*Institut Charles Gerhardt, UMR 5253 CNRS-Université de Montpellier, Université de Montpellier, 34095 Montpellier, France*

<sup>2</sup>*Centre for Theoretical and Computational Chemistry (CTCC), Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, 0315 Oslo, Norway*

<sup>3</sup>*Department of Chemistry and Applied Biosciences ETH Zürich, Vladimir-Prelog-Weg 1-5, 8093 Zürich, Switzerland*

NMR is one of the main characterization tools in molecular experimental chemistry, because it provides information on both structure and dynamics. Since the NMR chemical shift reflects the electronic structure of the NMR active nuclei in molecules, one may expect that NMR signatures can provide relation between structure and reactivity.

Here, we will present a combined experimental/computational study on the <sup>13</sup>C chemical shifts in metal alkylidene[1][2] and metallacyclobutane[3] complexes. Measurements of chemical shift tensors by solid-state NMR combined with four-component and/or two-component DFT calculations of these chemical shift tensors allows for a molecular orbital analysis of the principal components of the shielding tensors of the determinant carbons. With this analysis, we will discuss the relation between the factors that determine the shape of the shielding tensor of the metal-alkylidene and metallacyclobutane carbons and the nature and properties of metal-alkylidene and metallacyclobutane in the context of alkene metathesis.

[1] S. Halbert, C. Copéret, C. Raynaud, O. Eisenstein *J. Am. Chem. Soc.* **138**, 2261-2272 2016.

[2] K. Yamamoto, C. P. Gordon, W.-C. Liao, C. Copéret, C. Raynaud, O. Eisenstein *Angew. Chem. Int. Ed.* 2017, DOI: [10.1002/anie.201701537](https://doi.org/10.1002/anie.201701537)

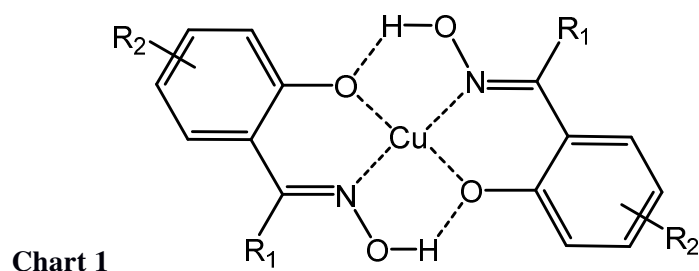
[3] C. P. Gordon, K. Yamamoto, W.-C. Liao, F. Allouche, R. A. Andersen, C. Copéret, C. Raynaud, O. Eisenstein, *ACS Central Science* 2017, DOI:10.102/acscentsci.7b00174

## Exploring NMR properties of paramagnetic Cu phenolic oxime complexes.

Michael Bühl, Zhipeng Ke, Daniel M. Dawson, Sharon E. Ashbrook

University of St. Andrews, School of Chemistry and Centre of Magnetic Resonance,  
North Haugh, St Andrews, UK

Copper (II) phenolic oxime complexes (Chart 1) are important intermediates during liquid-liquid extraction of copper from ores, being an alternative to energy-intensive techniques involving smelting. In conjunction with Density Functional Theory (DFT) calculations, solid-state nuclear magnetic resonance (NMR) can probe the local environment and give insights into the structure, symmetry and bonding in diamagnetic materials.<sup>[1]</sup> The paramagnetism of the Cu(II) complexes poses challenges to both experiment and theory. We have been using state-of-the-art DFT methods (at the PBE0-1/3/IGLO-II level) to simulate the  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts in these complexes and report on the detailed effect of temperature, intermolecular aggregation and substituents ( $\text{R}_1$  and  $\text{R}_2$  in Chart 1) on these parameters.<sup>[2]</sup>



- [1] S. E. Ashbrook, D. M. Dawson, J. M. Griffin, in *Local Structural Characterisation: Inorganic Materials Series*, (Eds.: D. W. Bruce, D. O'Hare, R. I. Walton), Wiley, West Sussex, 1st Ed., pp. 1–88 (2013).
- [2] (a) M. Bühl, S. E. Ashbrook, D. M. Dawson, R. A. Doyle, P. Hrobárik, M. Kaupp, I. A. Smellie, *Chem. Eur. J.* **22**, 15328 (2016); (b) S. E. Ashbrook, G. P. M. Bignami, M. Bühl, D. B. Cordes, D. M. Dawson, R. A. Doyle, Z. Ke, F. M. Mack, A. M. Z. Slawin, I. A. Smellie, in preparation.

## NMR spectroscopic parameters of HB containing molecules and aggregates of DNA base pairs

**Fernando Martínez, Marcos Montero and Gustavo A. Aucar**

*Physics Department - Northeastern University of Argentina and Institute for Modeling and Innovative Technology, IMIT (CONICET-UNNE). Corrientes. Argentina.*

The nature of the hydrogen bond, HB, as such, is still unknown, though some of its most fundamental features are being precisely described. Among the spectroscopic methods available to study molecules containing HBs, the NMR could give deeper insights about the electronic origin of properties and phenomena associated with them. One can mention two phenomena: resonance assisted HBs and charge assisted HBs.[1]

During the last few years we have been studying the dependence of NMR spectroscopic parameters with the type of HB in malonaldehyde and its derivatives.[2] They could arise from both, electronic and geometric factors. In this presentation we will show how the NMR spectroscopic parameters can be incorporated as descriptors of the magnetic nature of HBs.

On the other side,  $\pi$ - $\pi$  stacking or interbase interactions were recently studied to get a deeper understanding of the stacking forces necessary to break fragments of DNA base-pairs while leaving hydrogen bonds intact, at the level of individual pairs.[3] These studies are of great interest due to its applied use.

We are then interested to study the likely effects of the stacking interactions on the NMR spectroscopic parameters. One of our main interest is to describe the effect of piling up Watson-Crick base-pairs on the magnetic properties of a given pair, using two different systems: guanine-cytosine-rich sequences and adenine-thymine-rich sequences.[4] We are also interested to answer the question about whether stacking interactions may support the appearance of cooperativity effects transmitted through the fragments of DNA.

In this communication we will describe the dependence of nuclear magnetic shieldings and J-couplings with cooperativity effects, in addition to that of stacking and HB in short complexes of DNA base-pairs.

**Acknowledgments:** The argentinian research council, CONICET and the argentinian agency for science and technology, FONCYT are greatly acknowledged for financial support.

[1] P. Gilli, V. Bertolasi, L. Pretto, A. Lycka and G. Gilli. *J. Am. Chem. Soc.* **124**, 13554 (2002).

[2] M. Montero, F. Martínez and G. A. Aucar, *J. Phys. Chem. A*. Submitted.

[3] F. Kilchherr, C. Wachauf, B. Pelz, M. Rief, M. Zacharias and H. Dietz, *Science* **353**, aaf5508 (2016).

[4] F. Martínez and G. A. Aucar, *Phys. Chem. Chem Phys.* Submitted.

## Anion-Anion and Cation-Cation Halogen and Hydrogen Bonded complexes.

Ibon Alkorta<sup>1</sup>, David Quiñonero<sup>2</sup>, Ignasi Mata<sup>3</sup>, Elies Molins<sup>3</sup>, Enrique Espinosa<sup>4</sup>

<sup>1</sup>*Instituto de Química Médica, CSIC. Juan de la Cierva, 3. 28006-Madrid, Spain.*

<sup>2</sup>*Dep. de Química, Universitat de les Illes Balears, Crta. de Valldemossa km 7.5, 07122 Palma de Mallorca, Spain*

<sup>3</sup>*Institut de Ciència de Materials de Barcelona (CSIC), Campus UAB, 08193 Bellaterra, Spain*

<sup>4</sup>*Laboratoire de Crystallographie, Résonance Magnétique et Modélisations (CRM2), UMR UL-CNRS 7036, Institut Jean Barriol, Université de Lorraine, BP 70239, 54506 Vandoeuvre-les-Nancy, France*

Stable minima showing halogen [1] or hydrogen bonds [2-5] between charged molecules with the same sign have been explored by means of theoretical calculations. In spite of the ionic repulsion, local energy minima are found both in the gas phase (Fig. 1a) and in aqueous solution. Electrostatic potential and electron density topologies, and the comparison with neutral complexes, reveal that the ionization has no significant effect on the properties of the halogen and hydrogen bonds that hold together the complexes. The stability of the complexes in the gas phase is explained by attractive forces localized in a volume situated in the intermolecular region and defined as the electrostatic attraction region (EAR) and determined by the topological analyses of the electron density and the electrostatic potential, and by the electric field lines (Fig. 1c). The nature of the interaction in the minima and TSs indicate the presence of local favorable electrostatic interactions in the minima that vanish in the TSs. A corrected binding energy profile by removing the charge-charge repulsion of the monomers shows a similar profile to the one observed for the dissociation of analogous neutral systems (Fig. 1b).

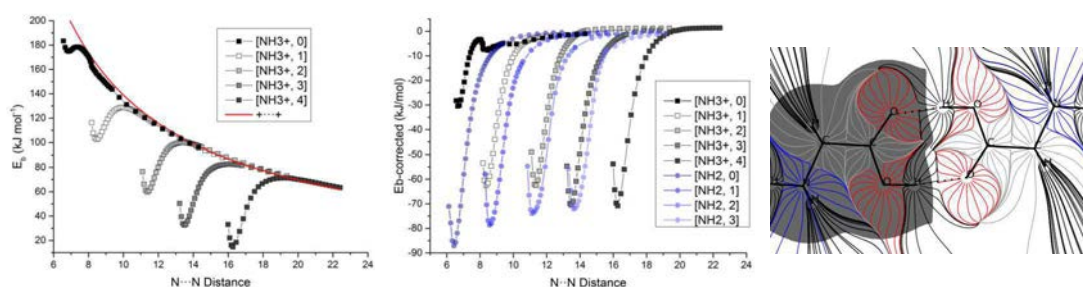


Fig. 1. (a) Dissociation profile versus the N...N intermolecular distance. (b) Coulombic repulsion removed from the profile. (c) Electric field in the dimer of the protonated glycine.

- [1] D. Quiñonero, I. Alkorta, J. Elguero, *Phys. Chem. Chem. Phys.* **18**, 27939 (2016).
- [2] I. Alkorta, I. Mata, E. Molins, E. Espinosa, *Chem. Eur. J.* **22**, 9226 (2016).
- [3] I. Mata, E. Molins, I. Alkorta, E. Espinosa, *J. Phys. Chem. A* **119**, 183 (2015).
- [4] I. Mata, I. Alkorta, E. Molins, E. Espinosa, *Chem. Phys. Lett.* **555**, 106 (2013).
- [5] I. Mata, I. Alkorta, E. Molins, E. Espinosa, *ChemPhysChem* **13**, 1421 (2012).

## Modeling of the spectroscopic signatures of water in different environments\*

Sotiris S. Xantheas

*Physical & Computational Sciences Division, Pacific Northwest National Laboratory,  
902 Battelle Boulevard, P.O. Box 999, MS K1-83, Richland, WA 99352 USA*

We report the linear and 2-D infrared spectra of liquid water and ice with the *ab-initio* based flexible, polarizable interaction potential for water. The potential is parametrized from high level *ab-initio* results for water clusters and incorporates an accurate description of the monomer's potential energy and non-linear dipole moment surfaces. The IR spectra of bulk water are reported from nuclear centroid molecular dynamics (CMD and semi-classical IVR simulations. The analysis of the 2-D IR spectra for the OH stretch and - for the first time - the HOH bend in liquid water provide insights regarding the molecular origin of the difference in the HOH bending region. For liquid water, the frequency fluctuation of the HOH bend is faster than that of the OH stretch. The later caused by the intermolecular HB stretch and the libration, while that of the HOH bend by the OH stretch as well as the intermolecular HB bend. The difference in the intensities of the HOH bend in the IR spectra between liquid water (larger intensity) and ice (smaller intensity) is attributed to (i) the strong anti-correlation between the water's permanent dipole moment and the induced dipole moment of its HB acceptor neighbor and (ii) the weakening of this anti-correlation by the disordered hydrogen bond network in liquid water compared to the one in ice.

This work was performed in collaboration with S. Imoto and S. Saito, Department of Theoretical and Computational Molecular Science, Institute for Molecular Science, Myodaiji, Okazaki, Japan.

---

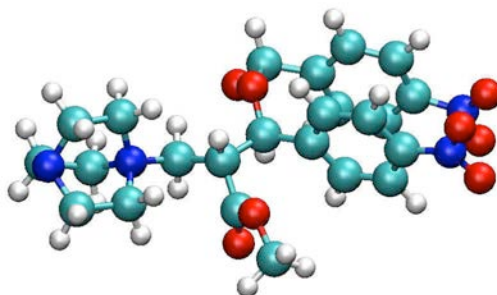
\* This work was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences. Pacific Northwest National Laboratory (PNNL) is a multi-program national laboratory operated for DOE by Battelle.

## Modelling Reaction Mechanisms and Kinetics in Homogeneous Catalysis: Challenges and Progress

Jeremy Harvey<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Division of Quantum Chemistry and Physical Chemistry, KU  
Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium*

In this talk, I will outline recent work in our group aimed at gaining insight into homogeneous catalysis based on computational chemistry. This is a broad area of research in which many groups are active, but to be more specific, our aim in recent years has been to try to build semi-quantitative models of the catalytic transformations based on predicting the rate and equilibrium constants for all relevant elementary steps involved in the mechanism. Doing so requires high accuracy in the treatment of solvation, of enthalpic and especially entropic thermal effects, and of course also in the quantum chemical characterization of the potential energy surfaces. Another challenging aspect is the need to carry out a comprehensive search of the chemical space accessible to the catalytic system – both in terms of the available conformations of each chemical species as well as the different chemical species that can be formed.



In my talk, I will focus especially on two transformations to illustrate these challenges: the Morita-Baylis-Hillman organocatalytic reaction [1,2], and the cobalt-catalyzed hydroformylation of alkenes [3,4]. The calculations are essentially standard molecular quantum chemistry combined with continuum solvent models and statistical rate theory.

- [1] R. Robiette, V. K. Aggarwal, J. N. Harvey, *J. Am. Chem. Soc.* **129**, 15513 (2007).
- [2] Z. Liu, C. Patel, J. N. Harvey, R. B. Sunoj, submitted.
- [3] L. E. Rush, P. G. Pringle, J. N. Harvey, *Angew. Chem. Int. Ed.* **53**, 8672 (2014), *Angew. Chem.* **126**, 8816 (2014).
- [4] E. N. Szlapa, J. Peters, J. N. Harvey, to be published.



## London Dispersion Effects in Molecular Chemistry

### – Reconsidering Steric Effects<sup>1</sup>

Peter R. Schreiner

*Institute of Organic Chemistry, Justus-Liebig University  
Heinrich-Buff Ring 17, 35392 Giessen, Germany, prs@uni-giessen.de*



The *Gecko* can walk up a glass window because of the adhesion in hydrophobic setae on its toes that convey van der Waals (vdW) interactions with the surface.<sup>2</sup> The attractive part of such vdW-interactions is an electron correlation effect referred to as *London dispersion*. Its role in the formation of condensed matter has been known since the work of van der Waals<sup>3</sup> and London<sup>4</sup> who related dispersion to polarizability. London dispersion has been underappreciated in molecular chemistry as a key element of structural stability, chemical reactivity, and catalysis. This negligence is due to the notion that dispersion is weak, which is only true for *one* pair of interacting atoms. For increasingly larger structures, the overall dispersion contribution grows rapidly and can amount to tens of kcal mol<sup>-1</sup>. This presentation shows selected examples that emphasize the importance of dispersion for molecules consisting mostly of first row atoms.<sup>5</sup> We note the synergy of experiment and theory that now has reached a stage where dispersion effects can be examined in fine detail. This forces us to re-consider our perception of steric hindrance and stereoelectronic effects, and even the transferability of chemical bond parameters from one molecule to another.

This work was supported by the DFG, priority program 1807 “dispersion”.

- (1) **Review:** Wagner, J. P.; Schreiner, P. R. *Angew. Chem. Int. Ed.* **2015**, *54*, 12274.
- (2) Autumn, K.; Sitti, M.; Liang, Y. A.; Peattie, A. M.; Hansen, W. R.; Sponberg, S.; Kenny, T. W.; Fearing, R.; Israelachvili, J. N.; Full, R. J. *Proc. Natl. Acad. Sci.* **2002**, *99*, 12252.
- (3) van der Waals, J. D., Leiden University, 1873.
- (4) London, F. *Z. Phys.* **1930**, *63*, 245.
- (5) **Experimental systems ideally suited for benchmarking theory:** a) Schreiner, P. R.; Chernish, L. V.; Gunchenko, P. A.; Tikhonchuk, E. Y.; Hausmann, H.; Serafin, M.; Schlecht, S.; Dahl, J. E. P.; Carlson, R. M. K.; Fokin, A. A. *Nature* **2011**, *477*, 308; b) Fokin, A. A.; Chernish, L. V.; Gunchenko, P. A.; Tikhonchuk, E. Y.; Hausmann, H.; Serafin, M.; Dahl, J. E. P.; Carlson, R. M. K.; Schreiner, P. R. *J. Am. Chem. Soc.* **2012**, *134*, 13641; c) Wagner, J. P.; Schreiner, P. R. *J. Chem. Theory Comput.* **2014**, *10*, 1353; d) Wagner, J. P.; Schreiner, P. R. *J. Chem. Theory Comput.* **2016**, *12*, 231; e) Rösel, S.; Balestrieri, C.; Schreiner, P. R. *Chem. Sci.* **2017**, *8*, 405; f) Rösel, S.; Quanz, H.; Logemann, C.; Becker, J.; Mossou, E.; Cañadillas-Delgado, L.; Caldeweyher, E.; Grimme, S.; Schreiner, P. R. *J. Am. Chem. Soc.* **2017**, *139*, 7428.

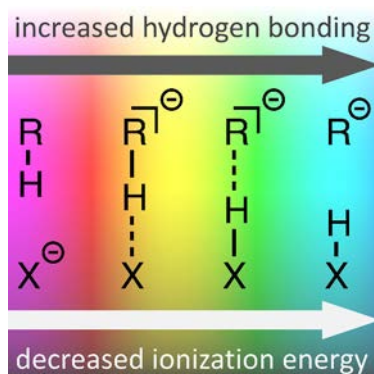
## Impact of Hydrogen Bonding on the Susceptibility of Peptides to Oxidation

Bun Chan,\* Damian Moran, Christopher J. Easton,\* and Leo Radom\*

*School of Chemistry, University of Sydney, Sydney, NSW 2006, Australia, Graduate School of Engineering, Nagasaki University, Nagasaki 852-8521, Japan, and Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia*

radom@chem.usyd.edu.au

The tendency of peptides to oxidize is intimately connected with their function and even their ability to exist in an oxidative environment. In this presentation, we use high-level computational quantum chemistry procedures to show how hydrogen bonding in model amino acids and small peptides can have a dramatic effect on the ionization energies and hence on the oxidative susceptibility.



**Isomerization Mechanisms Around E=E' (E,E'=C,Si) Bonds.****Experiment and Theory**

**Yitzhak Apeloig, Arseni Kostenko, Daniel Pinchuk, Lieby Zborovsky, D. Bravo-Zhivotovskii**

*Schulich Department of Chemistry, Technion- Israel Institute of Technology, Haifa 32000, Israel*

*E-mail: [apeloig@technion.ac.il](mailto:apeloig@technion.ac.il)*

The mechanism of isomerization around C=C bonds has been studied extensively both experimentally and theoretically. In contrast, relatively little is known about the isomerization mechanisms around E=E' (E,E'=C,Si) bonds.

In this lecture we discuss isomerization mechanisms around E=E' (E,E'=C,Si) bonds, for example in silenes (RR'C=SiRR') and in silenyl anions (RR'C=SiR<sup>-</sup>) and radicals, recently synthesized in our group [1]. The experimental and computational studies reveal interesting differences between the isomerization mechanism in alkenes and vinyl anions and their heavier congeners.

[1]. D. Pinchuk, J. Mathew, A. Kaushansky, D. Bravo-Zhivotovskii, Y. Apeloig, *Angew. Chem., Int. Ed.*, **55**, 10258 -10262 (2016).

## **Dynamics of Pericyclic Reactions**

**K. N. Houk and Zhongyue Yang**

*Department of Chemistry and Biochemistry  
University of California, Los Angeles 90095 USA*

Quasi-classical molecular dynamics of organic pericyclic reactions are reported for a variety of Diels-Alder reactions and Cope rearrangements, including reactions in water and in enzymes. Mechanisms are defined in terms of the time gap between the formation of two bonds for cycloadditions, or the time in the transition zone for the Cope rearrangement. When the time gap is less than 60fs the reaction is defined as dynamically concerted. Examples of dynamically concerted and stepwise reactions, as well as reaction mechanisms involving both types occurring simultaneously will be discussed. The influence of solvent and enzyme binding sites on the dynamics and mechanisms will be discussed for certain ambimodal reactions, where the transition state leads to two different products. Dynamics trajectories were propagated with B3LYP and M06-2X density functionals.

We have benefited greatly from collaborations with, and advice from, Charles Doubleday (Columbia) and Daniel Singleton (Texas A&M).

**Symmetry projected coupled cluster theory****Gustavo E. Scuseria**

*Department of Chemistry  
Department of Physics & Astronomy  
Department of Materials Science & Nano Engineering  
Rice University, Houston, Texas, USA*

Coupled cluster and symmetry projected Hartree-Fock are two central paradigms in electronic structure theory. However, they are very different. Single reference coupled cluster is highly successful for treating weakly correlated systems, but fails under strong correlation unless one sacrifices good quantum numbers and works with broken-symmetry wave functions, which is unphysical for finite systems. Symmetry projection is effective for the treatment of strong correlation at the mean-field level through non-orthogonal configuration interaction wavefunctions, but unlike coupled cluster, it is neither ideal for treating dynamic correlation nor size extensive beyond broken-symmetry field. This talk will examine two scenarios for merging these two dissimilar theories based on symmetry adapted and broken symmetry references. Benchmark results and will also be presented.

## Accurate treatment of long-range correlation effects in large molecules using explicitly correlated local coupled-cluster methods

Max Schwilk, Qianli Ma, Christoph Köppl, Hans-Joachim Werner

*Institute for Theoretical Chemistry, University of Stuttgart,*

*Pfaffenwaldring 55, D-70569 Stuttgart, Germany*

A well parallelized explicitly correlated local singles and doubles coupled-cluster method using pair natural virtual orbitals (PNO-LCCSD-F12) [1] is presented. This is an extension of our previous parallel PNO-LMP2 [2] and PNO-LMP2-F12 [3] methods. In the LCCSD the correlated orbital pairs are classified according to their PNO-LMP2 energy contributions as strong, close, weak, or distant. Close pair amplitudes are optimized using approximate LCCSD equations [4], in which slowly decaying terms that mutually cancel at long range are neglected. For weak pairs the same approximations are used, but in addition the non-linear terms are neglected. Distant pairs are treated by spin-component scaled (SCS)-LMP2 using multipole approximations [5]. This hierarchy leads to excellent accuracy for large systems, in particular when long-range dispersion interactions are important. The impact of the local approximations on reaction energies, barrier heights, and intermolecular interaction energies is investigated for 3-dimensional systems with up to 174 atoms (5168 basis functions). While the treatment of close and weak pairs by LMP2 or SCS-LMP2 strongly overestimates the long-range correlation contributions and can lead to large errors ( $> 5 \text{ kcal mol}^{-1}$ ) in relative energies, the errors caused by the new pair approximations were in all benchmarks less than  $0.2 \text{ kcal mol}^{-1}$ , using default thresholds. The domain errors are equally small if F12 terms are included. For extended one-dimensional systems the computational effort of the method scales almost linearly with the number of correlated electrons, but the linear scaling regime is usually not reached in real-life applications for three-dimensional systems. Nevertheless, due to the parallelization, which is efficient up to about 100-300 CPU cores (dependent on the molecular size), accurate PNO-LCCSD-F12 calculations for three-dimensional molecules with more than 100 atoms and cc-pVTZ-F12 basis sets can be carried out in 1-3 hours of elapsed time (depending on the molecular structure and the number of CPU cores).

- [1] M. Schwilk, Q. Ma, C. Köppl, H.-J. Werner, submitted for publication.
- [2] H.-J. Werner, G. Knizia, C. Krause, M. Schwilk, M. Dornbach, *J. Chem. Theory Comput.* **11**, 485 (2015).
- [3] Q. Ma, H.-J. Werner, *J. Chem. Theory Comput.* **11**, 5291 (2015).
- [4] M. Schwilk, D. Usyat, H.-J. Werner, *J. Chem. Phys.* **142**, 121102 (2015).
- [5] H.-J. Werner, *J. Chem. Phys.* **145**, 201101 (2016).

## Tensor Product Methods and Entanglement Measures for Strongly Correlated Molecular Systems

S. Szalay<sup>1</sup>, G. Barcza<sup>1</sup>, T. Szilvási<sup>2</sup>, Ö. Legeza<sup>1</sup>, L. Veis<sup>3</sup>, J. Brandejs<sup>3</sup>, J. Pittner<sup>3</sup>,  
F. Verstraete<sup>4</sup>, C. Krumnow<sup>5</sup>, J. Eisert<sup>5</sup>

<sup>1</sup>"Lendület" Research Group, Wigner Research Centre for Physics, Budapest, Hungary

<sup>2</sup>Department of Chemical and Biological Engineering, University of Wisconsin-Madison,  
United States

<sup>3</sup>J. Heyrovsky Institute of Physical Chemistry, Prague, Czech Republic

<sup>4</sup>Fakultät für Physik, Universität Wien, Vienna, Austria

<sup>5</sup>Dahlem Center for Complex Quantum Systems, Freie Universität, Berlin, Germany

We present general tensor network state techniques, that can be used for the treatment of strongly correlated molecular systems, and connect them to concepts already used in many-body quantum physics [1]. We will also discuss the controlled manipulation of the entanglement, which is in fact the key ingredient of such methods, and which provides relevant information about the correlation theory of the chemical bonds. Recent developments on fermionic orbital optimization [2], tree-tensor network states, multipartite entanglement in chemical systems [3], and accurate treatment of static and dynamic correlations based on the tailored coupled cluster (CC) theory [4] will be discussed. New results will be shown for various prominent multireference system, in particular transition metal clusters, extended periodic systems,  $\pi$ -conjugated polymers and graphene.

- [1] S. Szalay, M. Pfeffer, V. Murg, G. Barcza, F. Verstraete, R. Schneider, and Ö. Legeza, *Int. J. Quant. Chem.* **115**, 1342 (2015).
- [2] C. Krumnow, L. Veis, Ö. Legeza, J. Eisert, *Phys. Rev. Lett.* **117**, 210402 (2016).
- [3] S. Szalay, G. Barcza, T. Szilvási, L. Veis, Ö. Legeza, *Scientific Reports* **7**, 2237 (2017).
- [4] L. Veis, A. Antalík, J. Brabec, F. Neese, Ö. Legeza, J. Pittner, *J. Phys. Chem. Lett.* **7**, 4072 (2016).

## Wave Functions with Several Sets of Optimized Orbitals

Jeppe Olsen<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark*

Standard quantum chemical methods employ a single set of orthogonal or non-orthogonal orbitals. However, for a number of molecular systems such expansions are rather inefficient, as different parts of the wave function require different forms of orbitals. For example, a reasonable description of the ground state of the iron dimer is obtained only when the active space includes d-sets for both  $d^6$  and  $d^7$  configurations. In this talk, I will talk about our recent development and initial applications of a new method, where the wave function is a sum of several terms, with each term being a single or multi-configurational wave function with its own set of optimized orbitals. The method is extended to generate individual sets of orbitals for several states, thereby allowing MCSCF calculations on excited states to be formulated as minimizations.



## **Active Thermochemical Tables: What They Are, Why I Care About Them, and Why You Should, Too**

**John F. Stanton<sup>1</sup>**

*<sup>1</sup>Quantum Theory Project, Departments of Chemistry and Physics, University of Florida,  
Gainesville, FL 32611*

Developed during the last decade by Ruscic and collaborators at Argonne National Laboratory, Active Thermochemical Tables (ATcT) represents an entirely new and revolutionary way to approach the subject of thermochemistry. Traditional thermochemistry has advanced piecemeal and willy nilly, through individual spectroscopic, kinetic, calorimetric, etc. measurements often supplemented by ‘recommendation of ‘standard’ (in the non-thermodynamic sense) through the actions of various critical review committees (NIST-JANAF, CODATA, etc.). In contrast, ATcT is a holistic approach that views each molecule as connected – in principle – to all other species through within constructs called thermochemical networks. In ATcT, thermochemical parameters such as bond energies, ionization potentials, and enthalpies of formation are solved for self-consistently using all available relevant information. Many bond energies once known to, say, a few kcal mol<sup>-1</sup> have now been established with a precision that is at least an order of magnitude better than before, which clearly has enormous practical consequences for modelling studies. This talk reviews the surprisingly interesting topic of “where do these heats of formation come from?” and outlines the basic ideas in ATcT. Due to the high interconnectedness of many chemical species through the thermochemical network paradigm, it transpires that knowing any individual property (say, an ionization potential) can potentially impact properties of any number of different species. Hence, there is virtue to constantly improving our knowledge of fundamental molecular properties that goes well beyond just “putting another decimal place on it”. ATcT actively seeks accurate measurements and calculations for key quantities, which will be illustrated by a recent study of the photoelectron spectrum of hydrogen peroxide.

.

## **Localized Orbital Scaling Correction for Systematic Elimination of Delocalization Error in Density Functional Approximations.**

**Weitao Yang**

*<sup>1</sup> Department of Chemistry and Department of Physics, Duke University, Durham, North Carolina 27708, USA*

The delocalization error of popular density functional approximations (DFAs) leads to diversified problems in present-day density functional theory calculations. For achieving a universal elimination of delocalization error, we develop a localized orbital scaling correction (LOSC) framework, which unifies our previously proposed global and local scaling approaches. The LOSC framework accurately characterizes the distributions of global and local fractional electrons, and is thus capable of correcting system energy, energy derivative and electron density in a self-consistent and size-consistent manner. The LOSC–DFAs lead to systematically improved results, including the dissociation of cationic species, the band gaps of molecules and polymer chains, the energy and density changes upon electron addition and removal, and photoemission spectra.

[1] Chen Li,<sup>1</sup> Xiao Zheng, Neil Qiang Su, and Weitao Yang, “Localized Orbital Scaling Correction for Systematic Elimination of Delocalization Error in Density Functional Approximations”, arXiv:1707.00856v1

## Ultrafast Quantum/Molecular Mechanics: Thermodynamic Integration and van der Waals parameters

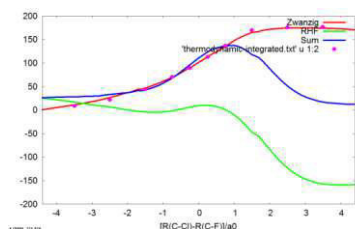
Krzysztof Wolinski,<sup>1</sup> Géza Fogarasi<sup>2</sup>, Peter Pulay<sup>3</sup>

<sup>1</sup>Faculty of Chemistry, Maria Curie-Skłodowska University, Pl. M. Curie-Skłodowskiej, 20-031 Lublin, Poland

<sup>2</sup>Institute of Chemistry, Eötvös University, Pázmány s. 1, Budapest 1117, Hungary

<sup>3</sup>Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR 72701, USA

In traditional Quantum/Molecular Mechanics (QM/MM), a large number ( $10^6$ - $10^7$ ) of configurations of the flexible solvent (or environment) must be sampled statistically for each geometry of the active region to obtain reliable free energies. This makes full QM/MM with *ab initio* or even DFT QM component very expensive. Ultrafast QM/MM [1] obviates the need to perform a QM run for each solvent configuration. As this is required only to calculate the polarization of the solute by the solvent, we precalculate once for a fixed solute, its Generalized Polarizabilities [2], i.e., the second derivatives of the energy with respect to the coefficients of the expansion basis functions *for the electric potential* within the solute. In the simulation phase the calculation of polarization energy requires only a fast matrix-vector product. With a few hundred explicit water molecules, Ultrafast QM/MM is about  $10^4$  times faster than traditional QM/MM, and is accurate to  $\sim 0.05$  kcal/mol [1]. Even this speed ( $\sim 10$  ms/config) is insufficient for mapping 2D potential surfaces by Free Energy Perturbation (FEP) for, e.g. a peptide model. We have implemented ultrafast free energy gradients with the help of Dr. T. Janowski. They allow



the use of Thermodynamic Integration (TI, or Potential of the Mean Force) instead of FEP. FEP is shown to be a finite-difference approximation to TI and it compares unfavorably with analytical derivatives. The accuracy of QM/MM depends on the solvent model, in particular on the van der Waals (vdW) parameters between the quantum and the MM systems. VdW parameters based on old RHF/3-21G calculations [3] are still widely used but not accurate enough. We have developed an Adaptive Force Fitting [4] program for state-of-the-art vdW parameters. Examples will be presented, and the method will be compared with MESS-E/H techniques [5], and with coarse-grained methods [6].

[1] Janowski, T.; Wolinski, K.; Pulay, P. *Chem. Phys. Lett.* **2012**, 530, 1.

[2] Pulay, P.; Janowski, T. *Int. J. Quantum Chem.* **2009**, 109, 2113.

[3] Freindorf, M.; Gao, J. *J. Comput. Chem.* **1996**, 17, 386-395.

[4] Akin-Ojo, O.; Song, Y.; Wang, F. *J. Chem. Phys.* 2008, 129, 064108/1-11.

[5] Sodt, A.J.; Mei, Y.; König, G.; Tao, P.; Steele, R. P.; Brooks, B. R.; Shao, Y. *J. Phys. Chem. A* **2015**, 119, 1511.

[6] Zhang, Y.; Liu, H.; Yang, W. *J. Chem. Phys.* **2000**, 112, 3483.

**Fast construction of the exchange operator in an atom-centered basis  
with concentric atomic density fitting**

**David S. Hollman<sup>a),1,2</sup>, Henry F. Schaefer<sup>1</sup>, and Edward F. Valeev<sup>2</sup>**

<sup>1)</sup>*Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia,  
30602, USA*

<sup>2)</sup>*Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061, USA*

An algorithm is presented for computing the Hartree–Fock (HF) exchange matrix using concentric atomic density fitting with  $O(N)$  data and instruction count complexities. The algorithm exploits the asymptotic distance dependence of the three-center Coulomb integrals along with the rapid decay of the density matrix to accelerate the construction of the exchange matrix. The new algorithm is tested with computations on systems with up to 1536 atoms and a quadruple-zeta basis set (up to 15585 basis functions). Our method handles screening of high angular momentum contributions in a particularly efficient manner, allowing the use of larger basis sets for large molecules without a prohibitive increase in cost.

Department of Energy, Office of Basic Energy Sciences, Computational and Theoretical Chemistry Program. Grand No. DE-SC0015512

<sup>a)</sup> Current address: Sandia National Laboratories, Livermore, CA 94551, USA

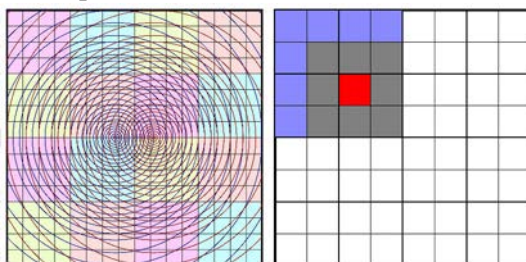
## Numerical Electronic Structure Theory Methods for Massively Parallel Computations on Molecules

Dage Sundholm<sup>1</sup>, Pauli Parkkinen<sup>1</sup>, Eelis Solala<sup>1</sup>, Wen-Hua Xu<sup>2</sup>

<sup>1</sup>Department of Chemistry, University of Helsinki, P.O. Box 55, A.I. Virtanens plats 1, FI-00014, Helsinki, Finland

<sup>2</sup>Department of Chemistry, Northwest University, Xian, China.

Algorithms and computational approaches for three-dimensional (3D) fully numerical electronic structure calculations on molecules will be discussed. In our approach, the steep parts of the functions are expanded in one-center functions (*bubbles*) consisting of numerical radial functions multiplied with spherical harmonics for the angular part. The difference between the bubbles and the 'exact' functions (the *cube*) is expanded on an equidistant 3D grid.[1] The methods have been implemented for massively parallel calculations on general purpose graphics processing units (GPGPU).[2] The presented algorithms include computational schemes for performing numerical calculations of electrostatic potentials and two-electron interaction energies as well as for calculations of the exchange correlation potentials and energies occurring in density-functional theory (DFT) calculations. The dual bubbles and cube basis renders accurate numerical calculations of the kinetic-energy contributions feasible. Orbital optimization is performed by integrating the Helmholtz kernel.[3] An implementation of a grid-based fast multipole method (FMM) for efficient calculations of electrostatic potentials and two-electron interactions is presented.[4] A generalized FMM algorithm based on the Helmholtz kernel is used for optimization of the numerical orbitals.[5]



The accuracy of the implemented numerical methods has been assessed by performing calculations on molecules for which benchmark data are available. The calculations show that the calculated energies systematically approach the basis-set limit when using large grids.

- [1] S. A. Losilla, D. Sundholm, *J. Chem. Phys.* **136**, 214104 (2012).
- [2] S. A. Losilla, M. A. Watson, A. Aspuru-Guzik, D. Sundholm, *J. Chem. Theory Comput.* **11**, 2053 (2015).
- [3] E. A. Toivanen, S. A. Losilla, D. Sundholm, *Phys. Chem. Chem. Phys.* **17**, 31480 (2015).
- [4] E. Solala, S. A. Losilla, D. Sundholm, W. H. Xu, P. Parkkinen, *J. Chem. Phys.* **146**, 084102 (2017).
- [5] P. Parkkinen, S. A. Losilla, E. Solala, E. A. Toivanen, W. H. Xu, D. Sundholm, *J. Chem. Theory Comput.* **13**, 654 (2017).

## Fourier transform of $1/r$ on graphical processing units – a promising tool for applications in nanolithography

Petr Čársky and Roman Čurík

*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic,  
Dolejšková 3, 18823 Prague 8, Czech Republic*

This contribution deals with the following issues:

1. Factorization of two-electron integrals to products of one-electron overlap integrals

$$\int g g \frac{1}{r_{12}} g g d\mathbf{r}_1 d\mathbf{r}_2 \rightarrow \frac{1}{2\pi^2} \sum (g g k)(k g g)$$

2. This factorization is an ideal task for graphical processing units. We show how to do it efficiently. The method is general and it can be profitable for use in quantum chemical calculations of various types.

3. We are interested primarily in exchange integrals of the type  $(g_1(1)k_1(1)|g_2(2)k_2(2))$ , where  $g$ 's and  $k$ 's, respectively, are gaussians and plane-wave functions that are needed in *ab initio* calculations on electron scattering by polyatomic molecules. Such an interest originates from our engagement in the international (mainly experimental) project CELINA (Chemistry for ELection Induced NAnolithography). In this project a new experimental technique is explored, in which decomposition of organometallics and subsequent deposition of metal on surface is imposed not by annealing but on electron impact. Achieved resolution is better and also the control of the process is better. Experimentalists need help from theory in selection of suitable precursors and experimental conditions. We briefly show what we can do in this respect, but the main attention in our presentation will be paid to issues 1 and 2.

## Open Systems Simulations of Macromolecular Solutes through Adaptive Resolutions Simulations (AdResS)

**Kurt Kremer**

*Max Planck Institute for Polymer Research, Theory Department,  
Ackermannweg 10, D-55128 Mainz, Germany*

The relation between atomistic structure, architecture, molecular weight and material properties is of basic concern of modern soft matter science. A typical additional focus is the relation between structure and function in nanoscopic molecular assemblies. Here computer simulations on different levels of resolution play an increasingly important role. This is achieved by two different approaches, namely by sequential multiscale descriptions or adaptive schemes, which allow for a free exchange of particles (atoms, molecules) between the different levels of resolution. The latter is the topic of the present lecture. The extension to open systems MD (grand canonical MD) as well as recent Hamiltonian based molecular dynamics and Monte Carlo adaptive resolution methods will be discussed.

Typical applications are solvation of polymers in mixed good solvents, called co(non)solvency, hydration layers of large solutes and the combination of all atom and elastic network description of proteins and protein ligand binding.

Part of this work has been supported by the ERC Advanced Grant MOLPROCOMP

- [1] M. Praprotnik et al., *Ann. Rev. Phys. Chem.* **59** (2008); General introductory review
- [2] S. Fritsch et al., *Phys. Rev. Lett.* **108**, 170602 (2012);
- [3] R. Potestio et al., *Phys. Rev. Lett.* **110**, 108301(2013), *Phys. Rev. Lett.* **111**, 060601 (2013);
- [4] D. Mukherji and K. Kremer, *Macrom.* **46**, 9158 (2013);
- [5] D. Mukherji, C. Marques, K. Kremer, *Nat. Comm.* **5**, DOI: 10.1038/ncomms 5882 (2014);
- [6] A.C. Fogarty, R. Potestio, K. Kremer, *J. Chem. Phys.* **142**, 195101 (2015)
- [7] K. Kreis, A.C. Fogarty, K. Kremer, R. Potestio, *EPJ –Spec. Top.* **224**, 2289 (2015)
- [8] K. Kreis, R. Potestio, K. Kremer, AC Fogarty, *JCTC*, **12**, 4067 (2016)
- [9] A.C. Fogarty, R. Potestio, K. Kremer, *Proteins – Struct. Funct. and Bioinf.* **84**, 1902 (2016)

## Multiscale molecular modelling of soft materials: The challenge of dynamics

**Florian Müller-Plathe**

*Technische Universität Darmstadt, Eduard-Zintl-Institut für Anorganische und  
Physikalische Chemie, Alarich-Weiss-Str. 8, D-64287 Darmstadt, Germany*

Moving from a fine-grained particle model to one of lower resolution leads, with few exceptions, to an acceleration of molecular mobility, higher diffusion coefficients, lower viscosities, and more. On top of that, the level of acceleration is often different for different dynamical processes as well as for different state points. While the reasons are often understood, the fact that coarse-graining almost necessarily introduces unpredictable acceleration of the molecular dynamics severely limits its usefulness as a predictive tool. There are several attempts under way to remedy these shortcomings of coarse-grained models. On the one hand, we follow bottom-up approaches. They attempt already when the coarse-graining scheme is conceived to estimate their impact on the dynamics. This is done by excess-entropy scaling. On the other hand, we also pursue a top-down development. Here we start with a very coarse-grained model (dissipative particle dynamics) which in its native form produces qualitatively wrong polymer dynamics, as its molecules cannot entangle. This model is modified by additional temporary bonds, so-called slip springs, to repair this defect. As a result, polymer melts and solutions described by the slip-spring DPD model show correct dynamical behaviour. Finally, we deal with the dynamics of the reactive formation of polymer networks near solid substrates (i.e. two-component adhesives) and with their glass transition in the interphase.

Read more:

Excess entropy scaling for the segmental and global dynamics of polyethylene melts, E. Voyiatzis, F. Müller-Plathe, and M.C. Böhm, *Phys. Chem. Chem. Phys.* **16**, 24301 (2014). [DOI: 10.1039/C4CP03559C]

Recovering the Reptation Dynamics of Polymer Melts in Dissipative Particle Dynamics Simulations via Slip-Springs, M. Langeloth, Y. Masubuchi, M. C. Böhm, and F. Müller-Plathe, *J. Chem. Phys.* **138**, 104907 (2013). [DOI: 10.1063/1.4794156].

The Glass Transition in Cured Epoxy Thermosets: A Comparative Molecular Dynamics Study in Coarse-Grained and Atomistic Resolution, M. Langeloth, T. Sugii, M. C. Böhm, and F. Müller-Plathe, *J. Chem. Phys.* **143**, 243158 (2015). [DOI: 10.1063/1.4937627]



**Exploring the mechanism and kinetics of nucleation processes:  
from crystallization to cavitation**

**Christoph Dellago**

*Faculty of Physics, University of Vienna, Boltzmannngasse 5, Vienna, Austria*

Computer simulations of first order phase transitions occurring via nucleation and growth are demanding for several distinct but related reasons. Particularly close to coexistence, the free energy barrier separating the metastable from the stable phase can be high, leading to nucleation times that vastly exceed the time scales accessible to molecular dynamics simulations. Other difficulties arising in the simulation of nucleation processes consist in detecting local structures characteristic for the stable and metastable phases and in identifying the degrees of freedom that capture the essential physics of the transition mechanism. In this talk, I will discuss simulation approaches to address these problems, using the crystallization of supercooled liquids and cavitation of water under tension as illustrative examples.

## **A multiscale simulation perspective on mineralization processes**

**Christine Peter<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, University of Konstanz, Universitätsstrasse 10, 78457 Konstanz, Germany*

How do biominerals form? Which factors steer the formation of particle shapes and morphologies? In recent years exciting experimental studies have shed new light on the processes and structures that occur during the early stages of mineralization. The traditional view - that had been dominated by classical nucleation theory and classical growth models - was significantly expanded. New pathways and intermediates have been investigated, such as liquid-like prenucleation species and metastable amorphous precursors which exist up to macroscopic length scales, requiring solid-solid phase transformations during mineralization.

Yet, molecular understanding and interpretation of these experimental data is often elusive. Here, molecular simulation can provide a microscopic structural interpretation. One can investigate the processes and transition states and dissect the observed thermodynamic behavior into contributions from various components. I will discuss several aspects related to models, methodologies, and challenges in simulating the early stages of mineralization. We start from an atomistic view on the formation of early precursor forms in solution and on the effect of biopolymer additives on nucleation. From there we move to a particle-based coarse-grained model, which is being developed to address the inherent time- and length-scale problems of mineral formation.

## Computational modeling of molecular processes in proteins.

**Alexander Nemukhin<sup>1,2</sup>, Bella Grigorenko<sup>1,2</sup>, Maria Khrenova<sup>1</sup>,  
Sofya Lushchekina<sup>2</sup>, Ekaterina Kots<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory 1-3,  
Moscow, Russian Federation*

<sup>2</sup>*Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Kosygina 4,  
Moscow, Russian Federation*

We consider molecular processes in proteins including chemical reactions catalyzed by enzymes and photo-induced transformations in photoreceptors. Quantum mechanics-molecular mechanics (QM/MM) and molecular dynamics (MD) methods are appropriate modeling tools for these simulations. We discuss the results of modeling [1] of the complete catalytic cycle of aspartoacylase responsible for cleavage of N-acetyl-L-aspartate, the major amino acid derivative in the mammalian brain. Starting from the crystal structure of the enzyme complexed with the intermediate analog, the QM/MM minimum energy geometry configurations and the corresponding transition states were located. The stages of substrate binding to the enzyme active site and release of the products were modeled by MD calculations with the replica-exchange umbrella sampling technique. We also analyze the results of the combined QM/MM and MD simulations aiming to model transient kinetic studies in several important proteins including aspartoacylase and guanosine triphosphate hydrolyzing enzymes [2]. One of the goals of these studies is to predict action of polymorphic variants of the most important human enzymes. Simulations of the fluorescent proteins [3] constitute another important direction of our studies using the QM/MM and MD approaches. We discuss novel results clarifying molecular mechanisms of chromophore formation and decomposition in the green fluorescent protein.

Support from the Russian Science Foundation (project 14-13-00124) is acknowledged,

- [1] E. D. Kots, M. G. Khrenova, S. V. Lushchekina, S. D. Varfolomeev, B. L. Grigorenko, A. V. Nemukhin, *J. Phys. Chem. B* **120**, 4221 (2016).
- [2] M. Khrenova, B. Grigorenko, A. Kolomeisky, A. Nemukhin, *J. Phys. Chem. B* **119**, 12838 (2015).
- [3] A. Acharya, A. M. Bogdanov, K. B. Bravaya, B. L. Grigorenko, A. V. Nemukhin, K. A. Lukyanov, A. I. Krylov, *Chem. Rev.* **117**, 758 (2017).

## Quantum dynamical and semiclassical calculations on chemical reactions with application to decomposition of nerve agents

David C. Clary<sup>\*</sup> and Xiao Shan

Department of Physical and Theoretical Chemistry  
University of Oxford  
South Parks Road  
Oxford OX1 3QZ, UK

<sup>\*</sup>email: david.clary@chem.ox.ac.uk

This lecture will describe research in our group on linking quantum dynamics and quantum chemistry methods to predict the kinetics and dynamics of reactions of polyatomic molecules from first principles. A reduced dimensionality (RD) approach is used that combines accurate quantum chemistry calculations of a small number of key points on the potential energy surface with a quantum-dynamical treatment of the bonds being broken and formed in a chemical reaction [1].

The quantum dynamics calculations of rate constants have been used to test the accuracy of a reduced-dimensional form of semiclassical transition state theory (SCTST) [2] for several hydrogen abstraction and exchange reactions such as H+cyclopropane and CH<sub>3</sub>+CH<sub>4</sub>. The results suggest that the RD SCTST should be a reliable and computationally inexpensive method for predicting the rate constants of polyatomic reactions from first principles [3].

The RD SCTST method is applied to calculate the decomposition rate for the nerve agent sarin which undergoes a unimolecular hydrogen transfer reaction. Excellent agreement with experiment is obtained.

[1] X. Shan and D. C. Clary, *J. Phys. Chem. A*, **118**, 10134 (2014).

[2] W. H. Miller, R. Hernandez, N. C. Handy, D. Jayatilaka and A. Willetts, *Chem. Phys. Lett.* **172**, 62 (1990).

[3] S. M. Greene, X. Shan and D. C. Clary, *J. Chem. Phys.*, **144**, 084113 (2016).

## High-dimensional quantum dynamics of functional organic polymer materials: Coherence, localization, and (dis)order

**Irene Burghardt<sup>1</sup>, Matthias Polkehn<sup>1</sup>, Robert Binder<sup>1</sup>, Hiroyuki Tamura<sup>2</sup>**

<sup>1</sup>*Institute for Physical and Theoretical Chemistry, Goethe University Frankfurt,  
Max-von-Laue-Str. 7, 60438 Frankfurt, Germany*

<sup>2</sup>*Department of Chemical System Engineering, School of Engineering,  
The University of Tokyo, Tokyo 113-8656, Japan*

This talk addresses quantum dynamical studies of ultrafast photo-induced exciton migration and dissociation in functional organic materials, in view of understanding the intricate interplay of electronic delocalization, coherent nonadiabatic dynamics, and trapping phenomena. Our approach combines first-principles parametrized Hamiltonians, based on TDDFT and/or high-level electronic structure calculations, with accurate quantum dynamics simulations using the Multi-Configuration Time-Dependent Hartree (MCTDH) method and its hierarchical multi-layer (ML-MCTDH) variant [1], as well as mixed quantum-classical techniques. The talk will specifically focus on (i) exciton dissociation and free carrier generation in donor-acceptor materials [2], including highly ordered oligothiophene-perylenediimide assemblies [3,4] (ii) exciton multiplication in acene materials [5] and (iii) the elementary mechanism of exciton migration and creation of charge-transfer excitons in polythiophene and poly-(p-phenylene vinylene) type materials [6]. Special emphasis is placed on the influence of structural (dis)order and molecular packing, which can act as a determining factor in transfer efficiencies. Against this background, we will comment on the role of temporal and spatial coherence along with a consistent description of the transition to a classical-statistical regime.

- [1] G. A. Worth, H.-D. Meyer, H. Köppel, L. S. Cederbaum, and I. Burghardt, *Int. Rev. Phys. Chem.* **27**, 569 (2008), H. Wang, *J. Phys. Chem. A* **119**, 7951 (2015).
- [2] M. Huix-Rotllant, H. Tamura, and I. Burghardt, *J. Phys. Chem. Lett.* **6**, 1702 (2015).
- [3] M. Polkehn, H. Tamura, P. Eisenbrandt, S. Haacke, S. Méry, and I. Burghardt, *J. Phys. Chem. Lett.* **7**, 1327 (2016).
- [4] L. Li, P. Eisenbrandt, T. Roland, M. Polkehn, P.-O. Schwartz, K. Bruchlos, B. Omiecienski, S. Ludwigs, N. Leclerc, E. Zaborova, J. Léonard, S. Méry, I. Burghardt, and S. Haacke, *Phys. Chem. Chem. Phys.* **18**, 18536 (2016).
- [5] H. Tamura, M. Huix-Rotllant, I. Burghardt, Y. Olivier, and D. Beljonne, *Phys. Rev. Lett.* **115**, 107401 (2015).
- [6] R. Binder, M. Polkehn, T. Ma, and I. Burghardt, *Chem. Phys.* **482**, 16 (2017).

## **Light-induced nonadiabatic dynamics: From isolated molecules to molecular assemblies and light-harvesting nanostructures**

**Roland Mitric<sup>1</sup>**

*<sup>1</sup>Institute for physical and theoretical chemistry, Julius-Maximilians-Universität Würzburg  
Emil-Fischer-Str. 42, D-97074 Würzburg, Germany*

The combination of mixed quantum-classical dynamics with efficient electronic structure methods was developed in order to simulate light-induced processes in complex molecules, multichromophoric aggregates and metallic nanostructures. We will demonstrate how the combination of nonadiabatic dynamics with experimental pump-probe techniques such as time-resolved photoelectron imaging (TRPEI) allows to fully resolve the mechanism of excited state relaxation through conical intersections in several prototype organic- and biomolecules.

Currently there is growing evidence that nonadiabatic relaxation processes also play a fundamental role in determining the efficiency of excitonic transfer or charge injection in multichromophoric assemblies. Since such systems are currently out of the reach of the state-of-the-art quantum chemistry a development of even more efficient quantum chemical approaches is necessary in order to describe the excited state dynamics in such assemblies. For this purpose we have recently developed long-range corrected time-dependent density functional tight binding (LC-TDDFTB) nonadiabatic dynamics and have applied it in order to simulate exciton relaxation and energy transfer dynamics in complex systems. The applications of the method to the investigation of the optical properties and dynamics in multichromophoric assemblies including stacked pi-conjugated organic chromophores, model molecular crystals as well as self-organized dye aggregates will be presented. Finally, we will address exciton transport dynamics coupled with the light propagation in hybrid exciton-plasmon nanostructures, which represent promising materials for the development of novel light-harvesting systems.

## New strategies for non-adiabatic dynamics with trajectories

I. Tavernelli<sup>1</sup>, F. Agostini<sup>2</sup>, S. K. Min<sup>3</sup>, E. K. U. Gross<sup>4</sup>

<sup>1</sup>IBM Research - Zurich, 8803 Rüschlikon, Säumerstrasse 4, Switzerland

<sup>2</sup>Department of Chemical Physics, University of Paris-Sud, Paris

<sup>3</sup>Department of Chemistry, UNIST, Ulsan 689-798, Korea

<sup>4</sup>Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany

Initially restricted to a single adiabatic state, DFT-based molecular dynamics was recently extended to the non-adiabatic regime becoming an important tool for the study of photophysical and photochemical processes. Among the most commonly used trajectory-based non-adiabatic MD (NAMD) schemes are Ehrenfest dynamics and Tully's fewest switching surface hopping (FSSH). Despite their enormous impact in the quantum chemistry community, these methods suffer from many limitations e.g., the impossibility to describe wavepacket branching in Ehrenfest dynamics and the presence of over-coherence in FSSH. These failures are mainly associated to the approximate character of these approaches, which can hardly be improved due to the lack of a solid theoretical background.

To overcome these limitations, several alternative trajectory-based methods have been developed, which all share the common feature of being derived from a well defined mixed quantum-classical limit of the underlying exact time-dependent Schrödinger equation. Among others, there are multiple spawning [1], Bohmian dynamics [2], exact factorization [3] and the conditional wavefunction approaches.

In this talk, I will present some novel and promising trajectory-based NAMD schemes derived from different rigorous mixed quantum-classical limits of the exact coupled electrons-nuclei quantum dynamics [4]. In particular, I will describe the derivation and the implementation of two approaches based on the exact factorization theorem and Bohmian dynamics, respectively. Their advantages and disadvantages with respect to classical FSSH will also be discussed. These methods will then be applied (with suited approximations) to the study of the ultrafast electron and nuclear dynamics in several molecular systems in the gas and condensed phases.

- [1] M. Ben-Nun, J. Quenneville, and T. J. Martínez, *J. Phys. Chem. A* **104**, 5161–5175 (2000).
- [2] B.F.E. Curchod, I. Tavernelli, *J. Chem. Phys.* **138**, 184112 (2013); I. Tavernelli, *Phys. Rev. A*, **87**, 042501 (2013).
- [3] A. Abedi, F. Agostini, E.K.U. Gross, *Europhysics Letters* **106**, 33001 (2014).
- [4] S.K. Min, F. Agostini, I. Tavernelli, E. K. U. Gross, *J. Phys. Chem. Lett.*, *accepted*.

## Quantum dynamics simulations of photo-excited molecules using the MCTDH method

Graham Worth<sup>1</sup>

<sup>1</sup>*School of Chemistry, University College London, WC1H 0AJ, U.K.*

The direct solution of the time-dependent Schrödinger equation has become an essential tool for the theoretical study of fundamental molecular processes. Traditionally, numerically exact solutions scale exponentially with system size, but the Multi-configuration time-dependent Hartree (MCTDH) method [2] provides a powerful quantum dynamics algorithm able to treat polyatomic molecules. This is particularly useful in the study of photochemistry where non-adiabatic effects can couple the motion of the electrons and nuclei and a full quantum treatment is required. Simulation of spectra can be used to benchmark excited-state calculations and provide an interpretation of the states involved. The population dynamics can then be followed to give timescales and pathways for relaxation dynamics.

A big problem is how to obtain potential energy surfaces for the coupled manifold of states of excited polyatomic molecules. Much success to date has been had with the vibronic coupling model Hamiltonian [3]. Examples are pyrrole [4], where simulations provided a new interpretation of the absorption spectrum and benzene [5], where a ultrafast intersystem crossing has been shown to be a possible pathway. Recent work aims to extend the utility and flexibility of quantum dynamics simulations by calculating the potential surfaces on-the-fly using a variational Gaussian wavepacket basis [6].

- [1] R. P. Feynman, *Phys. Rev.* **56**, 340 (1939).
- [2] M. Beck, A. Jäckle, G. Worth and H.-D. Meyer, *Phys. Rep.* **324**, 1 (2000).
- [3] G. A. Worth, H.-D. Meyer, H. Köppel, L. S. Cederbaum and I. Burghardt, *Int. Rev. Phys. Chem.* **27**, 569 (2008).
- [4] S. Neville and G. A. Worth, *J. Chem. Phys.* **140**, 034317 (2014).
- [5] T. J. Penfold, R. Spesyvtsev, O. Kirkby, R. S. Minns, D. Parker, H. H. F. Fielding and G. A. Worth, *J. Chem. Phys.* **137**, 204310 (2012).
- [6] G. W. Richings, I. Polyak, K. E. Spinlove, G. A. Worth, I. Burghardt and B. Lasorne, *Int. Rev. Phys. Chem.* **34**, 269 (2015).



## TADF efficiencies in coinage-metal coordination complexes and metal-free donor–acceptor systems

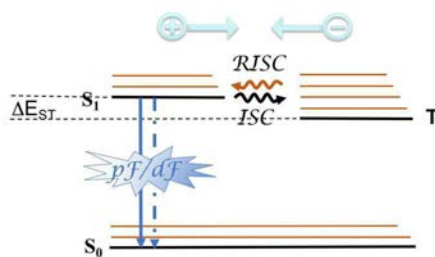
Christel M. Marian<sup>1</sup>, Jelena Föller<sup>1</sup>, Igor Lyskov<sup>1</sup>

<sup>1</sup>*Institute of Theoretical and Computational Chemistry, Heinrich-Heine-University Düsseldorf, Universitätsstraße 1, 40225 Düsseldorf, Germany*

Insight into the factors that determine the probability of thermally activated delayed fluorescence (TADF) is a key step toward the design and optimization of third-generation OLED emitters.

Despite intensive research on this topic in the last years, a consistent rationalization of TADF is still missing. A small singlet-triplet energy splitting  $\Delta E_{ST}$  of the electronically excited emitter states is considered to be a key parameter for efficient TADF. Charge-transfer (CT) states of many coinage-metal coordination complexes and metal-free donor–acceptor systems fulfill this requirement. However,

as will be outlined in this talk, a small  $\Delta E_{ST}$  alone is not sufficient for TADF to take place. The marginal overlap of the transition orbital densities that causes the exchange interaction and hence  $\Delta E_{ST}$  to be small leads to nearly vanishing electronic spin–orbit couplings (SOC) between the  $S_1$  and  $T_1$  states and to low  $S_1 \rightarrow S_0$  fluorescence rates.[1] In many TADF emitters, vibronic coupling of the CT states to nearby locally excited (LE) states plays a central role. For example,  $T_1 \leadsto S_1$  reverse intersystem crossing (RISC) in the assistant dopants ACRXTN [2] and ACRSA [3] is enhanced through vibronic spin–orbit coupling to LE  $^3(\pi\pi^*)$  and  $^3(n\pi^*)$  states of the acceptor moiety. In other compounds, such as the famous 4CzIPN emitter, torsional motions of the substituents are decisive. Phosphorescence and TADF are often competitive channels in metal-to-ligand charge-transfer (MLCT) states of Cu(I) coordination complexes.[4,5] In this talk, methods for determining spin-dependent excited-state properties of donor–acceptor systems and their application to some typical TADF emitters will be presented.



- [1] C. M. Marian, J. Föller, M. Kleinschmidt, M. Etinski, *Intersystem Crossing Processes in TADF Emitters*. In: Yersin (Ed.), *Highly Efficient OLEDs, Materials Based on Thermally Activated Delayed Fluorescence*. Wiley-VCH ISBN: 978-3-527-33900-6 (2018).
- [2] C. M. Marian, *J. Phys. Chem. C* **120**, 3715 (2016).
- [3] I. Lyskov, C. M. Marian, *J. Phys. Chem. C*, submitted (2017).
- [4] J. Föller, M. Kleinschmidt, C. M. Marian, *Inorg. Chem.*, **55**, 7508 (2016).
- [5] A. Liske, L. Wallbaum, J. Föller, M. Gernert, C. Ganter, C. M. Marian, A. Steffen, *Chem. Eur. J.*, submitted (2017).

## **New tools for the description of excited states of molecular systems in complex environment**

**Ilaria Ciofini<sup>1</sup>**

<sup>1</sup> *Chimie ParisTech, PSL Research University, CNRS, Institut de Recherche de Chimie Paris (IRCP), 75005 Paris, France*

With the aim of providing a simple but realistic description of excited state properties and evolution of molecular systems in gas and condensed phases, we report here examples of application of recently developed density based indexes for the description of excited states.

In particular, the possibility of using density based descriptors both to quantify the extent and magnitude of transferred charge associated to a charge transfer (CT) excitation and to describe excited state reactions and interconversions will be illustrated.

Special emphasis will be devoted to the possibility of providing a realistic description of the environmental effects (ex. solvent, absorption on a surface, encapsulation, molecular crystals) on the overall photophysical properties of these systems by the means of theoretical methods ranging from continuum polarisable models for solvent, cluster approaches, QM/QM' to fully periodic calculations.

A recently developed protocol allowing to efficiently model the effect of the environment (crystalline or amorphous) in a computationally affordable way will be used to disclose the origin of mechanochromism in organic molecular crystals. This work has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No 648558, Project STRIGES).

## Artificial Force Induced Reaction (AFIR) Method for Automated Search of Adiabatic and Nonadiabatic Pathways

Satoshi Maeda<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Faculty of Science, Hokkaido University, N10-W8 Kita-ku, Sapporo, Japan*

The mechanism of chemical reactions can be studied by calculating structures of reaction intermediate (IM) and transition state (TS) along reaction paths. Structures of minimum energy seam of crossing (MESX) and minimum energy conical intersection (MECI) have also been calculated as critical points along paths of nonadiabatic transition. Therefore, finding IMs, TSs, MESXs, and MECIs has great significance in computational chemistry. The geometry optimization is a powerful tool to obtain a structure of these critical points, starting from a given initial guess.

In this study, toward more systematic study and prediction, we have developed an automated method for searching of these structures [1,2]. The method, termed artificial force induced reaction (AFIR) method, has been applied most extensively to organic reactions including organo and organometallic catalysis [3]. Complicated reaction path networks generated by the AFIR method are analyzed by a kinetic approach developed in our group [4]. The AFIR method can be applied not only to the electronic ground state but also to PESs of electronic excited states and their crossings. Therefore, photoreactions have been one of important application targets [5]. In addition, recent developments that enables its applications to crystal structure exploration with periodic boundary conditions [6] and to enzyme with the QM/MM-ONIOM method [7] should also be mentioned. In my talk, these developments and some representative applications will be showcased.

- [1] S. Maeda, K. Ohno, K. Morokuma, *Phys. Chem. Chem. Phys.* **15**, 3683 (2013).
- [2] S. Maeda, Y. Harabuchi, M. Takagi, T. Taketsugu, K. Morokuma, *Chem. Rec.* **16**, 2232 (2016).
- [3] W. M. C. Sameera, S. Maeda, K. Morokuma, *Acc. Chem. Res.* **49**, 763 (2016).
- [4] Y. Sumiya, Y. Nagahata, T. Komatsuzaki, T. Taketsugu, S. Maeda, *J. Phys. Chem. A* **119**, 11641 (2015).
- [5] K. Saita, Y. Harabuchi, T. Taketsugu, O. Ishitani, S. Maeda, *Phys. Chem. Chem. Phys.* **18**, 17557 (2016).
- [6] M. Takagi, T. Taketsugu, H. Kino, Y. Tateyama, K. Terakura, S. Maeda, *Phys. Rev. B* **95**, 184110 (2017)
- [7] K. Suzuki, K. Morokuma, S. Maeda, *J. Comput. Chem.* (in press).

## The curious case of conical intersections in coupled cluster theory

Eirik F. Kjørnstad and Henrik Koch\*

Department of Chemistry, Norwegian University of Science and Technology, 7491  
Trondheim, Norway

### ABSTRACT

The motion of electrons and nuclei in photochemical events often involve conical intersections, degeneracies between electronic states. They serve as funnels for nuclear relaxation—on the femtosecond scale—in processes where the electrons and nuclei couple nonadiabatically. Accurate ab initio quantum chemical models are essential for interpreting experimental measurements of such phenomena. We have recently resolved a long-standing problem in coupled cluster theory<sup>1,2</sup>, presenting the first formulation of the theory that correctly describes conical intersections between excited electronic states of the same symmetry. This new development demonstrates that the highly accurate coupled cluster theory can be applied to describe dynamics on excited electronic states involving conical intersections.

\*henrik.koch@ntnu.no

1. “Crossing conditions in coupled cluster theory”, Eirik F. Kjørnstad, Rolf H. Myhre, Todd J. Martinez and Henrik Koch (submitted - <https://arxiv.org/abs/1708.01252>)
2. “Resolving the notorious case of conical intersections for coupled cluster dynamics”, Eirik F. Kjørnstad and Henrik Koch (submitted - <https://arxiv.org/abs/1708.01269>)

## Semiempirical quantum chemistry: Methodology and excited-state dynamics

Walter Thiel

*Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim,  
Germany*

Semiempirical quantum-chemical methods are well-established tools for computational studies of large molecules [1]. Methods with explicit orthogonalization corrections (OM1, OM2, OM3) offer better overall accuracy in standard statistical evaluations of ground-state properties as well as qualitative improvements for hydrogen bonding and conformational properties [2,3]. OMx-based studies of electronically excited states employ a general implementation of the GUGACI approach in a semiempirical framework which provides analytic gradients and nonadiabatic couplings. Comparisons with high-level ab initio benchmark data show that OMx/MRCI methods describe electronically excited states reasonably well [4]. They can thus be used in mixed quantum-classical dynamics to investigate fast nonradiative relaxation processes after photoexcitation [1,5].

The lecture will address the theoretical background of the OMx methods and report on recent comprehensive benchmarks and unpublished methodological enhancements. In addition, it will present selected OM2/MRCI studies of surface-hopping excited-state dynamics; recent examples include simulations on light-driven rotary molecular motors [6], GFP chromophores [7], arylazopyrazole photoswitches [8], and tetraphenylethene derivatives [9].

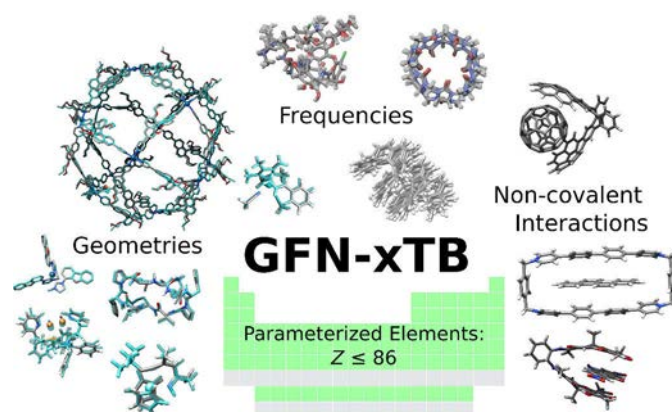
- [1] W. Thiel, *WIREs Comp. Mol. Sci.* **4**, 145-157 (2014).
- [2] P. O. Dral, X. Wu, L. Spörkel, A. Koslowski, W. Weber, R. Steiger, M. Scholten, W. Thiel, *J. Chem. Theory Comput.* **12**, 1082-1097 (2016).
- [3] P. O. Dral, X. Wu, L. Spörkel, A. Koslowski, W. Thiel, *J. Chem. Theory Comput.* **12**, 1097-1120 (2016).
- [4] D. Tuna, Y. Lu, A. Koslowski, W. Thiel, *J. Chem. Theory Comput.* **12**, 4400-4422 (2016).
- [5] L. Spörkel, W. Thiel, *J. Chem. Phys.* **144**, 194108 (2016).
- [6] A. Nikiforov, J. A. Gamez, W. Thiel, M. Filatov, *J. Chem. Phys. Lett.* **7**, 105-110 (2016).
- [7] X.-Y. Liu, X.-P. Chang, S.-H. Xia, G. Cui, W. Thiel, *J. Chem. Theory Comput.* **12**, 753-764 (2016).
- [8] Y.-T. Wang, X.-Y. Liu, G. Cui, W.-H. Fang, W. Thiel, *Angew. Chem. Int. Ed.* **55**, 14009-14013 (2016).
- [9] Y.-J. Gao, X.-P. Chang, X.-Y. Liu, Q.-S. Li, G. Cui, W. Thiel, *J. Phys. Chem. A* **121**, 2572-2579 (2017).

## Applications of the Extended Tight Binding Method (GFN-xTB)

Stefan Grimme<sup>1</sup>

<sup>1</sup>*Mulliken Center for Theoretical Chemistry, Institute for Physical and Theoretical Chemistry, University of Bonn, Berlingstraße 4, 53115 Bonn, Germany*

The computational treatment of large molecular systems in a multi-level scheme requires a quantum chemistry method which is able to provide good structures, vibrational frequencies as well as reasonable non-covalent interactions for more or less arbitrarily composed systems. We recently developed a special purpose self-consistent density functional TB scheme covering all spd-block elements and the lanthanides up to  $Z=86$ [1]. Key features of the Hamiltonian are the use of partially polarized Gaussian type orbitals, a double-zeta orbital basis for hydrogen, atomic-shell charges, diagonal third-order charge fluctuations, coordination number-dependent energy levels, a non-covalent halogen-bond potential, and the well established D3 dispersion correction. Application of this method to various problems in chemistry will be shown like optimization of large supramolecular systems, computation of electron ionization mass spectra[2], automated search for protomers[3], computation of the fractional orbital density for metallo-proteins[4], and conformation search for the automatic prediction of NMR spectra.



- [1] S. Grimme, C. Bannwarth, P. Shushkov, *J. Chem. Theory Comput.* **13**, 1989 (2017).
- [2] V. Asgeirsson, C. A. Bauer, S. Grimme, *Chem. Sci.* DOI:10.1039/C7SC00601B.
- [3] P. Pracht, C. A. Bauer, S. Grimme, *J. Comput. Chem.* submitted.
- [4] C. A. Bauer, A. Hansen, S. Grimme *Chem. Eur. J.* **23**, 6150 (2017).

## Developing Improved Force Fields.

**Frank Jensen**

*Department of Chemistry, University of Aarhus  
Langelandsgade 140, Aarhus, Denmark*

Molecular dynamics simulations rely on computational efficient energy functions, denoted force fields. As simulation times become longer, the accuracy of the force field may become the limiting factor. Production type force fields for biomolecular simulations rely on harmonic energy functions for the stretch and bend energy terms, a low-order Fourier expansion for the torsional energy and a combination of a Lennard-Jones and a Coulomb expression for the non-bonded interactions. The latter is often modelled by fixed atomic charges, but can be improved by higher order atomic multipoles and including polarization. We will present analyses and results for how to improve the description of the non-bonded interaction energies in a systematic fashion based on ab initio calculations [1-4].

- [1] S. Jakobsen, F. Jensen, *J. Chem. Theory Comp.* **10**, 5493 (2014)
- [2] S. Jakobsen, F. Jensen, *J. Chem. Theory Comp.* **12**, 1824, 2999 (2016)
- [3] E. Sedghamiz, B. Nagy, F. Jensen, *submitted*
- [4] P. P. Poier, F. Jensen, *in preparation*

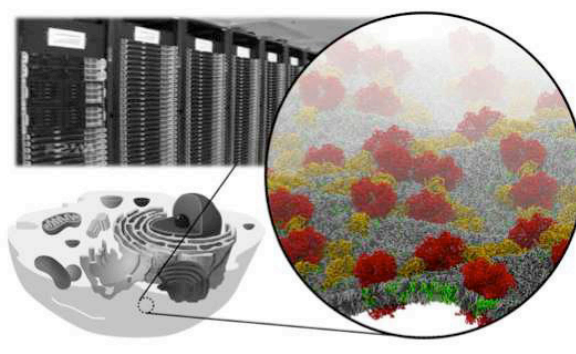
## Computational microscopy of (bio)molecular processes

Siewert J. Marrink<sup>1</sup>

<sup>1</sup>*GBB Institute, University of Groningen, The Netherlands.*

Computational ‘microscopy’ refers to the use of computational resources to simulate the dynamics of a molecular system, providing a spatio-temporal resolution that is unmatched by experimental microscopy methods [1]. Recent advances in coarse-grain modeling and multiscale methods [2] allow us to zoom out from individual atoms and molecules to supramolecular aggregates that contain tens of millions of particles and capture the complexity of realistic systems.

In this lecture I will describe the state-of-the-art of modelling (bio)molecular processes with the coarse-grain Martini model developed in our lab [3]. I will illustrate the power of the model by providing a few in-depth examples of large-scale simulations, including the formation of respiratory chain supercomplexes in mitochondrial membranes [4], the exchange of electron carriers in photosystems [5], and the formation of bulk heterojunction morphologies underlying organic solar cells [6].



- [1] H.I. Ingólfsson, C. Arnarez, X. Periole, S.J. Marrink. *J. Cell Science*, **129**, 257 (2016).
- [2] H.I. Ingólfsson, C.A. Lopez, J.J. Uusitalo, D.H. de Jong, S. Gopal, X. Periole, S.J. Marrink. *WIREs Comput. Mol. Sci.*, **4**, 225 (2014).
- [3] S.J. Marrink, D.P. Tieleman. *Chem. Soc. Rev.*, **42**, 6801 (2013).
- [4] C. Arnarez, S.J. Marrink, X. Periole. *Chem. Sci.*, **7**, 4435 (2016).
- [5] F.J. van Eerden, M.N. Melo, P.W.J.M. Frederix, X. Periole, S.J. Marrink. *Nature Commun.* **8**, 15214 (2017).
- [6] R. Alessandri, J.J. Uusitalo, A.H. de Vries, R.W.A. Havenith, S.J. Marrink. *J. Amer. Chem. Soc.*, **139**, 3697 (2017).



## **Using Semiempirical Methods for Fast and Automated Predictions.**

**Jan H. Jensen<sup>1</sup>**

*<sup>1</sup>Department of Chemistry, University of Copenhagen, Universitetsparken 5, Copenhagen,  
Denmark*

I'll talk about how semiempirical methods can be used to predict molecular properties such as pKa values and barrier heights and how to make such methods accessible to non-experts.

We will present several developments in the FCIQMC methodology, including a time-dependent generalization of the method, which allows the calculation of excitation spectra of *ab initio* Hamiltonians. We demonstrate the methodology to atomic and molecular systems, as well as to the calculation of (real-frequency) Green's functions of Hubbard models. Regarding recent applications, we will show results of large-scale CASSCF calculations on the spin energetics of Fe(II) porphyrins, and as well to cuprate systems, analyzing the results in terms of dynamical screening of on-site (Hubbard-like) repulsion through appropriate excitation channels.

## Multi-state effective Hamiltonian and size-consistency corrections for stochastic configuration interactions

Seiichiro Ten-no

*Graduate School of Science, Technology, and Innovation, Kobe University, Rokkodai-cho,  
Nada-ku, Kobe 657-8501, Japan*  
tenno@garnet.kobe-u.ac.jp

Model space quantum Monte Carlo (MSQMC) [1] is a stochastic approach to determine the effective Hamiltonian by sampling the contribution of Slater determinants outside the model space, facilitating the calculation of excited electronic states with quasi-degeneracy in a very large Hilbert space. We implemented massively parallel MSQMC by distributing walkers and model space determinants [2] within the framework of energy independent partitioning (EDP) of Lödwin, in which states in the vicinity of the target energy converges to the exact solutions. More recently, we have introduced a multi-state formalism [4] within MSQMC, which allows us to simultaneously obtain several roots in the effective Hamiltonian avoiding intruder states. This formalism is closely related to the dual partitioning [3], in which the efficiency of MSQMC is improved dramatically. We further introduce a new sampling criterion suitable for a series of size-consistency corrections including stochastic CEPA-type, a posteriori, and perturbative corrections [4].

- [1] S. Ten-no, *J. Chem. Phys.* **138**, 164126 (2013).
- [2] Y. Ohtsuka and S. Ten-no, *J. Chem. Phys.* **143**, 214107 (2015).
- [3] S. Ten-no, arXiv1512.03505.
- [4] S. Ten-no, to appear (2017).

## Stochastic Orbitals for Electronic Structure and Quantum Chemistry

Roi Baer<sup>1</sup>

<sup>1</sup>*Fritz Haber Center, Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

An *ab initio* Langevin dynamics approach is developed based on stochastic density functional theory (sDFT) within a new *embedded saturated fragment* formalism, applicable to covalently bonded systems. The forces on the nuclei generated by sDFT contain a random component natural to Langevin dynamics and its standard deviation is used to estimate the friction term on each atom by satisfying the fluctuation–dissipation relation. The overall approach scales linearly with system size even if the density matrix is not local and is thus applicable to ordered as well as disordered extended systems. We implement the approach for a series of silicon nanocrystals (NCs) of varying size with a diameter of up to 3nm corresponding to  $N_e = 3000$  electrons and generate a set of configurations that are distributed canonically at a fixed temperature, ranging from cryogenic to room temperature. We also analyze the structure properties of the NCs and discuss the reconstruction of the surface geometry. The method is extended to periodic boundary conditions and is shown highly efficient for studying warm dense matter. We show that the pressure-density and bulk moduli can be determined for WDM silicon. A transition from elastic to plastic material is described.

- [1] Roi Baer, Daniel Neuhauser, and Eran Rabani. Self-averaging stochastic kohn-sham density-functional theory. *Phys. Rev. Lett.*, 111:106402, Sep 2013.
- [2] Eitam Arnon, Eran Rabani, Daniel Neuhauser, and Roi Baer. Equilibrium configurations of large nanostructures using embedded-fragment stochastic density functional theory. *arXiv preprint*, arXiv:1702.02714, 2017.
- [3] Yael Cytter, Eran Rabani, Daniel Neuhauser, and Roi Baer. Orbital-less Kohn Sham method for warm dense matter *in preparation*.
- [4] Daniel Neuhauser, Yi Gao, Christopher Arntsen, Cyrus Karshenas, Eran Rabani, and Roi Baer. Breaking the theoretical scaling limit for predicting quasiparticle energies: The stochastic gw approach. *Phys. Rev. Lett.*, 113(7):076402, 2014.
- [5] Yi Gao, Daniel Neuhauser, Roi Baer, and Eran Rabani. Sublinear scaling for time-dependent stochastic density functional theory. *J. Chem. Phys.*, 142(3):034106, 2015.
- [6] Daniel Neuhauser, Eran Rabani, Yael Cytter, and Roi Baer. Stochastic optimally tuned range-separated hybrid density functional theory. *J. Phys. Chem. A*, 120(19):3071–3078, 2015.

**A New Formulation of Quantum Mechanics using Complex Trajectories:  
Application to Nonadiabatic Transitions and Optical Excitation**

**Werner Koch and David J. Tannor**

*Department of Chemical Physics, Weizmann Institute of Science, Rehovot, Israel*

Several years ago, we developed a formulation of the time-dependent Schrodinger equation (TDSE) using complex-valued classical trajectories. The method has a number of appealing features: 1) it has a simple and rigorous derivation from the TDSE with a precisely formulated approximation; 2) it treats classically allowed and classically forbidden processes on the same footing; 3) it allows the introduction of arbitrary time-dependent external fields into the dynamics seamlessly and rigorously. This talk will have three parts: 1) a review of the method and previous applications, including to barrier transmission, bound state dynamics and nonadiabatic dynamics; 2) two new methodological advances that open the door to multidimensional systems and long time dynamics, respectively; 3) applications made possible by these new advances, including long time wavepacket revivals and preliminary results on strong field attosecond tunneling ionization.

- [1] Y. Goldfarb, I. Degani and D.J. Tannor, *J. Chem. Phys.* **125**, 231103 (2006).
- [2] N. Zamstein and D. J. Tannor, *J. Chem. Phys.* **137**, 22A517-8 (2012).
- [3] N. Zamstein and D. J. Tannor, *J. Chem. Phys.* **140**, 041105 (2014).
- [4] W. Koch and D. J. Tannor, *Chem. Phys. Lett.* **683**, 306 (2017).

**Dispersion in Intermolecular Interactions****Mark S. Gordon, Emilie Guidez, Peng Xu**

*Department of Chemistry and Ames Laboratory  
Iowa State University  
Ames, IA 50014  
USA*

Dispersion plays a key role in a broad range of intermolecular interactions. Most dispersion formulations rely on empirically fitted parameters. In contrast, the effective fragment potential (EFP) treats dispersion via a series of first principles derivations that are based on frequency-dependent multipoles. This talk will discuss implementations of the EFP dispersion terms, the use of the EFP dispersion as a correction to computational methods that do not themselves include dispersion, and a consideration of the importance of three-body dispersion interactions.

## Photostability and Photodamage in DNA Building Blocks

**Leticia González**

*Institute of Theoretical Chemistry, University of Vienna,  
Währinger Strasse 17, 1090 Vienna (Austria),  
leticia.gonzalez@univie.ac.at*

Photoexcited DNA, as well as its constituting nucleobases, decay non-radiatively very efficiently thereby dissipating the excess of electronic energy to the ground state and avoiding detrimental excited state reactions. This so-called photostability is contrasted with the existence of long-lived singlet and triplet states in different purine and pyrimidine derivatives, which can lead to cytotoxicity. In this presentation, the efforts of our group in disentangling the deactivation pathways of nucleobases and particular nucleobases analogues will be presented [1]. Furthermore, the mechanism of one of the most common DNA photolesions, the thymine-thymine dimerization will be exposed [2]. A common methodology employed in all investigated systems is our surface-hopping molecular dynamics code including non-adiabatic and spin-orbit couplings [3].

- [1] S. Mai, N. Dunn, L. Martínez-Fernández, M. Pollum, P. Marquetand, I. Corral, C. Crespo-Hernández, L. González, *Nat. Commun.* **7**, 13077, (2016)
- [2] C. Rauer, J. J. Nogueira, P. Marquetand, L. González, *J. Am. Chem. Soc.* **138**, 15911, (2016)
- [3] M. Richter, P. Marquetand, J. González-Vázquez, I. Sola, L. González, *J. Chem. Theory Comput.* **7**, 1253 (2011).

## **Non-Adiabatic Chemiluminescent Dynamics of the Methyl-Substituted 1,2-Dioxetanes**

**Morgane Vacher<sup>1</sup>, Ignacio F. Galvan<sup>1</sup>, Anders Brakestad<sup>1</sup>, Hans O. Karlsson<sup>1</sup>, Roland Lindh<sup>1</sup>**

*<sup>1</sup>Dept. of Chemistry - Ångström, Uppsala University, Lägerhyddvägen 1, Uppsala, Sweden*

That the origin of chemi- and bioluminescence is a non-adiabatic process originating from the breakage of a peroxide bond is well understood. However, some details in the mechanisms of chemi- and bioluminescence are not well understood. In this lecture we will unravel one of these lesser understood experimental observations. That is, the intriguing and dramatic increase - 0.003 to 0.35 - of the quantum yield of the phosphorescence for the series of 1,2-dioxetane molecules substituted going from none up to four methyl groups. This changes of quantum yield, more than two orders of magnitude, is studied in a series of non-adiabatic surface hopping dynamics simulations using multi-configurational electron structure theory. The dynamics reveal how the seemingly innocent methyl groups retards the dynamic of the fragmentation process - 1,2-dioxetane thermally fragments to two formaldehyde - in a so-called entropic trap, there by enhancing the interstate crossing efficiency. The lecture will initially give a brief background to the field of chemi- and bioluminescence, followed by the details for the problem and simulations listed above.



## Simulation of Ultrafast Excited State Dynamics in Transition Metal Complexes

**Maria Fumanal, Julien Eng, Etienne Gindensperger, Chantal Daniel**

*Laboratoire de Chimie Quantique, Institut de Chimie Strasbourg, UMR-7177 CNRS/  
Université de Strasbourg, 1 Rue Blaise Pascal BP 296/R8, F-67008 Strasbourg, France*

The ultrafast luminescent decay of Rhenium(I) complexes, representative of  $\alpha$ -diimine photosensitizers, is interpreted by means of wavepacket propagations based on the multiconfiguration time-dependent Hartree (MCTDH) method.



On the basis of electronic structure data obtained at the time-dependent density functional theory (TD-DFT) level, the luminescence decay is simulated by solving a multi-state multi-mode problem including both vibronic and spin-orbit coupling (SOC) up to fifteen vibrational modes [1]. A careful analysis of the results provides the key features of the mechanism of the intersystem crossing (ISC) in this class of complexes used as building units in light activated long-range electron transfer in modified proteins [2]. The intermediate signals, detected by means of fs - ps time resolved spectroscopies [3], are assigned to specific excited states.

[1] M. Fumanal, E. Gindensperger, C. Daniel, *J. Chem. Theory. Comput.* **13**, 1293 (2017) ; Y. Harabuchi, J. Eng, E. Gindensperger, T. Taketsugu, S. Maeda, C. Daniel, *J. Chem. Theory Comput.* **12**, 2335 (2016); C. Gourlaouen, J. Eng, M. Otsuka, E. Gindensperger, C. Daniel, *J. Chem. Theory Comput.* **11**, 99 (2015); J. Eng, C. Gourlaouen, E. Gindensperger, C. Daniel, *Acc. Chem. Res.* **48**, 809 (2015).

[2] A. M. Blanco-Rodríguez, M. Busby, C. Grădinaru, B. R. Crane, A. J. Di Bilio, P. Matousek, M. Towrie, B. S. Leigh, J. H. Richards, A. Vlček Jr., H. B. Gray, *J. Am. Chem. Soc.* **18**, 4365 (2006); A. M. Blanco-Rodríguez, M. Busby, K. Ronayne, M. Towrie, C. Grădinaru, J. Sudhamsu, J. Sýkora, M. Hof, S. Záliš, A. J. Di Bilio, B. R. Crane, H. B. Gray, A. Vlček Jr. *J. Am. Chem. Soc.* **131**, 11788 (2009).

[3] A. M. Blanco-Rodríguez, M. Towrie, J. Sýkora, S. Záliš, A. Vlček Jr., *Inorg. Chem.* **50**, 6122 (2011); A. El Nahhas, C. Consani, A. M. Blanco-Rodríguez, K. M. Lancaster, O. Braem, A. Cannizzo, M. Towrie, I. P. Clark, S. Záliš, M. Chergui, A. Vlček Jr., *Inorg. Chem.* **50**, 2932 (2011); A. Vlček Jr. *Top. Organomet. Chem.* **29**, 73 (2010)

## Theories of SERS, TERS, Electrochemistry and Plasmon-Enhanced Energy Transfer

George C. Schatz<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Northwestern University, Evanston IL 60208 USA*

This talk will provide an overview of recent advances in the development of theoretical methods for characterizing SERS and TERS, with emphasis on electronic structure methods for plasmonic clusters, and including a recently developed semiempirical approach that enables us to determine the resonant charge transfer contribution to SERS, and to TERS measurements of single molecule electrochemistry. I will also describe a new approach to plasmon enhanced resonant energy transfer based on quantum electrodynamics.

The theory work begins with electronic structure methods for describing clusters of silver atoms with 10-200 atoms as such clusters have been demonstrated to exhibit plasmon-like excited states that consist of coherent superpositions of many particle-hole excitations. Our past work with such clusters has demonstrated (using TDDFT) that the cluster plasmon energies red shift with increasing cluster size, and extrapolate smoothly to plasmons that are well known for silver nanoparticles in the 20 nm and larger regime. These clusters are therefore useful for describing surface enhanced Raman spectroscopy (SERS), wherein a molecule like pyridine is adsorbed on a cluster, and the Raman intensity of the molecule is evaluated at frequencies that are resonant with the plasmon. However self-interaction errors lead to charge transfer states that often have unphysically low energies, and this sometimes leads to unphysical features in the spectra. Recently we have developed improved INDO-based methods that generate the same spectral properties as TDDFT but the charge transfer states are physically meaningful. This has enabled us to generate a meaningful description of both the electromagnetic and chemical mechanisms of SERS and the tip-enhanced variant, TERS. In addition, this approach can be used to mimic electrochemistry experiments, and we demonstrate the utility of this by showing how this can be applied to single-molecule electrochemistry measurements that have recently been reported in the Van Duyne lab at Northwestern.

In another direction, we have recently developed a method for calculating the rate of energy transfer between donor and acceptor molecules that are in the presence of a complex dispersive dielectric medium that can include plasmonic nanoparticles. This method involves full quantum electrodynamics, but the computational effort is simply that of a standard classical Maxwell equation solver, such as the finite difference time-domain method. We demonstrate the application of this approach to plasmon-mediated energy transfer, where the rates can be enhanced by orders of magnitude compared to standard energy transfer dynamics in the absence of nanoparticles.

## Electrochemistry and Nonadiabatic Dynamics at Metal Surfaces:

### The importance of electron-electron correlation

Joseph E Subotnik<sup>1</sup>, Wenjie Dou<sup>1</sup>, Gaohan Miao<sup>1</sup>

<sup>1</sup>*Dept of Chemistry, University of Pennsylvania*

<sup>2</sup>*231 S. 34th Street, Philadelphia PA 19104 USA*

There are many unanswered questions regarding the dynamics of molecules sitting on metal surfaces, which can be probed either with scattering experiments (more directly) or with electrochemical measurements (more indirectly). Many, many, many advances will be required to understand these dynamics fully, including embedding theories for electronic structure, nonadiabatic quantum dynamics to describe the motion of nuclei, and statistical mechanics to describe the distribution of binding sites at the interface. Understanding these dynamics will be a key challenge for the next generation of theorists.

In this talk, I will highlight our recent work with the two standard techniques for treating nuclear motion (**electronic friction** vs. **surface hopping**). Even with these very simple methods, several interesting features emerge including: (i) non-intuitive vibrational relaxation rates and (ii) exotic friction tensors in the presence of electron-electron interactions. I will introduce these phenomena and focus especially on **how electron-electron correlation affects nuclear dynamics near surfaces.**

## Many-body potentials for water and protonated water clusters and VSCF/VCI calculations of IR spectra

**Qi Yu, Chen Qu, Yimin Wang, Kee Wang, Joel Bowman**

*Department of Chemistry, Emory University,  
1515 Dickey Drive, Atlanta, GA 30322 USA*

High-level, *ab initio*-based many-body potentials and dipole moment surfaces for water and protonated water clusters enable quantum and semi-quantum calculations of vibrational dynamics that would be prohibitive using “on-the-fly” approaches. The development of these surfaces will be briefly reviewed and several recent applications will be given. These include addressing the controversy about whether the experimental IR spectrum of the  $\text{H}_9\text{O}_4^+$  cluster is of the Eigen or Zundel motif and the far IR spectra of small water clusters. Time permitting, applications to hydrate clathrates of several molecules will also be presented.

## What molecules can reveal about fundamental interactions

Robert Berger<sup>1</sup>

<sup>1</sup>*Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Str. 4, 35032 Marburg, Germany*

Electroweak quantum chemistry accounts for the unification of electromagnetic and (fundamental) weak interactions and thereby allows to predict tiny effects in molecules that are due to the violation of parity (P), the symmetry with respect to spatial inversion. This symmetry violation is a signature of the weak interaction and is predicted to lead in open-shell diatomic molecules to a P-odd hyperfine coupling contribution that can in principle be detected in the spin-rotational spectrum. Beyond such P-odd effects, one can also attempt to search for intriguing P,T-odd effects, with T referring to time-reversal symmetry. For instance open-shell diatomic molecules that contain heavy nuclei are expected to strongly enhance effects of the long-sought electric dipole moment of an electron (eEDM). This P,T-odd moment is considered as one of the most sensitive probes for physics being at odds with the well-established standard model of particle physics. By that token, combined theoretical and spectroscopic studies of molecular systems have the potential to complement or even outperform traditional high-energy physics experiments.

Here we discuss how such violations of fundamental symmetries can be taken into account within a quasi-relativistic (two-component) zeroth order regular approximation approach to electroweak quantum chemistry and highlight challenges and opportunities in the high-resolution spectroscopy of heavy-elemental compounds. Select applications will include the molecule radium monofluoride (RaF, see [1,2]) and other promising molecular systems [3] that are predicted to be favourable for a search of fundamental symmetry violations in general and an eEDM in particular.

- [1] T. A. Isaev, R. Berger, *arXiv:1302.5682*.
- [2] A. D. Kudashov, A. N. Petrov, L. V. Skripnikov, N. S. Mosyagin, T. A. Isaev, R. Berger, A. V. Titov, *Phys. Rev. A* **90**, 052513 (2014); *arXiv:1405.6391*.
- [3] K. Gaul, R. Berger, *J. Chem. Phys.* **117**, 014109 (2017); *arXiv:1703.06838*.

## **Computational Vibrational Spectroscopy: Anharmonic Algorithms and Determination of 3D Structures of Biomolecular Conformers**

**R. Benny Gerber**

*Institute of Chemistry, The Hebrew University of Jerusalem, Israel and  
Department of Chemistry, University of California, Irvine, CA, USA*

Recent progress in anharmonic calculations of vibrational spectroscopy of macromolecules is described. New variants of the VSCF approximation are used to compute the vibrational spectroscopy of individual conformers of peptides, and in combination with high-resolution experimental data this leads to determination and validation of the 3D structures of the conformers. Anharmonic effects in the spectroscopy play a crucial role in the structure determination. A major highlight of the results in the determination of the structures of three conformers of the doubly hydrated decapeptide GramicidinS---( $\text{H}_2\text{O}$ )<sub>2</sub>. This yields important insights into peptide-water interactions. Another challenging structure determination is that of the structure of a conformer of a particular type of Enkephalin, a linear pentapeptide.

Another line of progress is the development of the CSP method for quantum vibrational dynamics in time of large molecules. CSP is a mean-field method as is time-independent VSCF, but the effective single mode potentials in CSP are approximated by classical dynamics. In principle, CSP can be used to compute vibrational linewidths and lineshapes. The usefulness of linewidth in structure determination is currently being explored.

With the above developments vibrational spectroscopy emerges as a potentially powerful tool for biomolecular structure determination.

**On systems with and without excess energy in environment  
ICD and other interatomic mechanisms.**

**Lorenz S. Cederbaum<sup>1</sup>**

*<sup>1</sup>Theoretical Chemistry Department/Institute of Physical Chemistry/University of  
Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany*

How does a microscopic system like an atom or a small molecule get rid of the excess electronic energy it has acquired, for instance, by absorbing a photon? If this microscopic system is isolated, the issue has been much investigated and the answer to this question is more or less well known. But what happens if our system has neighbors as is usually the case in nature or in the laboratory? In a human society, if our stress is large, we would like to pass it over to our neighbors.

Indeed, this is in brief what happens also to the sufficiently excited microscopic system. A new mechanism of energy transfer has been theoretically predicted and verified in several exciting experiments. This mechanism seems to prevail “everywhere” from the extreme quantum system of the He dimer to water and even to quantum dots. The transfer is ultrafast and typically dominates other relaxation pathways.

Can there be interatomic/intermolecular processes in environment when the system itself (again, an atom or small molecule) does not possess excess energy? The answer to this intriguing question is yes. The possible processes are introduced and discussed. Examples and arguments are presented which make clear that the processes in question play a substantial role in nature and laboratory.

**Work on the interatomic processes discussed can be found in the Bibliography:**

<http://www.pci.uni-heidelberg.de/tc/usr/icd/ICD.refbase.html>

## Theoretical molecular line lists for atmospheric characterizations of exoplanets

Sergey Yurchenko and Jonathan Tennyson

*Department of Physics and Astronomy, University College London, Gower Street, WC1E  
6BT, London, UK*

As part of the ExoMol project [1] we develop computational methodology to produce lists of spectroscopic transitions (line lists) for hot molecules. There is a major demand from astrophysics and elsewhere of comprehensive line lists for molecules important in the atmospheres of cool stars and extrasolar planets. This methodology is based on a combination of high level *ab initio* (electronic structure) calculations, high level nuclear motion (variational) calculations and empirical refinement to the highly accurate experimental data (e.g. line positions) [2]. Over the past years there have been a rapid improvement in variational nuclear motion approaches to solving spectroscopic problems, which has been described as the fourth age of quantum chemistry [3]. The main challenge is that very high rotational and vibrational excitations are needed for accurate descriptions of high-temperature molecular spectra. This in turn requires larger basis sets and therefore larger Hamiltonian matrices, with associated increase of the calculation costs in terms of memory (both RAM and storage) and time. The ExoMol project has already produced more than 20 such line lists [4], which complement or even replace measured data. In this presentation, we will review our recent work in the field of theoretical spectroscopy of hot molecules, discuss our methods and present applications to different systems. We will also show examples of some key spectroscopic problems, which are still challenging for the modern *ab initio* spectroscopy.

[1] J. Tennyson and S. N. Yurchenko, *Mon. Not. R. Astron. Soc.* **425**, 21 (2012).

[2] J. Tennyson and S.N. Yurchenko, *Int. J. Quant. Chem.* **117**, 92, (2017).

[3] A. G. Császár, C. Fabri, T. Szidarovszky, E. Mátyus, T. Furtenbacher, and G. Czako, *Phys. Chem. Chem. Phys.* **14**, 1085 (2012).

[4] J. Tennyson, S. N. Yurchenko, A. F. Al-Refaie, et al., *J. Mol. Spectrosc.* **327**, 73 (2016).



## Attochemistry: imaging and controlling electron dynamics in molecules

**Fernando Martín<sup>1</sup>**

<sup>1</sup>*Departamento de Química, Módulo 13, Universidad Autónoma de Madrid, 28049 Madrid, Spain.*

<sup>2</sup>*Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA Nano), Campus de Cantoblanco, 28049 Madrid, Spain.*

<sup>3</sup>*Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, 28049 Madrid, Spain.*

Attosecond light pulses allow one to probe the inner workings of atoms, molecules and surfaces on the timescale of the electronic motion. For example, in molecules, sudden ionization by an attosecond pulse is followed by charge redistribution on a time scale from a few-femtoseconds down to hundreds attoseconds, which is usually followed by fragmentation of the remaining molecular cation. Such complex dynamics arises from the coherent superposition of electronic states covered by the broadband attosecond pulse and from rearrangements in the electronic structure of the molecular cation due to electron correlation. To investigate these ultrafast processes, attosecond pump-probe and transient absorption spectroscopies have been shown to be very valuable tools [1-3]. In this talk I will present the results of molecular attosecond pump-probe experiments and theoretical simulations in which several molecules, from the simplest H<sub>2</sub> one to the aminoacids phenylalanine and tryptophan, are ionized with a single attosecond pulse (or a train of attosecond pulses) and are subsequently probed by one or several infrared or xuv few-cycle pulses. In all cases, the evolution of the electronic and nuclear densities in the photo-excited molecule or remaining molecular ions can be inferred from the measured (or calculated) ionization or fragmentation yields with attosecond time-resolution, and can be visualized by varying the delay between the pump and probe pulses. The results of these pioneering works will certainly serve as a guide of future experimental efforts in more complicated molecules and may open the door to the control of charge transfer in biologically relevant processes [3].

[1] G. Sansone et al, *Nature* **465**, 763 (2010).

[2] F. Calegari et al, *Science* **346**, 336 (2014)

[3] M. Nisoli, P. Decleva, F. Calegari, A. Palacios, and F. Martín, *Chem. Rev.* DOI: 10.1021/acs.chemrev.6b00453

## Novel Multidimensional Spectroscopy of Conical Intersections with X-ray Pulses and Quantum Light

Shaul Mukamel, Markus Kowalewski, and Kochise Bennett

*Department of Chemistry and Department of Physics and Astronomy, University of California, Irvine,  
1102 Natural Sciences II, Irvine, California 92697-2025, USA*

### Abstract:

Multidimensional spectroscopy uses sequences of optical pulses to study dynamical processes in complex molecules through correlation plots involving several time delay periods. Extensions of these techniques to the x-ray regime will be discussed. Ultrafast nonlinear x-ray spectroscopy is made possible by newly developed free electron laser and high harmonic generation sources. The attosecond duration of X-ray pulses and the atomic selectivity of core X-ray excitations offer a uniquely high spatial and temporal resolution. We demonstrate how stimulated Raman detection of an X-ray probe may be used to monitor the phase and dynamics of the nonequilibrium valence electronic state wavepacket created by e.g. photoexcitation, photoionization and Auger processes. Conical intersections (CoIn) dominate the pathways and outcomes of virtually all photophysical and photochemical molecular processes. Despite extensive experimental and theoretical effort CoIns have not been directly observed yet and the experimental evidence is being inferred from fast reaction rates and some vibrational signatures. Novel ultrafast X ray probes for these processes will be presented. Short X-ray pulses can directly detect the passage through a CoIn with the adequate temporal and spectral sensitivity. The technique is based on a coherent Raman process that employs a composite femtosecond/attosecond X-ray pulse to directly detect the electronic coherences (rather than populations) that are generated as the system passes through the CoIn.

Strong coupling of molecules to the vacuum field of micro cavities can modify the potential energy surfaces thereby manipulating the photophysical and photochemical reaction pathways. The photonic vacuum state of a localized cavity mode can be strongly mixed with the molecular degrees of freedom to create hybrid field-matter states known as polaritons. Simulations of the avoided crossing of sodium fluoride in a cavity which incorporate the quantized cavity field into the nuclear wave packet dynamics will be presented. Numerical results show how the branching ratio between the covalent and ionic dissociation channels can be strongly manipulated by the optical cavity.

### References

- [1] Markus Kowalewski , Kochise Bennett, Konstantin Dorfman, and Shaul Mukamel. *Phys. Rev. Lett.* **115**, 193003 (2015).
- [2] Kowalewski, M., Bennett, K., Rouxel, J., and Mukamel, S., *Phys. Rev. Lett.* **117**, 043201 (2016)
- [3] Markus Kowalewski, Kochise Bennett, and Shaul Mukamel. *J. Phys. Chem. Lett.*, **7**, 2050-2054 (2016)
- [4] Konstantin E. Dorfman, Frank Schlawin, and Shaul Mukamel. *Rev. Mod. Phys.* **88**, 045008 (2016)
- [5] Markus Kowalewski , Benjamin Fingerhut, Konstantin Dorfman, Kochise Bennett and Shaul Mukamel. *Chem Rev* (Submitted, 2017).

**The 11<sup>th</sup> Triennial Congress of the World Association of Theoretical and Computational Chemists (WATOC) 27 August-1 September 2017, Munich, Germany**

## Angular Dependence of Ionization by Short, Intense Pulses of Linear and Circularly Polarized Light

**H. Bernhard Schlegel, Pascal Krause, Qing Liao and Wen Li**

*Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA*

The availability of short, intense laser pulses has opened up new frontiers in chemistry and physics. Attosecond laser pulses can directly explore electron dynamics, image molecular orbitals and probe bond making and breaking processes. The response of molecules to short, intense laser pulses cannot be treated by the perturbative methods used for ordinary spectroscopy. Direct simulation of the quantum dynamics is needed to understand the behavior of molecules under these extreme conditions. Short, intense laser pulses in the optical range cause rapid ionization by barrier suppression. We have used time-dependent configuration interaction with an absorbing boundary to simulate the ionization of a series of small molecules by 7 cycle 800 nm pulses of linear and circularly polarized light with intensities ranging from  $1.44 \times 10^{14} \text{ W cm}^{-2}$  to  $5.05 \times 10^{14} \text{ W cm}^{-2}$  [1-4]. The shapes of the ionization yield for linearly polarized light can be understood primarily in terms of the nodal structure of the highest occupied orbitals [1-3]. Depending on the orbital energies, ionization from lower lying orbitals may also make significant contributions to the shapes. The shapes of the ionization yield for circularly polarized light can be readily explained in terms of the shapes for linearly polarized light. Averaging the results for linear polarization over orientations perpendicular to the direction of propagation yields shapes that are in very good agreement with direct calculations of the ionization yield by circularly polarized light [4].

- [1] Krause, P; Schlegel, H. B.; *J. Phys. Chem. Lett.* **2015**, 6, 2140.
- [2] Krause, P; Schlegel, H. B.; *J. Phys. Chem. A* **2015**, 119, 10212.
- [3] Liao, Q.; Li, W.; Schlegel, H. B.; *Can. J. Chem.* **2016**, 94, 989.
- [4] Hoerner, P., Schlegel, H. B.; *J. Phys. Chem. A* **2017**, 121, 1336.

## Light-driven processes in molecular systems: From photophysics to photochemistry

Peter Saalfrank<sup>1</sup>, Shiladitya Banerjee<sup>1</sup>, Tillmann Klamroth<sup>1</sup>, Pascal Krause<sup>1</sup>,  
Boyke Schönborn<sup>1</sup>, Evgenii Titov<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of Potsdam, Karl-Liebknecht-Straße 24-25, D-14476  
Potsdam, Germany*

Modern laser technology and ultrafast spectroscopies have pushed the timescales for detecting and manipulating dynamical processes in molecules from the picosecond over femtosecond domains ( $1\text{ fs} = 10^{-15}\text{ s}$ ), to the so-called attosecond regime ( $1\text{ as} = 10^{-18}\text{ s}$ ). This way, real-time dynamics of electrons and nuclei after their photoexcitation became accessible experimentally. On the theory side, powerful (quantum) dynamical tools have been developed to rationalize experiments on photon-driven molecular species. In this talk, three classes of examples for light-induced processes in molecular systems – two from “photophysics”, one from “photochemistry” – will be presented.

In a first, “photophysical” example the creation of electron wavepackets in molecules by ultrashort laser pulses and their attosecond dynamics will be followed with the help of time-dependent configuration interaction (TD-CI) methods [1]. Stochastic pulse optimization is suggested as a tool to tailor non-linear responses (high harmonic signals) of small molecules such as  $\text{H}_2$  [2]. Much bigger molecules, *e.g.*, diamondoids will be considered in a second example, where the vibronic finestructure in electronic absorption and emission spectra is determined within a time-dependent correlation function approach [3]. This approach has been suggested several decades ago by Heller and coworkers, and is now an efficient method for spectroscopy in complex molecular systems. Also, non-radiative transitions can be treated in this way. Finally, the step to “photochemistry” is made by considering photoswitching of azobenzene molecules in an environment. Here, non-adiabatic molecular dynamics with surface hopping allow for detailed insight into the mechanism of photoinduced *trans*-to-*cis* isomerization [4].

[1] P. Krause, T. Klamroth, P. Saalfrank, *J. Chem. Phys.* **127**, 034107 (2007).

[2] J.B. Schönborn, T. Klamroth, P. Saalfrank, *J. Chem. Phys.* **144**, 044301 (2016).

[3] S. Banerjee, T. Stüker, P. Saalfrank, *Phys. Chem. Chem. Phys.* **17**, 19656 (2015).

[4] E. Titov, G. Granucci, M. Persico, J.P. Götze, P. Saalfrank, *J. Phys. Chem. Lett.* **7**, 3591 (2016).

## On the Perturbative Computation of Ionization Energies

**Peter J. Knowles<sup>1</sup>**

*<sup>1</sup>School of Chemistry, Cardiff University, Park Place, Cardiff CF10 3AT, United Kingdom*

Ionization energies and electron affinities are traditionally calculated either as energy differences between separate computations on the ion and its parent neutral, or through perturbative and other schemes based on a single reference state that is usually the Hartree-Fock wavefunction of the parent. This talk will discuss the relationship between these approaches and the Extended Koopmans Theorem, and outline a new alternative method.

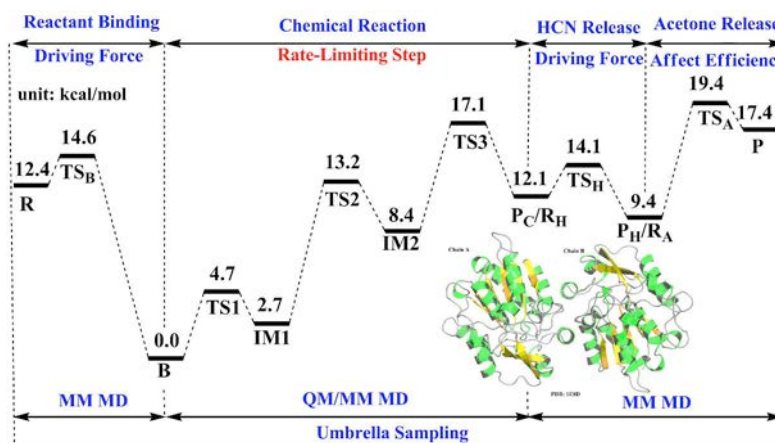
## Global Simulation of Cyanohydrin Cleavage by Hydroxynitrile Lyases

Yuan Zhao and Zexing Cao\*

Department of Chemistry, Xiamen University, Xiamen, China

E-mail: zxcao@xmu.edu.cn

The highly homologous hydroxynitrile lyases (HNLs) from *Manihot esculent* (*MeHNL*) and *Hevea brasiliensis* (*HbHNL*) are both belong to the  $\alpha/\beta$ -hydrolase superfamily, and they convert cyanohydrins into corresponding ketone (aldehyde) and hydrocyanic acid. Based on extensive MM and ab initio QM/MM MD simulations, one-dimensional and two-dimensional free energy profiles on the whole enzymatic catalysis by *MeHNL* and *HbHNL* have been explored, and the effects of key residues around the channel on the delivery of substrate and product have been discussed [1-2]. The residue Trp128 plays an important gate-switch role to manipulate the substrate access to the active site and product release. In particular, the release of acetone and HCN has been firstly detected to follow a stepwise mechanism. The release of HCN is quite facile, while the escaping of acetone experiences a barrier of  $\sim 10$  kcal/mol. The chemical reaction is an endergonic process with the free energy barrier of  $\sim 17.1$  kcal/mol, which dominates the whole enzymatic efficiency. Such energy costs can be compensated by the remarkable energy release during the initial substrate binding. Here the carbon-carbon cleavage is the rate-determined step, differing from *HbHNL* with the rate-limiting step of HCN formation. The protonation state of Lys237 also plays an important role in the carbon-carbon bond cleavage by restoring Ser80Ala mutant system of *MeHNL* into its wild system, which explains the discrepancy between *MeHNL* and *HbHNL* at the molecular or atomic scale. The present results provide a basis to understand the similarity and difference in the enzymatic catalysis by *MeHNL* and *HbHNL*.



### References

- [1] Y Zhao, NH Chen, CJ Wang, ZX Cao, *ACS Catal.*, **2016**, 6, 2145-2157.
- [2] Y Zhao, NH Chen, YR Mo, ZX Cao, *Phys. Chem. Chem. Phys.*, **2014**, 16, 26864-26875.

## Metadynamics Simulations of G-Protein Coupled Receptors

Timothy Clark

*Computer-Chemie-Centrum, Friedrich-Alexander-Universität Erlangen-Nürnberg,  
Nägelsbachstrasse 25, 91052 Erlangen, Germany*

The human genome contains 800 G-protein coupled receptors (GPCRs), that convert extracellular signals (proteins, peptide hormones, small molecules, light ....) into an intracellular action. GPCRs are the targets of approximately 40% of all marketed drugs. Despite their importance, the exact mechanisms of GPCR action are not fully understood. GPCRs can control one or more signaling pathways and GPCR-ligands may be agonists, antagonists, inverse or partial agonists and often show bias for one of the pathways controlled by the receptor. The first X-ray structure of a GPCR was published in 2000 and even today only approximately 40 are available. Classical (force-field) molecular-dynamics simulations therefore play an important role in GPCR-research.

We have used a common metadynamics protocol, in which the multiple-walker technique allows efficient simulations on massively parallel supercomputers, to investigate the mechanisms of activation of a series of GPCRs. [1]

The simulations quite generally reveal multiple binding sites, both for natural peptide hormones [2] and for drug-like molecules. [3] Remarkably, binding free energies can be calculated with a standard error of approximately 1 kcal mol<sup>-1</sup> for all types of ligands and regardless of which binding site the ligand occupies. [1] The effect (agonist, antagonist etc.) and the functional bias of drug-like ligands can be predicted. [4] The role of the intracellular binding partner (usually a G-protein or  $\beta$ -arrestin) is an essential component of activation mechanisms. [5]

[1] N. Saleh, P. Ibrahim, G. Saladino, F. L. Gervasio and T. Clark, *J. Chem. Inf. Model.*, **57**, DOI: 10.1021/acs.jcim.6b00772, (2017)

[2] N. Saleh, E. Haensele, L. Banting, J. Sopkova-de Oliveira Santos, D. C. Whitley, G. Saldino, F. L. Gervasio, R. Bureau and T. Clark, *Angew. Chemie Int. Ed.*, **55**, 8008–8012 (2016).

[3] L. Milanos, N. Saleh, R. C. Kling, J. Kaindl, N. Tschammer and T. Clark, *Angew. Chemie Int. Ed.*, **55**, 15277-15281(2016)

[4] N. Saleh, G. Saladino, F. L. Gervasio and T. Clark, *Chem. Sci.*, **8**, 4019-4026 (2017).

[5] N. Saleh, P. Ibrahim and T. Clark, *Angew. Chemie Int. Ed.*, **56**, DOI: 10.1002/anie.201702468R1 (2017).

## Quantitative Atomistic Simulations for Chemical and Biological Applications

**Markus Meuwly<sup>1</sup>**

*<sup>1</sup>Department of Chemistry, University of Basel, Switzerland*

In this talk I will give an overview of current developments in atomistic simulations to quantitatively investigate condensed-phase systems and phenomena. Examples include 1- and 2-dimensional infrared spectroscopies of labels in proteins, the thermodynamics of halogenated compounds and applications to protein stability and design, and the structural interpretation of metastable states in proteins. Central to all these quests is the availability of flexible and accurate intermolecular interactions to study, analyze and interpret the molecular dynamics of complex systems in solution. Such improved intermolecular interactions and force fields can be obtained from including multipolar interactions or from representing energies from electronic structure calculations by reproducing kernels. The results suggest that atomistic simulations have matured to a degree which allows to use them for interpretation of state-of-the art experiments of chemical and biological systems in the condensed phase.



## Replica-Exchange Enveloping Distribution Sampling (RE-EDS) to Calculate Relative Binding Free Energies

Sereina Riniker<sup>1</sup>

<sup>1</sup>*Laboratory of Physical Chemistry, ETH Zürich, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland*

Enveloping distribution sampling (EDS) [1] allows the calculation of free-energy differences between multiple end states from a single simulation. A reference-state Hamiltonian is simulated which envelopes the Hamiltonians of the end states. The challenge when using EDS is the determination of optimal parameters for the reference-state Hamiltonian. Previously, the choice of parameters for an EDS simulation with multiple end states was a non-trivial problem that limited the application of the methodology [2]. To overcome these limitations, we have generalized the replica-exchange EDS (RE-EDS) methodology proposed in the literature for constant-pH molecular dynamics (MD) simulations [3] to arbitrary systems [4,5]. By exchanging configurations between replicas with different parameters for the reference-state Hamiltonian, major parts of the problem to choose optimal parameters are circumvented. Algorithms to estimate the energy offsets and optimize the replica distribution have been developed. Our approach was tested successfully using a system consisting of nine inhibitors of phenylethanolamine *N*-methyltransferase (PNMT), which were studied previously with thermodynamic integration and pairwise EDS.

[1] C. D. Christ, W. F. van Gunsteren, *J. Chem. Phys.* **126**, 184110 (2007).

[2] S. Riniker, C. D. Christ, N. Hansen, A. E. Mark, P. C. Nair, W. F. van Gunsteren, *J. Chem. Phys.* **135**, 024105 (2011).

[3] J. Lee, B. T. Miller, A. Damjanovic, B. R. Brooks, *J. Chem. Theory Comput.* **10**, 2738-2750 (2014).

[4] D. Sidler, A. Schwaninger, S. Riniker, *J. Chem. Phys.* **145**, 154114 (2016).

[5] D. Sidler, M. Cristófol-Clough, S. Riniker, *J. Chem. Theory Comput.*, online, DOI: 10.1021/acs.jctc.7b00286 (2017).

## Kinetics-Controlled Molecular Self-Assembly Processes Elucidated by Kinetic Network Models

**Xuhui Huang<sup>1</sup>**

*<sup>1</sup>Department of Chemistry, the Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong*

Amphiphile self-assembly is an essential bottom-up approach of fabricating advanced functional materials. Self-assembled materials with desired structures are often obtained through thermodynamic control. Here, we demonstrate that the selection of kinetic pathways can lead to drastically different self-assembled structures, underlining the significance of kinetic control in self-assembly. As the self-assembly process is often highly heterogeneous, systematic elucidation of the dominant kinetic pathways of self-assembly is challenging. Here, based on mass flow, we developed a new method for the construction of kinetic network models and applied it to identify the dominant kinetic pathways from large-scale molecular dynamics simulations. We show that two largely similar amphiphiles, 1-[11-oxo-11-(pyren-1-ylmethoxy)-undecyl]pyridinium bromide (PYR) and 1-(11-((5a1,8a-dihydropyren-1-yl)methylamino)-11-oxoundecyl)pyridinium bromide (PYN), prefer distinct kinetic assembly pathways. While PYR prefers an incremental growth mechanism and forms a nanotube, PYN favors a hopping growth pathway leading to a vesicle. Such preference was found to originate from the subtle difference in the distributions of hydrophobic and hydrophilic groups in their chemical structures, which leads to different rates of the adhesion process among the aggregating micelles. Our results are in good agreement with experimental results, and accentuate the role of kinetics in the rational design of amphiphile self-assembly.

## **New Methods and Models for Condensed Phase Simulation**

**Teresa Head-Gordon**

<sup>1</sup>*Kenneth S. Pitzer Center for Theoretical Chemistry,* <sup>2</sup>*Department of Chemistry,*  
<sup>3</sup>*Department of Chemical and Biomolecular Engineering,* <sup>4</sup>*Department of Bioengineering,*  
*University of California Berkeley*  
<sup>5</sup>*Chemical Sciences Division, Lawrence Berkeley National Labs*  
*Berkeley, California 94720, USA*

I will discuss new theoretical models and extended Lagrangian methods that addresses accuracy and tractability for using atomistic polarizable force fields and linear scaling AIMD. These models and their implementations are opening up new abilities for allowing larger scales of study for molecular simulation with more complex potential energy surfaces. I will highlight a recent application of polarizable models to improve the rate of catalysis by 50X by optimizing electric field environments.

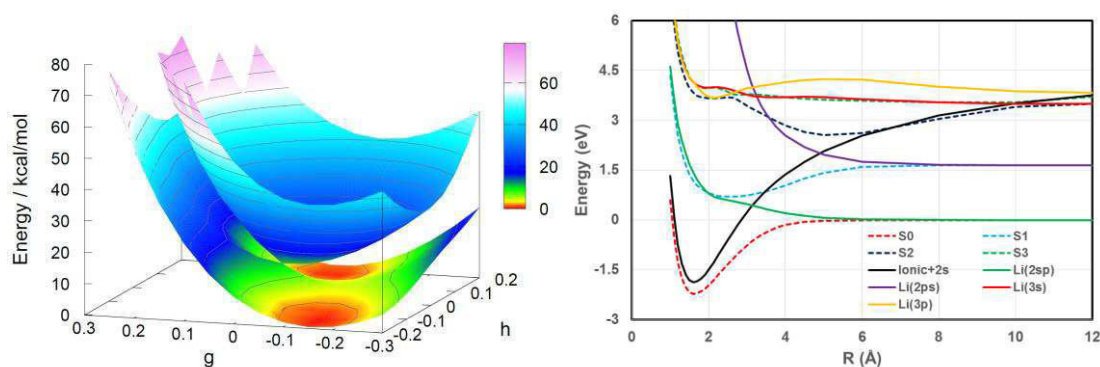
## Methods and applications of multistate density functional theory (MSDFT)

Jiali Gao<sup>1,2</sup>

<sup>1</sup>Theoretical Chemistry Institute, Jilin University, Changchun, 130023, P.R. China

<sup>2</sup>Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA

Charge transfer and energy transfer processes are ubiquitous in chemistry and biological systems. To adequately model these reactions through atomistic simulations, it is useful to define charge localized electronic states. Furthermore, it is of interest to develop methods to represent the potential energy surfaces in terms of relevant diabatic states. In this paper, I will present a block-localization scheme for defining diabatic states by construction (DAC). In particular, a multistate density functional theory (MSDFT) is described to model the ground and excited states of chemical and photochemical processes.



[1] Jiali Gao, Adam Grofe, Haisheng Ren, and Peng Bao, “Beyond Kohn–Sham Approximation: Hybrid Multistate Wave Function and Density Functional Theory”, *Journal of Physical Chemistry Letters*, **7**, 5143–5149 (2016).

[2] Adam Grofe, Zexing Qu, Donald G. Truhlar, Hui Li, and Jiali Gao “Diabatic-At-Construction (DAC) Method for Diabatic and Adiabatic Ground and Excited States Based on Multistate Density Functional Theory”, *Journal of Chemical Theory and Computation*, **13**, 1176–1187 (2017).

## DNA. A FASCINATING MULTISCALE PROBLEM

Modesto Orozco. IRB Barcelona and University of Barcelona

Dna is the paradigm of a multiscale problem. At the smallest scale, DNA needs to be represented at sub-Angstrom resolution level requiring the use of quantum mechanical approaches, while at the largest scale macroscopic methods able to represent a fiber measuring more than a meter need to be used. To tackle this  $10^{10}$  scale problem multi-physic approaches need to be used and coupled with restraints derived from experimental measures. I will summarize during my talk our more recent approaches to approach the multiscale problem in DNA, illustrating how they can provide clues on the epigenetic mechanisms of gene regulation.

- 1) Reference: P.D.Dans, J.Walther, H.Gómez and M.Orozco. "Multiscale simulation of DNA". *Current Opin. Struct. Biol.*, (2016), **37**, 29-45

## Dynamics, Flexibility, Cooperativity and the Evolution of Enzyme Function

**Shina Caroline Lynn Kamerlin**

*Science for Life Laboratory, Department of Cell and Molecular Biology, Uppsala University, BMC Box 596, S-751 24 Uppsala, Sweden*

Recent years have seen an explosion of interest in both experimental and computational studies of the evolution of enzyme function [1,2]. In particular, it has been argued that conformational selection plays a major role in allowing old enzymes to acquire new activities [3]. My group and I have performed detailed computational studies of a broad range of catalytically promiscuous enzymes, in order to probe the molecular origins of both their multifunctionality and its implications for their functional evolution [4-7]. These include alkaline phosphatases [4], organophosphate hydrolases [5,6], aldolases [7] and Kemp eliminases, to name a few examples. Based on this work, we present a molecular model for enzyme evolution, highlighting the critical importance of a fine-tuned interplay between enzyme dynamics, electrostatic cooperativity and conformational selection in allowing for the acquisition of new activities, as well as the ability to select more than one possible reaction from a pool of given substrates.

- [1] O. Khersonsky and D. S. Tawfik, *Annu. Rev. Biochem.* **79**, 471 (2010).
- [2] A. Pabis, F. Duarte and S. C. L. Kamerlin, *Biochemistry* **55**, 3061 (2016).
- [3] N. Tokuriki and D. S. Tawfik, *Science* **324**, 203 (2009).
- [4] A. Barrozo, F. Duarte, P. Bauer, A. T. P. Carvalho and S. C. L. Kamerlin, *J. Am. Chem. Soc.* **137**, 9061 (2015).
- [5] M. Purg, A. Pabis, F. Baier, N. Tokuriki, C. Jackson and S. C. L. Kamerlin, *Phil. Trans. R. Soc. A* **374**, 20160150 (2016).
- [6] D. Blaha-Nelson, D. M. Krüger, K. Szeler, M. Ben-David and S. C. L. Kamerlin, *J. Am. Chem. Soc.* **139**, 1155 (2017).
- [7] H. Ma, K. Szeler, S. C. L. Kamerlin and M. Widersten, *Chem. Sci.* **7**, 1415 (2016).

## **Towards a mechanistic understanding of ribosomal function**

**Lars V. Bock<sup>1</sup>, Michal H. Kolar<sup>1</sup>, Andrea C. Vaiana<sup>1</sup>, Helmut Grubmüller<sup>1</sup>**

*<sup>1</sup>Theoretical and Computational Biophysics Department, Max Planck Institute for Biophysical Chemistry, Am Fassberg 11, Göttingen, Germany*

During protein synthesis, tRNA molecules move from the ribosome's aminoacyl to peptidyl to exit sites, with the two ribosomal subunits remaining associated through a complex network of intersubunit bridges, despite rapid large-scale intersubunit rotation. Using molecular dynamics simulations, we investigated conformational motions during spontaneous translocation, as well as the underlying energetics and kinetics. We asked how binding affinity between the two subunits is controlled and maintained at a quite constant level despite large-scale motions and highly dynamic changes. Indeed, intersubunit rotations exhibit remarkably fast intrinsic submicrosecond dynamics, which requires a fine-tuned flat free energy landscape, as any larger barrier would slow down the conformational motions. The total contribution of the tRNAs to the intersubunit binding enthalpy is almost constant, despite their changing positions in the ribosome during translocation. These mechanisms keep the intersubunit interaction strong and steady during rotation, thereby preventing dissociation and enabling rapid rotation. We further describe a new combined allosteric mechanism for erythromycin-induced translational stalling of the antibiotics sensor peptide ErmB as well as nascent peptide dynamics in the ribosomal exit tunnel.

## Recent Progress in Density Functional Theories

**Donald G. Truhlar<sup>1</sup> and coworkers**

<sup>1</sup>*Department of Chemistry, Chemical Theory Center, and Minnesota Supercomputing Institute, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN55455-0431, USA*

This lecture will include both Kohn-Sham density functional theory (KS-DFT)[1-15] and multiconfiguration pair-density functional theory (MC-PDFT)[16-23]. My group's work on MC-PDFT is collaborative effort with the group of Laura Gagliardi. Other recent coauthors are named in the references below, which highlight our recent emphasis on electronically excited states and transition metals. Different components of the work were supported in part by the Department of Energy, the National Science Foundation, and the Air Force Office of Scientific Research.

- [1] H. S. Yu, X. He, S. L. Li, D. G. Truhlar, *Chem. Sci.* **7**, 5032 (2016).
- [2] P. Verma, R. Maurice, D. G. Truhlar, *J. Phys. Chem. C* **120**, 9933 (2016).
- [3] J. Borycz et al., *Inorg. Chem.* **55**, 4924-4934 (2016).
- [4] S. Huang et al., *J. Phys. Chem. C* **120**, 9637 (2016).
- [5] P. Verma, D. G. Truhlar, *Theor. Chem. Acc.* **135**, 182 (2016).
- [6] H. S. Yu, S. L. Li, D. G. Truhlar, *J. Chem. Phys.* **145**, 130901 (2016).
- [7] S. T. Akin et al., *J. Phys. Chem. Lett.* **7**, 4568 (2016).
- [8] K. Duanmu, D. G. Truhlar, *J. Chem. Theory Comput.* **117**, 835 (2017).
- [9] P. Verma, D. G. Truhlar, *J. Phys. Chem. Lett.* **8**, 380 (2016).
- [10] J. L. Bao, X. Zhang, X. Xu, D. G. Truhlar, *Phys. Chem. Chem. Phys.* **19**, 5839 (2017).
- [11] A. Grofe, Z. Qu, D. G. Truhlar, H. Li, J. Gao, *J. Chem. Theory Comput.* **13**, 1176 (2017).
- [12] P. Verma, D. G. Truhlar, *J. Phys. Chem. C* **121**, 7144 (2017).
- [13] Y. Shu, K. Parker, D. G. Truhlar, *J. Phys. Chem. Lett.* **8**, 2017 (2017).
- [14] P. Verma, D. G. Truhlar, *Phys. Chem. Chem. Phys.* **19**, 12898 (2017).
- [15] P. Verma, Z. Varga, J. E. M. N. Klein, C. J. Cramer, L. Que, Jr., D. G. Truhlar, *Phys. Chem. Chem. Phys.* **19**, 13049 (2017).
- [16] S. Odoh, G. Li Manni, R. Carlson, D. G. Truhlar, L. Gagliardi, *Chem. Sci.* **7**, 2399 (2016).
- [17] C. E. Hoyer, S. Ghosh, D. G. Truhlar, L. Gagliardi, *J. Phys. Chem. Lett.* **7**, 586 (2016).
- [18] J. L. Bao, A. Sand, L. Gagliardi, D. G. Truhlar, *J. Chem. Theory Comput.* **12**, 4274 (2016).
- [19] L. Gagliardi, D. G. Truhlar, G. Li Manni, R. K. Carlson, C. E. Hoyer, J. L. Bao, *Acc. Chem. Res.* **50**, 66 (2017).
- [20] J. L. Bao, S. O. Odoh, L. Gagliardi, D. G. Truhlar, *J. Chem. Theory Comput.* **13**, 616 (2017).
- [21] A. M. Sand, D. G. Truhlar, L. Gagliardi, *J. Chem. Phys.* **146**, 034101 (2017).
- [22] S. Ghosh, C. J. Cramer, D. G. Truhlar, L. Gagliardi, *Chem. Sci.* **8**, 2741-2750 (2017).
- [23] L. Wilbraham, P. Verma, D. G. Truhlar, L. Gagliardi, I. Ciofini, *J. Phys. Chem. Lett.* **8**, 2026 (2017).



**Non-empirical double-hybrid functionals:  
more theoretical constraints, better performances?**

**Carlo Adamo<sup>1</sup>**

<sup>1</sup> *Institut de Recherche de Chimie Paris, PSL Research University, CNRS, Chimie  
ParisTech, 11 rue Pierre et Marie Curie, F-75005 Paris, France*

Density Functional Theory (DFT) emerged in the last two decades as one of the most reliable approach the description and prediction of properties of molecular systems and extended materials, coupling in an unprecedented way high accuracy and reasonable computational cost. However, the Achilles' heel of DFT is represented by the exchange-correlation contribution to the total energy, which, being unknown, must be approximated. Since the beginning of the '90s, global hybrids (GH) functionals, imposed themselves as the most reliable DFAs for chemical applications. However, if these functionals normally provide results of sufficient accuracy for most of the cases analyzed, some properties, such as thermochemistry or dispersive interactions, can still be significantly improved. A possible way out is represented by the inclusion, into the exchange-correlation functional, of an explicit dependence on virtual Kohn-Sham orbitals via Perturbation Theory. This leads to a new class of functionals, called double-hybrid (DH) density-functionals. In this talk, we describe our non-empirical approach to DHs, which, starting from some theoretical considerations, allows for the definition of DH (QI-DH) method [1], competitive with other -more empirical- DHs [2].

Discussion of selected cases, ranging from thermochemistry and reactions to excitations energies, not only show the large range of applicability of non empirical DHs, but also underline how increasing the number of theoretical constraints in the definition of the exchange-correlation functional parallel with an improvement of the numerical performances [3,4].

[1] E. Brémond, M. Savarese, A. J. Pérez-Jiménez, J. C. Sancho-García, C. Adamo *J. Chem. Phys.* **141**, 031101 (2014)

[2] E. Brémond, I. Ciofini, J. C. Sancho-García, C. Adamo *Acc. Chem. Res.* **49**, 1503 (2016).

[3] E. Brémond, M. Savarese, A.J. Perez-Jimenez, J.C. Sancho-Garcia, C. Adamo *J. Phys. Chem. Lett.* **6**, 3540 (2015).

[4] E. Brémond, M. Savarese, J.C. Sancho-García, A.J. Pérez-Jiménez, C. Adamo, *J. Chem. Phys.* **144**, 124104 (2016).

# Reliable DFT results for spin-crossover complexes

Suhwan Song,<sup>†</sup> Min-Cheol Kim,<sup>†</sup> Eunji Sim,<sup>\*,†</sup> Anouar Benali,<sup>‡</sup> Olle Heinonen,<sup>¶</sup> and Kieron Burke<sup>§</sup>

<sup>†</sup>*Department of Chemistry, Yonsei University, 50 Yonsei-ro Seodaemun-gu, Seoul 03722, Korea* <sup>‡</sup>*Argonne Leadership Computing Division, Argonne National Laboratory, 9700 S. Cass Ave, Argonne, IL 60347, USA* <sup>¶</sup>*Material Science Division, Argonne National Laboratory, 9700 S. Cass Ave, Argonne, IL 60347, USA* <sup>§</sup>*Departments of Chemistry and of Physics, University of California, Irvine, CA 92697, USA*

E-mail: esim@yonsei.ac.kr

## Abstract

DFT is used throughout nanoscience, especially when modelling spintronics. But standard self-consistent semilocal density functional calculations fail badly for spin-crossover complexes. For Fe(II) complexes, we show that density-corrected DFT, using Hartree-Fock densities (HF-DFT), greatly improves accuracy and reduces dependence on approximations. We use fixed-node diffusion Monte Carlo to benchmark our calculations, as even CCSD(T) is insufficient for these complexes. We show the improvement by calculating the Fe-Porphyrin complex. The “parameter-dilemma” of needing different amounts of mixing for different properties is eliminated by HF-DFT.

## Cooperativity of Non-covalent Interactions

G. Narahari Sastry

*Centre for Molecular Modeling, CSIR-Indian Institute of Chemical Technology,  
Hyderabad-500 007, India*

*Website: <http://cmm.osdd.net/gnsmmg> Email: [gnsastry@gmail.com](mailto:gnsastry@gmail.com)*

**Abstract:** Non-covalent interactions control the three dimensional structure of macromolecules and the supramolecular assemblies. Thus, atomic level understanding of condensed phase structure warrants a clear understanding of the role, strength and relevance non-covalent interactions and how do they mutually influence each other. The role, range and relevance of cation- $\pi$  and  $\pi$ - $\pi$  interactions in determining the macromolecular structure will be explained. In our efforts to employ rigorous computations on the molecules of medium sizes which involve non-covalent interactions several interesting features were unraveled. In this talk we describe the studies on stacking interactions of Buckybowls, the metal ion interactions in chemical and biological systems and the ion transport in the membrane proteins. The alkali and alkaline earth metal interactions in biological system is analyzed using computational methods and also through analyzing databases. Energy decomposition analysis is used to explore the nature of non-covalent interactions. Further, we focus our attention on how a pair of non-covalent interactions mutually influences each other's strength, through computational and structural analyses. The extent of cooperativity among the non-covalent interactions is analyzed and its effect on controlling the 3D-structure.

### References:

- [1] A. S. Mahadevi, G. N. Sastry, *Chem. Rev.* **116**, 2775 (2016).
- [2] S. Saha and G. N. Sastry, *J. Phys. Chem. B*, **119**, 11121 (2015).
- [3] B. Sharma, H. K. Srivastava, G. Gayatri and G. N. Sastry, *J. Comp. Chem.* **36**, 529 (2015).
- [3] D. Vijay, G. N. Sastry, *Chem. Phys. Lett.* **485**, 235 (2010).
- [4] A. Srinivas Reddy, G. Madhavi Sastry and G. N. Sastry, *Proteins: Struct. Funct. Bioinform.* **67**, 1179 (2007).
- [5] A. S. Reddy, D. Vijay, G. M. Sastry and G. N. Sastry, *J. Phys. Chem. B.* **110**, 2479 (2006).
- [6] A. S. Reddy and G. N. Sastry, *J. Phys. Chem. A.* **109**, 8893 (2005).

## Large Datasets for Benchmarking Noncovalent Interactions

C. David Sherrill<sup>1</sup>

<sup>1</sup>*DSchool of Chemistry and Biochemistry, Georgia Institute of Technology, 901 Atlantic Dr. NW, Atlanta, Georgia, U.S.A.*

Advances in theoretical chemistry methods, algorithms, and computer hardware have led to a dramatic increase in the ability to generate large sets of high-quality benchmark data at levels such as coupled-cluster through perturbative triples in the complete basis set limit [CCSD(T)/CBS]. For example, our group's first paper on the benzene dimer [1] reported just three high-quality benchmark values. Several years later, we were able to extend our studies to eight entire potential energy curves of van der Waals dimers, for 148 benchmark-quality energies [2]. Most recently, in collaboration with Kenneth Merz, Alex MacKerell, and others, we have obtained benchmark interaction energies [3] for approximately 3400 sidechain-sidechain and 100 backbone-backbone interactions extracted from the Protein DataBank. Various approximate methods---from force-fields to semi-empirical to ab initio approaches---are assessed against the CCSD(T)/CBS benchmarks. This talk will summarize the results of our analysis (involving ~1M datapoints) and will also discuss how quantum chemistry must change its standard workflow to handle the generation, management, analysis, storage, and sharing of databases with hundreds of thousands or millions of datapoints.

[1] M. O. Sinnokrot, E. F. Valeev, and C. D. Sherrill, *J. Am. Chem. Soc.* **124**, 10887 (2002).

[2] C. D. Sherrill, T. Takatani, and E. G. Hohenstein, *J. Phys. Chem. A* **113**, 10146 (2009).

[3] L. A. Burns, J. C. Faver, Z. Zheng, M. S. Marshall, D. G. A. Smith, V. Vanommeslaeghe, A. D. MacKerell, K. M. Merz, and C. D. Sherrill, submitted.

## Enhanced sampling for chemistry

**Michele Parrinello<sup>1</sup>**

*<sup>1</sup>Department of Chemistry and Applied Biosciences, ETH Zurich, and Facoltà di Informatica, Istituto di Scienze Computazionali, Università della Svizzera italiana, Via Giuseppe Buffi 13, 6900 Lugano, Switzerland*

The study of chemical reactions in condensed phases poses severe difficulties and requires adapting the classical approach based on the study of the potential energy surface and the determination of reaction paths. We suggest that in complex systems a description in terms of collective variables and the associated free energy surfaces is a fruitful alternative. We discuss simple, yet effective and general collective variables that are suitable to study chemical reactions. Based on such collective variables we use metadynamics and variationally enhanced sampling to accelerate *ab-initio* molecular dynamics and explore reaction paths and determine reaction rates. We also show how to improve the collective variables, so as to speed up sampling and express concisely and clearly the chemical processes underlying the reaction being studied. We demonstrate the fruitfulness of this approach on a few examples.

## Comparison of quantum-mechanical approaches to calculate ligand-binding affinities with free-energy perturbation

Martin A. Olsson, Ulf Ryde<sup>1</sup>

<sup>1</sup> *Theoretical Chemistry, Lund University, P. O. Box 124, SE-221 00 Lund, Sweden*

One of the largest challenges of computational chemistry is to estimate the binding free energy of a small molecule to a biomacromolecule (e.g. a drug candidate to its receptor). Currently, the best results are typically obtained by free-energy perturbation (FEP) methods, with free energies estimated by exponential averaging, thermodynamic integration, or by the Bennett acceptance ratio [1]. Such methods require extensive sampling and therefore they have been mainly used with molecular-mechanics (MM) methods. However, it is well-known that such methods have severe limitations. Therefore, there have been much interest to improve binding-affinity estimates using quantum-mechanics (QM) methods [2]

We have tried to employ QM methods to in FEP estimates of binding affinities for both proteins and more simple host-guest models. Initial attempts failed, because the perturbations did not converge [3,4]. We have compared reference-potential methods with explicit QM/MM FEP calculations [5]. For the former, which are based on FEP calculations at the MM level, combined with MM→QM/MM FEP calculations, we have tried to avoid QM/MM simulations by employing single-step exponential averaging or non-Boltzmann Bennett acceptance ratio method. For convergence ~700 000 QM energy calculations were needed [6]. However, more stable and reliable results can be obtained with running a few QM/MM simulations. Currently, we investigate how such calculations can be sped up, retaining the accuracy. In this talk, I will discuss and compare these approaches.

- [1] N. Hansen, W. E. van Gunsteren, *J. Chem. Theory Comput.* 2014, 10, 2632
- [2] Ryde, U.; Söderhjelm, P. *Chem. Rev.*, 2016, 116, 5520.
- [3] P. Mikulskis, et al. *J. Comp.-Aided Mol. Design*, 2014, 28, 375
- [4] S. Genheden, et al. *J. Comput. Chem.*, 2015, 36, 2114
- [5] M. A. Olsson, U. Ryde *J. Chem. Theory Comput.*, 2017, submitted.
- [6] M. A. Olsson, et al. *J. Comput. Chem.* 2016, 37, 1589

## Automated Reaction Pathway Sampling Using Stochastic Surface Walking Method for Predicting Chemical Reactions

Zhi-Pan Liu

Department of Chemistry, Fudan University, Shanghai 200433, China  
<http://homepage.fudan.edu.cn/fdzpliu>

In this talk, I will introduce our latest progress for the SSW package, including Stochastic Surface Walking method (SSW) and Double-Ended Surface Walking (DESW) method, and apply the package for resolving the reaction pathways in catalysis and solid phase transition. The SSW method is designed for the global optimization of structure on potential energy surface (PES), while maintaining the pathway information during structure search. By adding bias potentials and performing local relaxation repeatedly, SSW method can perturb smoothly the structure from one minimum to another following a random direction. The SSW method in combination with DESW method can be utilized for finding unknown structures and predicting chemical reactivity from molecules to solids. Using these methods, we recently studied a number of important systems, e.g. water-gas shift reaction on Cu, ZrO<sub>2</sub> tetragonal-to-monoclinic phase transition, heterophase junction structures in photocatalysts, and dynamic catalyst structure evolution in H<sub>2</sub> evolution.

Related references :

1. Xie, Yao-Ping; Zhang, Xiao-Jie; Liu Zhi-Pan\* "Graphite to Diamond: Origin for Kinetics Selectivity", J. Am. Chem. Soc. 2017, 139, 2545–2548
2. Li, Ye-Fei\*; Zhu, Sheng-Cai; Liu, Zhi-Pan\*, "Reaction Network of Layer-to-Tunnel Transition of MnO<sub>2</sub>", J. Am. Chem. Soc., 2016, 138, 5371
3. Zhu, Sheng-Cai; Xie, Song-Hai; Liu, Zhi-Pan\* "Nature of Rutile Nuclei in Anatase-to-Rutile Phase Transition", J. Am. Chem. Soc., 2015, 137, 11532
4. Guan, Shu-Hui ; Zhang, Xiao-Jie; Liu, Zhi-Pan\*, "Energy Landscape of Zirconia Phase Transitions", J. Am. Chem. Soc., 2015, 137, 8010
5. Zhao, Wei-Na; Zhu, Sheng-Cai; Li, Ye-Fei, Liu, Zhi-Pan\* "Three-phase Junction for Modulating Electron-Hole Migration in Anatase/Rutile Photocatalysts", Chem. Sci., 2015, 6, 3483
6. Wei, Guang-Feng; Liu, Zhi-Pan\* "Restructuring and Hydrogen Evolution on Pt Nanoparticle", Chem. Sci., 2015, 6, 1485

## Time-dependent density-functional theory for open system and its applications.

GuanHua Chen<sup>1</sup>

<sup>1</sup>*Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, P. R. China*

With our proof of the holographic electron density theorem for time-dependent systems, a first-principles method for any open electronic system is established. By introducing the self-energy for the dissipative interactions between the reduced system and its environment, we develop a time-dependent density-functional theory for open system (TDDFT-OS) based on an equation of motion for the Kohn-Sham reduced single-electron density matrix of the reduced system. Being implemented with state-of-the-art linear scaling techniques, the TDDFT-OS method is not only accurate but also very efficient in numerical calculations. The method has been successfully applied to address a very broad spectrum of problems in different research areas, including quantum electron transport, molecular electronics, photovoltaic, electroluminescence, and chemical reactions.

- [1] X. Zheng, F. Wang, C.Y. Yam, Y. Mo and G.H. Chen, *Phys. Rev. B* **75**, 195127 (2007).
- [2] X. Zheng, G.H. Chen, Y. Mo, S. K. Koo, H. Tian, C. Y. Yam, and Y. J. Yan, *J. Chem. Phys.* **133**, 114101 (2010).
- [3] S. G. Chen, Y. Zhang, S. K. Koo, H. Tian, C. Y. Yam, G.H. Chen, and M. A. Ratner, *J. Phys. Chem. Lett.* **5**, 2748 (2014).
- [4] Y. Zhang, L.Y. Meng, C. Y. Yam, G.H. Chen, *J. Phys. Chem. Lett.* **5**, 1272 (2014).
- [5] R. L. Wang, Y. Zhang, F. Z. Bi, T. Frauenheim, G.H. Chen, and C. Y. Yam, *Nanoscale*. **8**, 13168 (2016).



## Real and Imaginary-Time Electron Dynamics of Open Quantum Subsystems.

**Michele Pavanello**

*Department of Chemistry, Rutgers University, Newark, NJ, U.S.A.*

In an effort to allow first principle simulations to approach realistic time- and length-scales, and to shed light on the dynamical behavior of complex systems, we have developed an open-source density embedding software called *embedded Quantum-ESPRESSO* (eQE). eQE is capable of approaching periodic and molecular systems alike [1,2,3], their Born-Oppenheimer dynamics, and electron dynamics through a real-time time-dependent subsystem DFT implementation [4]. We present applications to liquid water [5], crystalline oligoacenes, and organic-metal interfaces. The density embedding treatment allows us to quantify cooperative and anticooperative excitonic effects in the electronic spectra of these complex systems as well as a non-Markovian electron dynamics, which is particularly important when molecules interact with metal surfaces. Specifically, we find the non-Markovian electron dynamics to be responsible for peak broadening and peak shift in the optical spectra of molecules interacting with infinite systems such as metals. By carrying out the dynamics in imaginary time, the correlation energy of interaction between subsystems can be evaluated. We show how this method reproduces the S22 and S22-5 benchmark sets [6,7], and provides a clear prescription for improving current force fields which are based on RPA.

- [1] Krishtal, A., Sinha, D., Genova, A. and Pavanello, M., J. Phys.: Condens. Matter, **27**, 183202 (2015)
- [2] Genova, A. and Pavanello, M. J. Phys.: Condens. Matter, **27**, 495501 (2015)
- [3] Genova, A., Ceresoli, D., Krishtal, A., Andreussi, O., DiStasio Jr., Robert A. and Pavanello, M., Int. J. Quantum Chem. **117**, e25401 (2017)
- [4] Krishtal, A. and Pavanello, M., J. Chem. Phys., **144**, 124118 (2016)
- [5] Kumar P., S., Genova, A., Pavanello, M., arXiv:1706.03260v2 (2017)
- [6] Kevorkyants, R., Eshuis, H. and Pavanello, M., J. Chem. Phys., **141**, 044127 (2014)
- [7] Sinha, D. and Pavanello, M., J. Chem. Phys., **143**, 084120 (2015)

## A comprehensive view on the Claisen rearrangement of chorismate via a new quantum chemical toolbox

Elfi Kraka<sup>1</sup>, Dieter Cremer<sup>†</sup>, Yunwen Tao<sup>1</sup>, Marek Freindorf<sup>1</sup>

<sup>1</sup>Computational and Theoretical Chemistry Group (CATCO) <http://smu.edu/catco>

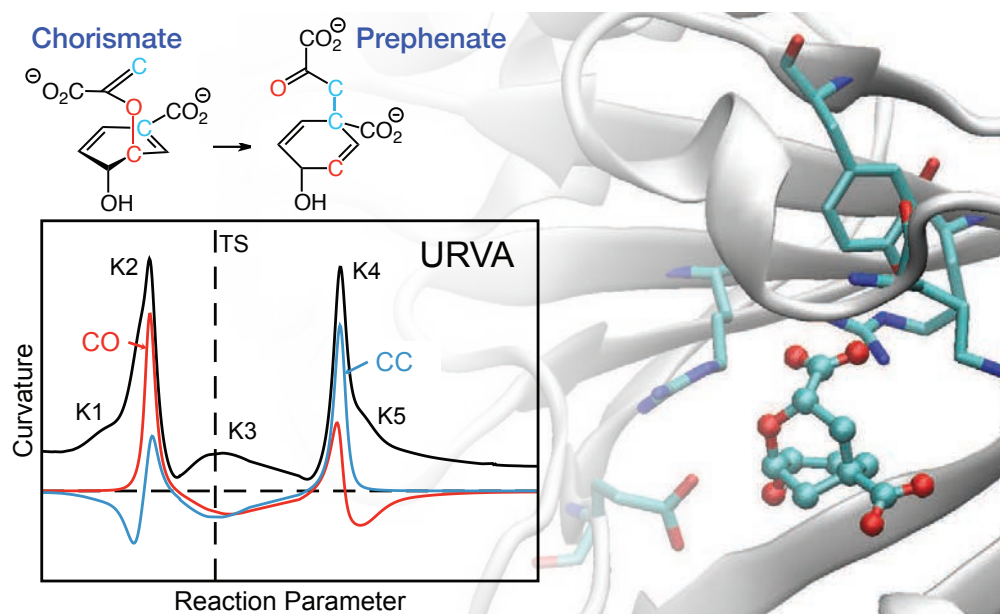
Southern Methodist University, 3215 Daniel Ave, Dallas, 75275, USA

<sup>†</sup> In Memoriam

The *Bacillus subtilis* Chorismate Mutase (BsCM) catalyzed Claisen rearrangement of chorismate to prephenate is one of the few pericyclic processes in biology, and as such provides a rare opportunity for understanding how Nature promotes such rearrangements so successfully.

In this talk we will i) Examine the hypothesis that the mechanism of the chorismate rearrangement is the same in the gas phase, solution and in the enzyme, e.g. space confinement does not play a role; ii) Investigate current suggestions that the enzyme lowers the barrier via transition state stabilization; iii) Elucidate the role of conformational changes during the rearrangement via a puckering analysis along the reaction path; iv) Compare Nature's way of catalyzing this reaction with gold(I) catalyzed Claisen rearrangements, and v) Make suggestions for BsCM based metalloenzyme analogues.

We use for this purpose the Reaction Valley Approach (URVA) combined with the Local Mode Analysis, the Cremer-Pople Ring-Puckering Analysis and a new QM/MM vibrational analysis, recently developed in the CATCO group, which allows at each point on the reaction path to single out the QM vibrational modes for further analysis. This new toolbox can efficiently be used for the quantum chemical investigation of enzyme reactions as well as for a direct comparison of chemical reactions in different environments.



## Massive Search of Planar Hypercoordinate Carbon Atoms

Gabriel Merino<sup>1</sup>

<sup>1</sup> *Departamento de Física Aplicada, Centro de Investigación y de Estudios Avanzados, Km. 6 Antigua carretera a Progreso Apdo. Postal 73, Cordemex, 97310, Mérida, México*  
*gmerino@cinvestav.mx*

Thinking about a planar tetracoordinate carbon atoms (ptC) (or even planar pentacoordinate carbon atom) may look like an aberration in organic chemistry or simply a figment of the imagination of a theoretician, but in the last forty years, a plethora of such compounds have been synthesized or detected experimentally. As mentioned by Roald Hoffmann, “the purpose of studying nonclassical molecules is to learn from the abnormal... the making of molecules that are untypical or abnormal test our understanding of that fundamental yet fussy entity –the chemical bond” and the ptC is one of the best examples.

Schleyer and Boldyrev carried out theoretical investigations on other pentatomic systems such as  $\text{Al}_4\text{O}$ ,  $\text{Al}_4\text{N}^-$ ,  $\text{Al}_3\text{SiN}$ , *cis*- $\text{Al}_2\text{Si}_2\text{C}$ , *trans*- $\text{Al}_2\text{Si}_2\text{C}$ , and  $\text{AlSi}_3\text{B}$ . Their planar structures with a tetracoordinate carbon atom in the center of a four membered ring are lower in energy than the corresponding tetrahedral ones. And another thing that they all have in common is 18 valence electrons. That electron count is so prevalent in low energy ptCs that it has come to be seen as a “magic number” for planar geometries.

Herein, we exploit the “18 valence electron rule” to do a massive search on the potential energy surfaces of clusters meet the following rules:

- 1) They are comprised of C and maximum other two different elements from the main group of the periodic table.
- 2) Systems are either pentaatomic or hexaatomic.
- 3) Charges are equal to 0,  $\pm 1$  or  $\pm 2$ .

Following these restrictions, the PESs of 508 pentaatomic and 424 hexaatomic species were systematically explored. For each case, 150 singlets and 80 triplets initial motifs were considered. A total of 428720 optimizations were carried out. Our computations show that the global minima of 156 pentaatomic clusters have a ptC. In hexaatomic species, 50 ptC and 18 planar pentacoordinate carbons were found to be global minima. It is the first time that such number of hypercoordinate planar systems is predicted. We also used statistical data analysis tools (Random Forests, Support Vector Machines) to rank and quantify the most important features that determine if a compound will be a global or local minima, with a prediction accuracy of 90%.

## Non-covalent Interactions in Asymmetric Catalysis: A Mechanistic Voyage from Rationalizations to Predictions

Raghavan B. Sunoj

*Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076  
India*

Computational quantum chemistry has been increasingly employed toward rationalizing the stereochemical outcome in catalytic reactions.<sup>1</sup> The approach typically involves the identification of kinetically significant transition states and intermediates. In our laboratory, *ab initio* as well as DFT methods are employed to gain insights into carbon-carbon and carbon-heteroatom bond-forming reactions of immediate practical significance.<sup>2</sup> The key objective of our research is to gain molecular insights on the factors responsible for stereoselectivity and to exploit such insights toward *in silico* design of novel asymmetric catalysts.<sup>3</sup>

A number of examples wherein the conventional transition state models required systematic refinements toward accounting the observed product distribution and stereochemical outcome will be presented. Through this talk, we intend to propose the need for a timely rethink on a number of working hypotheses on asymmetric induction that places an over-emphasis on steric interaction. In general, the presentation would encompass a few contemporary themes in the domain of asymmetric multi-catalytic reactions.<sup>4</sup> Interesting interpretations/rationalizations of experimental observations besides meaningful guidelines for rational improvements in the design of asymmetric catalysts would remain the key focus of the presentation. The contents are designed to cater to a broad and diverse group of audience; hence, the chemical insights would be emphasized, rather than a labyrinth of technical details.

[1] (a) P. H. -Y. Cheong, C. Y. Legault, J. M. Um, N. Celebi-Olcum, K. N. Houk, *Chem. Rev.* **111**, 5042 (2011). (b) R. B. Sunoj, *Wiley Interdisciplinary Reviews: Comput. Mol. Sci.* **1**, 920 (2011).

[2] (a) G. Jindal, R. B. Sunoj, *Angew. Chem., Int. Ed.* **53**, 4432 (2014). (b) R. B. Sunoj, *Acc. Chem. Res.* **49**, 1019 (2016).

[3] (a) C. B. Shinisha, R. B. Sunoj, *Org. Biomol. Chem.* **5**, 1287 (2007). (b) G. Jindal, Sunoj, R. B. *Org. Biomol. Chem.* **12**, 2745 (2014).

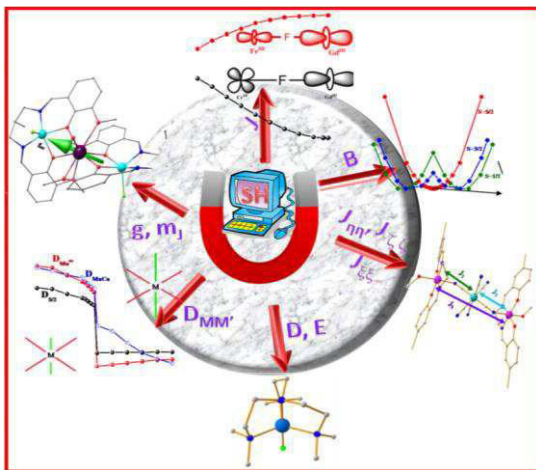
[4] (a) G. Jindal, R. B. Sunoj, *J. Am. Chem. Soc.* **136**, 15998 (2014). (b) G. Jindal, H. K. Kisan, R. B. Sunoj, *ACS Catal.* **5**, 480 (2015). (c) B. Bhaskararao, R. B. Sunoj, *J. Am. Chem. Soc.* **137**, 15712 (2015).

## Are Single Molecule Magnets Predictable? Learning from Ab initio Calculations on Lanthanide and Transition Metal Molecular Magnets

Gopalan Rajaraman

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai-400076, India. Email: rajaraman@chem.iitb.ac.in

Molecular magnetism is one of the vastly growing research fields with an aim to design the molecules and materials with tunable magnetic and electronic properties.<sup>1</sup> Their synthesis, characterization and implementation as devices which creates lively crossroad among chemistry, physics and material science: a multidisciplinary research field. These molecules have wide spread potential applications ranging from magnetic storage devices, spintronics, Q-bits in quantum computing to magnetic coolants. Single-molecule magnets (SMMs) are the molecules which show slow relaxation of magnetization below the critical temperature and exhibit hysteresis loop similar to classical magnets. SMMs offer key advantage over classical magnets due to their light weight, solubility and multifunctional behavior. Theoretical tools are indispensable in this arena<sup>2</sup> for understanding the observed magnetic properties. The strength of these methods is not only limited rationalization but also to predict novel molecules which can exhibit superior magnetic properties. In this presentation, I will present some of our research effort in modelling lanthanide and transition metal based molecular magnets employing ab initio CASSCF/PT2 methods undertaken in our group towards achieving this goal.<sup>2</sup>



[1] R. Sessoli, et al. **Nature**, 365, 141 (1993).

[2] S. K. Singh and G. Rajaraman, **Nature Commun.** 7:10669 (2016), S. K. Gupta, T. Rajeshkumar, G. Rajaraman, R. Murugavel, R. **Chem. Sci.**, 7, 5181 (2016); M. K. Singh, N. Yadav, G. Rajaraman, **Chem. Commun.** 51, 17732 (2015). T. Gupta, G. Rajaraman **Chem. Comm.**, 52, 8972 (2016).

## Computationally Guided Discovery of Metal-Decorated Metal–Organic Frameworks Active for Catalysis

Laura Gagliardi

*Department of Chemistry, Chemical Theory Center, and Supercomputing  
Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431, United States*

Metal-organic frameworks (MOFs) are attracting the attention of many scientists because of their high selectivity in gas separations, catalytic activity, and magnetic properties. We have combined theory and experiment to understand the activity of nickel, cobalt, and rhodium catalysts supported on  $Zr_6$  nodes in metal–organic frameworks (MOFs) for reactions related to natural gas conversion. For Ni and Co,[1],[2] computational studies provide important insights with respect to the catalytic mechanism(s) for observed ethylene dimerization after metal-decoration of the MOF NU-1000. Rh complexes have been installed on the  $Zr_6$  nodes of not only NU-1000, but also the related metal–organic framework UiO-67, and the zeolite DAY; influences of the supports on ethylene hydrogenation and dimerization have been assessed.[3] A library of transition metals (TMs), ranging from first row TMs to noble metals, is now being screened computationally to search for optimal catalysts, and structure-function relationships are beginning to emerge from this theory-driven approach.

[1] V. Bernales, A. B. League, Z. Li, N. M. Schweitzer, A. W. Peters, R. K. Carlson, J. T. Hupp, C. J. Cramer, O. K. Farha, and L. Gagliardi, *J. Phys. Chem. C*, **120**, 23576–23583 (2016).

[2] Z. Li, N. M. Schweitzer, A. B. League, V. Bernales, A. W. Peters, A. B. Getsoian, T. C. Wang, J. T. Miller, A. Vjunov, J. L. Fulton, J. A. Lercher, C. J. Cramer, L. Gagliardi, J. T. Hupp, O. K. Farha, *J. Am. Chem. Soc.*, **138**, 1977-1982 (2016).

[3] V. Bernales, D. Yang, J. Yu, G. Gümüşlü, C. J. Cramer, B. C. Gates, and L. Gagliardi *ACS Appl. Mater. Interfaces* DOI: 10.1021/acsami.7b03858 (2017)

## **Projector Augmented Wave Method Incorporated into Gauss-type Atomic Orbital Based Density Functional Theory**

**Takeshi Yanai<sup>1</sup> and Xiao-Gen Xiong<sup>2</sup>**

*<sup>1</sup>Institute for Molecular Science, Okazaki, 444-8585 Aichi, Japan*

*<sup>2</sup>Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China*

The Projector Augmented Wave (PAW) method developed by Blöchl is well recognized as an efficient, accurate pseudopotential approach in solid-state density functional theory (DFT) calculations with plane-wave basis. In this presentation, we will describe an approach to incorporate the PAW method into the Gauss-type function (GTF) based DFT implementation. The nodal and high-exponent GTF components of valence molecular orbitals (MOs) are removed or pseudized by the ultrasoft PAW treatment, while there is elaborate transparency to construct accurate and well-controlled pseudopotential from all-electron atomic description and to reconstruct all-electron form of valence MOs from the pseudo MOs. This smoothness should benefit the efficiency of GTF-based DFT calculations in terms of elimination of high-exponent primitive GTFs and reduction of grid points in the numerical quadrature. The present scheme is implemented by incorporating them into the conventional GTF-based DFT solver. The test calculations are shown for illustrating the performance.

[1] X.-G. Xiong and T. Yanai, submitted.

## From evaluation of methodology to error bars in computational materials science

Claudia Draxl<sup>1,2</sup>

<sup>1</sup>*Humboldt-Universität zu Berlin, Zum Großen Windkanal 6, 12489 Berlin*

<sup>2</sup>*Fritz-Haber-Institut Berlin, Faradayweg 4-6, 14195 Berlin*

While in quantum chemistry, assessing the precision of calculations has been playing a role for decades, in computational condensed-matter physics such efforts are just gaining momentum. A first step towards reproducibility, was only recently demonstrated by an impressive community effort [1]. The reproducibility of equilibrium properties of bulk elemental solids obtained by semi-local density-functional theory (DFT) [1] is, however, only a first step. We demonstrate the basically exact numerical solution of the Kohn-Sham equations for atoms, molecules and solids on the same footing [2], based on the full potential linearized augmented planewave plus local-orbital method as implemented in the **exciting** code [3].

To address the issue of uncertainty introduced by computational parameters, we have created a database, populated with data from elemental and binary solids, from four conceptually different codes and several numerical settings, amounting to approximately 100,000 calculations. A prediction model for the error bars as a function of the basis set size is proposed and validated by a systematic analysis of our results [4].

The project received funding from the European Union's Horizon 2020 research and innovation program under grant agreement no. 676580 with The Novel Materials Discovery (NOMAD) Laboratory, a European Center of Excellence [5].

[1] K. Lejaeghere et al., *Science* **351**, aad3000 (2016).

[2] A. Gulans, A. Kozhevnikov, and C. Draxl, preprint.

[3] A. Gulans, S. Kontur, C. Meisenbichler, D. Nabok, P. Pavone, S. Rigamonti, S. Sagmeister, U. Werner, and C. Draxl, *J. Phys: Condens. Matter* **26**, 363202 (2014).

[4] C. Carbogno, et al., preprint.

[5] The NOMAD Laboratory, Center of Excellence for Computing Applications, <https://nomad-coe.eu>



## The method of increments applied to weakly bound systems

Beate Paulus<sup>1</sup>

<sup>1</sup>*Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany*

Material properties are mainly determined on the first principle level applying density functional methods. But there exists materials, especially weakly bound systems, where present-day density functionals reveal problems to describe the binding accurately enough. The application of the method of increments [1] for the correlation energy in extended systems is based on the determination of local correlation increments with any size-extensive correlation method like coupled cluster. In the contribution various examples are presented. The first one is the binding in the halogen molecular crystals of chlorine, bromine and iodine[2]. Another topic it the physisorption of atoms and molecules. Here the curvature dependent adsorption of water inside and outside of carbon nanotubes[3] and the adsorption of metal atoms on graphene[4] are presented. In a last example the folding of alkanes in comparison to their partially and fully fluorinated analogons. In all cases highly accurate binding properties could be obtained which can be used as benchmarks for computational cheaper methods like dispersion corrected DFT functionals or as highly accurate data for the determination of force fields for classical MD simulations[3].

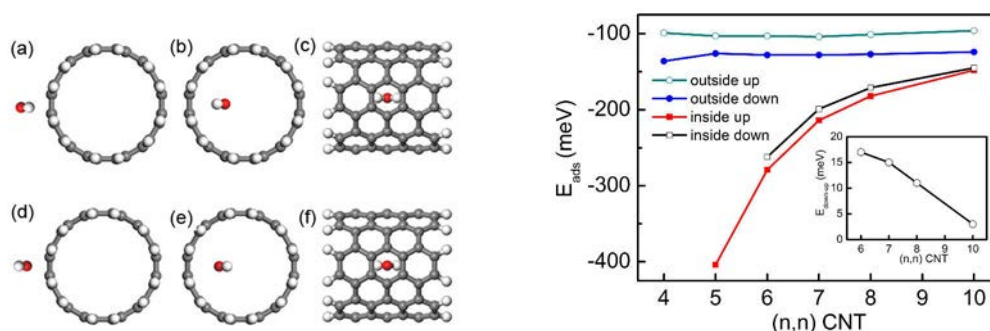


Figure 1: Curvature dependence of the adsorption energy of water inside and outside an arm-chair carbon nanotube, calculated at the LCCSD(T) level.

- [1] B. Paulus, *Phys. Rep.* **428**, 1 (2006); C. Müller, B. Paulus, *Phys. Chem. Chem. Phys.* **14**, 7605 (2012).
- [2] K. G. Steenbergen, N. Gaston, C. Müller, B. Paulus, *J. Chem. Phys.* **141**, 124707 (2014).
- [3] S. Lei, B. Paulus, *Z. Phys. Chem.* **230**, 651 (2016); S. Lei, B. Paulus, S. Li, B. Schmidt, *J. Comp. Chem.* **37**, 1313 (2016).
- [4] F. Weber, C. Müller, B. Paulus, P. Reinhardt, *Mol. Phys.* **114**, 1098 (2016).

## Physics-based intermolecular potentials for material design

Krzysztof Szalewicz

*Department of Physics and Astronomy,  
University of Delaware, Newark, Delaware 19716*

Computer modeling and the design of materials has become a mainstream method in engineering and is expected to become even more important as computers pass the exaflop performance threshold. Currently, such modelling is performed either by using biomolecular empirical potential energy surfaces (PESs) or calculating the potential energies on-the-fly using density-functional theory (DFT) methods. We have developed an alternative approach which will allow new materials to be designed with higher accuracy, by as much as a factor of 100 compared to today's state-of-the-art methods and be of comparable costs to methods based on empirical potentials. Our approach is physics-based, i.e., it starts from accurate solutions of Schrödinger's equation (SE) using symmetry-adapted perturbation theory (SAPT) and does not invoke any empirical information. SAPT interaction energies are represented by analytic PESs that can be applied in any molecular dynamics (MD) simulations. Such first-principles-based PESs are much more accurate than the currently used empirical PESs and more accurate than predictions of electronic structure methods used in on-the-fly MD simulations. Our approach will require computer resources orders of magnitude lower than needed for on-the-fly simulations with DFT. A recently developed method for automatic fitting of PESs will be used. With PESs, it is possible to perform MD simulations for systems with millions of atoms. The use of physics-based PESs is expected to overcome the problem that empirical PESs work well for the typical systems considered in biomolecular modelling and for some simple condensed phases, but often perform poorly in engineering applications (such as in designing composites, photovoltaics, etc.).

## **Analytic Energy Gradient and Hessian of TD-DFT/MM Excited-State: Implementation and Applications**

**WanZhen Liang**

*Department of Chemistry, Xiamen University, China*

To develop the computationally efficient theoretical tools to obtain the vibrational frequencies and vibrational spectra of the excited state, and explore the excited-state potential energy surfaces of molecules in condensed phases, we have implemented the analytic energy gradient and Hessian of TDDFT/MM excited-state into quantum chemistry software package. Here I will present the performance and the applications of those efficient approaches for the photo-physical and photochemical properties of some fluorescent proteins. By applying the developed codes, we characterized the excited-state proton transfer (ESPT) process and identified the states involved in ESPT of red fluorescent protein LSSmKate1, and calculated vibrationally-resolved one- and two-photon absorption spectra of YFP Citrine. Some interesting insights on the origin of large stokes shift in RFP LSSmKate1 and the effect of protein environment on absorption spectra of YFP Citrine were thus revealed.

## Quantum computing for quantum chemistry.

**Alán Aspuru-Guzik<sup>1</sup>**

<sup>1</sup>*Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street,  
Room M138, Cambridge, MA, USA*

<sup>2</sup>*E-mail: [aspuru@chemistry.harvard.edu](mailto:aspuru@chemistry.harvard.edu), <http://aspuru.chem.harvard.edu>,*

*Twitter: @A\_Aspuru\_Guzik*

The *numerically exact* solution of Schrödinger's equation is out of reach for classical computers. This fact, originally suggested by Dirac, has inspired generations of computational chemists to develop powerful, yet *approximate* methods for the electronic structure of atoms and molecules. Richard Feynman originally suggested that controllable quantum systems, also known as quantum simulators could simulate physics and chemistry efficiently. Based on algorithms originally developed by Seth Lloyd and co-workers, in 2005 we proposed an algorithm for simulating quantum chemistry on quantum computers in a *numerically exact* manner in polynomial time. In 2010, the first quantum computer experiment for quantum chemistry was realized using two qubits. Just this year, IBM researchers have carried out a six-qubit quantum simulation of BeH<sub>2</sub> using one of their early quantum computers. With regards to algorithmic development, several groups, including ours, have lowered the algorithmic costs by several polynomial orders and prefactors. Currently, several researchers in the field consider quantum computing for quantum chemistry as one of the most promising early applications of quantum computers. Adding to the excitement for this field, several commercial research groups are actively developing hardware for quantum computation and algorithms for quantum chemistry. In this talk, I will try to review this field and provide a perspective of what's to come.

In terms of an accessible reference, I refer you to a recent report of an NSF workshop on the subject [1].

- [1] J. Olson, et al., [arXiv 1706.05413](#) (2017).

## Machine-learning unifies the modelling of materials and molecules

Michele Ceriotti<sup>1</sup>, Sandip De<sup>1</sup>, Albert Bartok<sup>2</sup>, Gabor Csanyi<sup>2</sup>,  
Carl Poelking<sup>2</sup>, Noam Bernstein<sup>3</sup>, James Kermode<sup>4</sup>

<sup>1</sup>EPFL Lausanne, Switzerland

<sup>2</sup>Cambridge University, UK

<sup>3</sup>US Naval Research Laboratory, USA

<sup>4</sup>Warwick University, UK

Determining the stability of molecules and condensed phases is the cornerstone of atomistic modelling, underpinning our understanding of chemical and materials properties and transformations. Here we show that a machine-learning model, based on a local description of chemical environments and Bayesian statistical learning, provides a unified framework to predict atomic-scale properties. It captures the quantum mechanical effects governing the complex surface reconstructions of silicon, predicts the stability of different classes of molecules with chemical accuracy, and distinguishes active and inactive protein ligands with more than 99% reliability. The universality and the systematic nature of our framework provides new insight into the potential energy surface of materials and molecules.

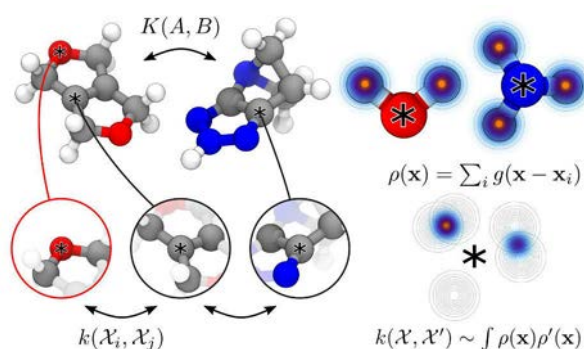


Figure 1: Machine-learning based on a mathematically-sound representation of chemical environments provides the basis for an universally-applicable framework to predict the properties of materials and molecules

- [1] S. De, A. P. Bartók, G. Csányi, and M. Ceriotti, *Phys. Chem. Chem. Phys.* **18**, 13754 (2016).
- [2] A. P. Bartok, S. De, C. Poelking, N. Bernstein, J. Kermode, G. Csanyi, and M. Ceriotti, *arXiv:1706.00179* (2017).

## Interactive and Automated Exploration of Reaction Mechanisms.

**Markus Reiher<sup>1</sup>**

<sup>1</sup>*Lab. f. Phys. Chem., ETH Zurich, Vladimir-Prelog-Weg 2, Zurich, Switzerland*

A prominent focus of molecular science has been the understanding and design of functional molecules and materials. This brings about new challenges for theoretical chemistry. We are faced with the necessity to obtain theoretical results of predictable accuracy for molecules of increasing size and number. Moreover, the molecular composition, which is required as input for a quantum chemical calculation, might not be known, but the target of a design attempt. Then, the relevant chemical processes are not necessarily known, but need to be explored and identified. Whereas parts of these challenges have already been addressed by the development of specific methods (such as linear scaling or high-throughput screening), the fact that an enormous multitude of structures needs to be considered calls for integrated approaches. This holds particularly true for predictions on complex chemical processes that encode function (e.g., through reaction networks). In my talk, I will review our recent work on these challenges that range from automated and interactive explorative approaches with error control for density functional theory to automated benchmarking based on black-box density matrix renormalization group calculations including dynamic correlation[1].

[1] for references and demonstrations see: <http://www.reiher.ethz.ch/publications.html> and <http://www.reiher.ethz.ch/software.html>

## **Big Data of the Chemical Physics of Materials: Discovering Interpretable Patterns, Correlations, and Causality**

**Matthias Scheffler** (\*)

*Fritz-Haber-Institut der Max-Planck-Gesellschaft,  
Faradayweg 4-6, D-14195 Berlin, Germany*

Recent years have seen an impressive complement of the traditional, experimental “trial and error” approach for discovering new materials or determining so far unknown properties of already known materials by high-throughput density functional theory (DFT) computations. The amount of already existing data (experimental and theoretical) is huge.

The NOMAD (Novel Materials Discovery) Laboratory Center of Excellence, [1] creates, collects, stores, and cleanses a large volume of computational materials science data, derived from all important materials science codes available today. Presently NOMAD holds results of more than 20 million DFT total-energy calculations. In addition, the NOMAD Laboratory CoE develops tools for mining this data in order to find structure, correlations, and novel information that could not be discovered from studying smaller data sets. Indeed, it is now increasingly becoming clear that big data of materials does not only provide direct information but that the data is structured. This enables interpolation, (modest) extrapolation, and new routes towards understanding [see Ref. 2-4 and references therein].

The talk will address how to exploit big data of materials for research and engineering, how to find (hidden) structure in the data in order to advance materials science, identify new scientific phenomena, and provide support towards industrial applications.

[1] The NOMAD (Novel Materials Discovery) Laboratory, a European Centre of Excellence (CoE): <https://NOMAD-CoE.eu> .

[2] L.M. Ghiringhelli, J. Vybiral, S.V. Levchenko, C. Draxl, and M. Scheffler, *Phys. Rev. Lett.* **114**, 105503 (2015).

[3] L.M. Ghiringhelli, J. Vybiral, E. Ahmetcik, R. Ouyang, S.V. Levchenko, C. Draxl, and M. Scheffler, *New J. Phys.* **19**, 023017 (2017).

[4] B.R. Goldsmith, M. Boley, J. Vreeken, M. Scheffler, and L.M. Ghiringhelli, *New J. Phys.* **19**, 013031 (2017).

(\*) Work performed in collaboration with Luca Ghiringhelli, Runhai Ouyang and many other collaborators of the NOMAD Laboratory: <https://NOMAD-CoE.eu>.

## Ultra-Coarse-Graining and Its Applications

Gregory A. Voth<sup>1</sup>

<sup>1</sup>*Department of Chemistry, James Franck Institute, and Institute for Biophysical Dynamics, The University of Chicago, 5735 South Ellis Avenue, Chicago, USA*

<sup>1</sup>*5735 South Ellis Avenue, SCL 231, Chicago, IL, USA*

Recent advances in theoretical and computational methodology will be presented that are designed to simulate complex (biomolecular and other soft matter) systems across multiple length and time scales. The approach provides a systematic connection between all-atom molecular dynamics, coarse-grained modeling, and mesoscopic phenomena. At the heart of these concepts are methods for deriving coarse-grained models from molecular structures and their underlying atomic-scale interactions. This particular aspect of the work has strong connections to the procedure of renormalization, but in the context of CG models it is developed and implemented for more heterogeneous systems. An important new component of our work has been the concept of the “ultra-coarse-grained” (UCG) model and its associated computational implementation. In the UCG approach, the CG sites or “beads” can have internal states, much like quantum mechanical states. These internal states help to self-consistently quantify a more complicated set of possible interactions within and between the CG sites, while still maintaining a high degree of coarse-graining in the modeling. At present, the UCG equations of motion can be solved in two limits, one of which has similarities to quantum surface hopping in the case of rare internal CG site state transitions, while the other limit is akin to Born-Oppenheimer or Ehrenfest dynamics in the limit of rapid local equilibration of the CG internal states. In either case, the presence of the CG site internal states greatly expands the possible range of systems amenable to accurate CG modeling, including quite heterogeneous systems such as aggregation of hydrophobes in solution, liquid-vapor and liquid-solid interfaces, and complex self assembly processes such as occurs for large multi-protein complexes.



## Oriented Electric Fields as Future Smart Reagents in Chemistry.

**Sason Shaik<sup>1</sup>, Debasish Mandal<sup>1</sup>, Rajeev Ramanan<sup>1</sup>,**

*<sup>1</sup>Institute of Chemistry and the Lise Meitner Minerva Center, The Hebrew University of Jerusalem, Edmond J. Safra Campus @ Givat Ram, Jerusalem, Israel*

Oriented external-electric-fields (OEEFs) as “smart reagents” are no longer a theoretical dream. The talk discusses the wide-ranging potential of using OEEFs to catalyze and control a variety of non-redox reactions and impart selectivity at will.<sup>[1]</sup> An OEEF along the direction of electron reorganization, the so-called “reaction axis”, will catalyze nonpolar reactions, control regioselectivity and induce spin-state selectivity. Simply flipping the direction of the OEEF or orienting it off of the reaction-axis, will control at will, the *endo/exo* ratio in Diels-Alder reactions and steps in enzymatic catalytic cycles. The talk will try to highlight these outcomes using theoretical results for H-abstraction reactions, epoxidation of double bonds, C-C bond making reactions, proton transfers, and the cycle of the enzyme cytochrome P450, as well as recent experimental data. We postulate that, as experimental techniques mature, chemical syntheses may become an exercise in zapping oriented molecules with OEEFs!

[1] S. Shaik, D. Mandal, R. Ramanan, *Nature Chem.* **8**, 1091 (2016).

## Bringing Volcano Plots as a Tool to Understand and Predict Homogenous Catalysts

Michael Busch,<sup>1,2</sup> Matthew D. Wodrich,<sup>1</sup> Clémence Corminboeuf<sup>1</sup>

<sup>1</sup>Laboratory for Computational Molecular Design, Institute of Chemical Sciences and Engineering, Ecole polytechnique fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.

<sup>2</sup>National Center for Computational Design and Discovery of Novel Materials (MARVEL), Ecole Polytechnique fédérale de Lausanne, Station 12, 1015 Lausanne, Switzerland

Volcano plots are common tools used by the heterogeneous catalysis and electrochemistry communities to compare the thermodynamic profiles of different catalysts. These plots pictorially represent Sabatier's principle, which states that the interaction between a substrate and a catalyst should be neither too weak nor too strong[1] Despite their inherent ability to identify attractive catalysts and to facilitate understanding of the roles that metal and ligand choice have on cycle energetics, volcano plots describing homogeneous catalytic processes have only recently been realized[2] To meet the unique challenges of homogeneous catalysis, these plots must be further extended beyond the simple thermodynamic picture[3]. Most recently, we have sought to systematically gauge the impact of multiple factors (*e.g.*, a transmetallation partner) that influence catalytic cycle energetics through the creation of three-dimensional volcano plots.[4] Using cross-coupling reactions as a prototypical model, these 3D plots allowed us to uncover a kind of "cross-coupling genome" that not only enhances fundamental understanding of this important class of chemical reactions, but also reveals strategies for developing new catalytic systems.



- [1] P. Sabatier, *La Catalyse en Chimie Organique*, Librairie Polytechnique, Paris, 1913.
- [2] M. Busch, M.D. Wodrich, C. Corminboeuf, *Chem. Sci.* **6**, 6754 (2015).
- [3] M.D. Wodrich, M. Busch, C. Corminboeuf, *Chem. Sci.* **7**, 5723 (2016).
- [4] M. Busch, M.D. Wodrich, C. Corminboeuf, submitted for publication.

## **"Nucleobases: from the prebiotic world to self-healing polymers"**

**Julia E. Rice<sup>1</sup>, William C. Swope<sup>1</sup>, Hans W. Horn<sup>1</sup>, Timothy E. Long<sup>2</sup>,  
Partha P. Bera<sup>3</sup>, Timothy J. Lee<sup>3</sup>**

<sup>1</sup> *IBM Almaden Research Center, 650 Harry Road, San Jose, Ca 95120, United States*

<sup>2</sup> *Macromolecules Innovation Institute, Department of Chemistry, Virginia Tech,  
Blacksburg, Virginia 24061, United States*

<sup>3</sup> *Space Science and Astrobiology Division, NASA Ames Research Center, MS 245-6,  
Moffett Field, CA 94035, United States*

Abstract: Laboratory experiments have shown that the UV photo-irradiation of low-temperature ices of astrophysical interest, with addition of pyrimidine, leads to the formation of nucleobases: uracil, cytosine and thymine [1]. In the first part of this talk we investigate a possible route to the formation of cytosine via the irradiation of pyrimidine in the presence of water and ammonia ices.

In the second part, we investigate the strength of hydrogen bonding interactions between two cytosine molecules as a preliminary step to evaluating their use in polymer networks.

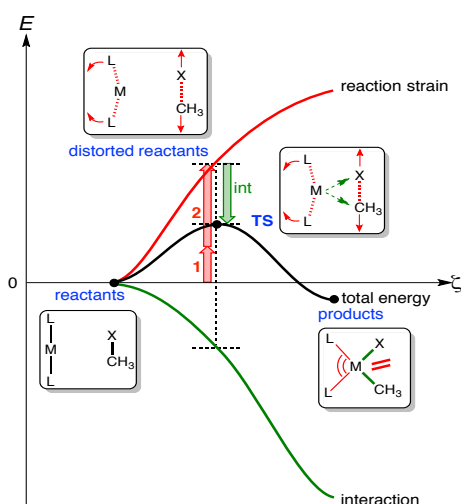
[1] M. Nuevo, S. N. Milam, S. A. Sandford, *Astrobiology* **12** 295 (2012); C. K. Materese, M. Nuevo, P. P. Bera, T. J. Lee, S. A. Sandford, *Astrobiology* **13**, 948 (2013).

## Rational Design of Chemical Reactions

F. Matthias Bickelhaupt<sup>1</sup>

<sup>1</sup>*Amsterdam Center for Multiscale Modeling (ACMM), Vrije Universiteit Amsterdam, and  
Institute for Molecules and Materials (IMM), Radboud University, Nijmegen,  
The Netherlands. E-mail: f.m.bickelhaupt@vu.nl*

The aim of this talk is to convey a way of understanding the factors that determine bonding and reactivity in the framework of quantitative Kohn-Sham molecular orbital theory. To this end, I will first discuss the activation strain model (ASM, also known as distortion/interaction model, D/I-M) which creates causal relationships between reactivity trends, on one hand, and the physical properties of reactants and the type of chemical transformation, on the other hand [1-3]. The ASM covers not only the interaction between reactants but also the energy needed to distort them as they proceed along the reaction coordinate. A typical activation strain diagram (ASD) can be found in the illustration, showing the strain associated with distortion of reactants as well as the interaction between the ever more distorted reactants for a metal-mediated bond-activation reaction. In this presentation, examples of ASM applications to organic and inorganic chemistry comprise S<sub>N</sub>2 substitution and E2 elimination, oxidative addition as well as selected pericyclic reactions. Our reactivity model is causative, transparent, and, within the accuracy of the employed compute engine, it is also exact.



**Figure 1.** Schematic activation strain diagram (ASD) for bond activation via oxidative addition.

- [1] F. M. Bickelhaupt, K. N. Houk, *Angew. Chem. Int. Ed.*, DOI: 10.1002/anie.201701486.
- [2] L. P. Wolters, F. M. Bickelhaupt, *WIREs Comput. Mol. Sci.* **5**, 324 (2015).
- [3] I. Fernandez, F. M. Bickelhaupt, *Chem. Soc. Rev.* **43**, 4953 (2014).

## Development and Applications of Direct Dynamics Simulations

William L. Hase<sup>1</sup>

<sup>1</sup>*Department of Chemistry and Biochemistry, Texas Tech University,  
Lubbock, Texas, United States*

Direct dynamics is a classical chemical dynamics simulation in which the potential energy, gradient, and possibly Hessian are obtained directly from an electronic structure theory [1,2]. The simulations are computationally demanding and approaches for enhancing their execution will be discussed. Comparisons with experiment are important and accurate potential energy surfaces (PESs) are necessary, as well as proper initial conditions for the simulation's trajectories. The ability of DFT methods to accurately represent multi-dimensional properties of the PES, and not only stationary points, will be discussed. Applications to gas-phase S<sub>N</sub>2 reactions, including micro-solvation, and collision-induced dissociation of peptide ions will be emphasized.

[1] M. Paranjothy, R. Sun, Y. Zhuang, and W. L. Hase, *WIREs Comput. Mol. Sci.* **3**, 296 (2013).

2. S. Pratihari, X. Ma, Z. Homayoon, G. L. Barnes, and W. L. Hase, *J. Am. Chem. Soc.* **139**, 3570 (2017)

## Refining First-Principles Photo-Electrocatalysis

**Karsten Reuter<sup>1</sup>**

*<sup>1</sup>Chair for Theoretical Chemistry and Catalysis Research Center,  
Technical University of Munich, Lichtenbergstr. 4, 85747 Garching, Germany*

First-principles based computational modelling assumes an ever increasing role in understanding and partly already optimizing catalysts for photo-electrochemical reactions. The success of prevalent approaches like the computational hydrogen electrode (CHE) thereby relies largely on a numerical efficiency sufficiently high as to allow for large-scale screening of catalyst materials. Such efficiency arises out of well-chosen descriptors that ideally condense the mechanistic understanding of the ongoing catalytic reactions at the solid-liquid interface.

In recent years, there is increasing evidence that this understanding needs further scrutiny. Critical aspects in this respect are the neglect of solvation effects, the assumption of pathways that exclusively proceed via proton-coupled electron transfer steps, and the neglect of any kinetic limitations in the CHE approach. In this talk I will review our recent activities in addressing these issues with detailed first-principles based multiscale modeling approaches. Thereby, in particular embedding approaches – both on the solid and the liquid side of the interface – have the potential for a refined description without sacrificing computational efficiency.

## Challenges in modeling electronic structure, optical and transport properties of conjugated molecular materials

Fabrizia Negri<sup>1</sup> and Sofia Canola<sup>1</sup>

<sup>1</sup> *Dipartimento di Chimica "G. Ciamician", University of Bologna,  
via F. Selmi 2, Bologna, Italy.*

Developments in organic electronics, following a bottom-up chemical approach, have contributed to an increase in the number of potential semiconductors and to tuning of their properties.[1] The interplay between intramolecular properties and intermolecular interactions governs, among others, charge conduction mechanisms, energy transfer and optical properties of the condensed phases. Among conjugated dyes, those characterized by a singlet biradical character are also very interesting since they generally have a small energy gap and can therefore find applications as near-infrared dyes and ambipolar semiconductors.[2] Over the past few years we have modelled, with computational tools, structural, electronic, optical and charge transport properties of a number of core-extended conjugated molecules, paying increasing attention to the effects that condensed phase and aggregation can have on the properties of the molecular material.[3] We model charge transport in molecular materials by means of an integrated computational approach including quantum-chemical (QC) evaluation of intra-molecular properties and electronic couplings followed by propagation of the charge carriers through the material, via Kinetic Monte Carlo simulations. When thermal effects become relevant, molecular dynamics simulations combined with the QC evaluation of electronic couplings are also carried out to capture the effect of non-local electron-vibration couplings. Moving to semiconductors with biradical character, the presence of a low-lying double exciton state in their electronic absorption spectra (similarly to oligoenes), is a major fingerprint[4]. The large dimension of most of these systems however, often limits the applicability of multi-reference correlated methods and we discuss a possible cheap alternative approach to model this peculiar spectroscopic feature for large conjugated biradical systems. Finally, we outline our recent investigations on the excited states of chromophore's aggregates with the aim of disclosing the role of charge transfer states on their optoelectronic properties and showing the need to go beyond the exciton model.

[1] Gao X., Zhao Z. *Sci. China Chem.* **58**, 947 (2015); Cinar M. E., Ozturk T. *Chem. Rev.* **115**, 3036 (2015)

[2] Zeng Z., Shi X., Chi C., Lopez Navarrete J.T., Casado J., Wu J., *Chem. Soc. Rev.* **44**, 6578 (2015); Sun Z., Zeng Z., Wu J., *Acc. Chem. Res.* **47**, 2582 (2014)

[3] Canola S., Negri F., *Phys. Chem. Chem. Phys.* **16**, 21550 (2014); Canola S., Negri F., *J. Phys. Chem. C* **119**, 11499 (2015)

[4] Di Motta S., Negri F., Fazzi D., Castiglioni C., Canesi E. V. *J. Phys. Chem. Lett.*, **1**, 3334 (2010)

## From dye-sensitized TiO<sub>2</sub> to dye-Sensitized NiO heterointerfaces: a new challenge for theory.

Simone Piccinin,<sup>1</sup> Dario Rocca,<sup>2</sup> Mariachiara Pastore<sup>2</sup>

<sup>1</sup> CNR-IOM DEMOCRITOS c/o SISSA, Via Bonomea 265, 34136 Trieste, Italy

<sup>2</sup> CNRS - Universite de Lorraine, Boulevard des Aiguillettes, BP 70239 54506

Vandoeuvre-les-Nancy Cedex, France

In the context of solar energy exploitation, dye-sensitized solar cells (DSCs)<sup>1</sup> and dye-sensitized photoelectrosynthetic cells (DSPECs)<sup>2</sup> offer the promise of cost effective sunlight conversion and storage, respectively. Dye-functionalization of p-type semiconductors (like NiO) can be either exploited to build p-type DSC architectures (Figure 1) or employed in a water splitting cell at the photocathode for water reduction. Despite the huge interest in developing efficient p-type electrodes, up to now the solar-energy-to-electric-energy conversion efficiency of the n-type DSC is still one order of magnitude higher than the inverse counterpart.<sup>3</sup> Moreover, the characterization of the electronic and structural properties of the complex NiO/solvent/dye/electrolyte (catalyst) interface is still poor when compared to the level of understanding reached for TiO<sub>2</sub> sensitized photoanodes, from both the experimental and computational point of view.<sup>4,5</sup> In an effort to improve the predictive power of theoretical simulations and the fundamental understanding for these systems, here we tackle the dynamical modelling of a full dye-sensitized NiO heterointerface, including the water environment.<sup>6</sup> We will discuss the main methodological limitations of state-of-the art DFT methodologies in predicting the energy level alignment across the dye/semiconductor interface and the challenging definition of a proper structural model needed to reliably capture the interface complexity.

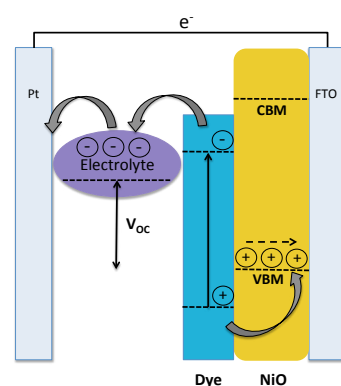


Figure 1. Operational mechanism of a p-type DSC

### References.

- [1] M. Grätzel, *Acc. Chem. Res.*, **42**, 1788 (2009).
- [2] W. J. Youngblood, S.-H. A. Lee, K. Maeda, T. E. Mallouk, *Acc. Chem. Res.*, **42**, 1966 (2009).
- [3] F. Odobel, L. Le Pleux, Y. Pellegrin, E. Blart, *Acc. Chem. Res.*, **43**, 1063 (2010).
- [4] M. Pastore, F. De Angelis, *Top. Curr. Chem.*, Springer Berlin Heidelberg: 1- 86 (2014)
- [5] M. Pastore, F. De Angelis, *J. Am. Chem. Soc.* **137**, 5798 (2015)
- [6] S. Piccinin, D. Rocca, M. Pastore (in preparation)

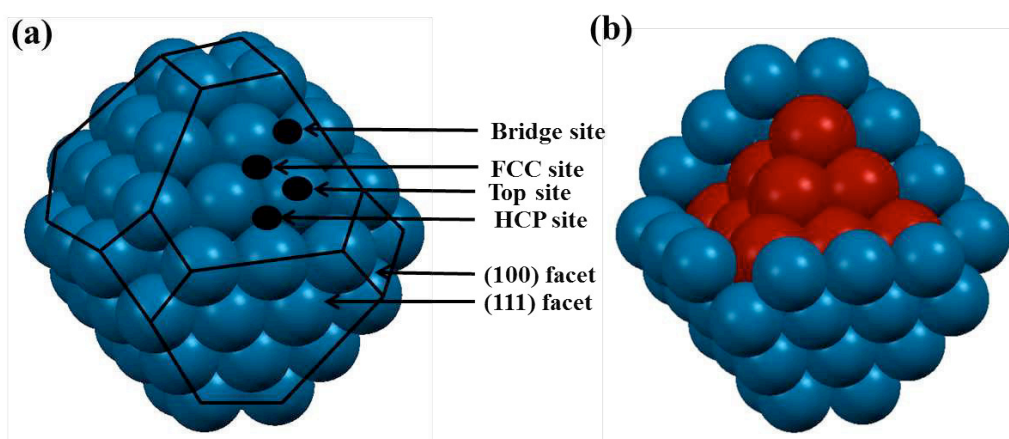


## Atomistic Modeling of Nanocluster Based Electrodes for Fuel Cell Applications

Arup Mahata<sup>1</sup>, Biswarup Pathak<sup>1</sup>

<sup>1</sup>*Discipline of Chemistry, Indian Institute of Technology Indore, Indore, India*

Proton exchange membrane (PEM) fuel cells are promising sources of clean energy due to their high efficiency, low operating temperature, and zero carbon emission. However, the performance of such fuel cell largely depends on the performance of the oxygen reduction reaction (ORR) at the cathode. The slow kinetics of ORR and expensive Pt metal in the Pt/C based electrodes prevents the commercialization of PEM fuel cells. Therefore, lowering Pt loading without compromising the performance of a fuel cell can be challenging. In order to lower the Pt loading, Pt-nanocluster based electrodes [Figure] are best alternatives and may improve the performance of such fuel cell. However, stability can be an issue for such cases. For this, alloying Pt with other metals may improve the stability with compromising the performance. So, the main objective of this talk is to discuss all these aspects [1-6] towards the nanocluster based electrodes for fuel cell applications.



- [1] A. Mahata, I. Choudhuri, B. Pathak, *Nanoscale* **7**, 13438 (2015).
- [2] A. Mahata, K. S. Rawat, I. Choudhuri, B. Pathak, *Catalysis Science and Technology*, **6**, 7913 (2016).
- [3] A. Mahata, P. Bhauriyal, K. S. Rawat, B. Pathak, *ACS Energy Letters*, **1**, 797 (2016).
- [4] A. Mahata, K. S. Rawat, I. Choudhuri, B. Pathak, *Journal of Materials Chemistry A*, **4**, 12756 (2016).
- [5] A. Mahata, K. Singh Rawat, I. Choudhuri, B. Pathak, *Scientific Reports*, **6**, 25590 (2016).
- [6] A. Mahata, B. Pathak, *Journal of Materials Chemistry A*, **5**, 5303 (2017).

## Understanding Intramolecular Singlet Fission Process in D-A Polymer From Correlated Wavefunction Perspective

Zhigang Shuai and Jiajun Ren

*Department of Chemistry, Tsinghua University, Beijing, China*

Singlet fission (SF) phenomena has aroused strong interests in recent years due to the possible application in enhancing the photovoltaic efficiency. The intermolecular SF process has been investigated widely and a comprehensive picture has been emerged recently. However, the intramolecular SF process discovered by Busby et al. [1] is full of controversies, especially regarding the role of the dark  $2Ag$  state. The fact that the double-excitation (dark  $2Ag$  state) lies below single excitation ( $1Bu$ ) discovered experimentally by Hudson and Kohler demonstrated the essential role of electron correlation effect for excited states. Regarding the role of the dark  $2Ag$  state, two conflicting mechanisms have been proposed: (i) pros mechanism: the dark state  $2Ag$  symmetry broken which led to direct photoabsorption followed by splitting into two triplet states [2], namely  $2Ag < 1Bu$  is essential; (ii) cons mechanism: then the dark  $2Ag$  state serves as a deactivation pathway, detrimental for iSF [3], namely,  $2Ag > 1Bu$  is required for iSF. Targetting such  $2Ag$  state for large molecule becomes intractable because of the multireference difficulty. Density matrix renormalization group theory has been shown to be nearly exact for conjugated linear chain, even for the low-lying excited states. We here propose a novel mechanism through DMRG study along with correlation functions analysis [4]. We find that (i) the  $2Ag$  is of intrinsically TT character and (ii) it serves as an active pathway for iSF instead of deactivation channel; and (iii) according to this model, the much lower iSF quantum yield for oligomer is due to the larger non-adiabatic coupling between  $2Ag$  and  $1Ag$  than in polymer.

- [1] E. Busby, J. Xia, Q. Wu, J. Z. Low, R. Song, J. R. Miller, X.Y. Zhu, L. M. Campos, M. Y. Sfeir, *Nature Mater.* **14**, 426 (2015).
- [2] K. Aryanpour, T. Dutta, U. N. Huynh, Z. V. Vardeny, S. Mazumdar, *Phys. Rev. Lett.* **115**, 267401 (2015).
- [3] E. Busby, J. Xia, J. Z. Low, Q. Wu, J. Hoy, L. M. Campos, M. Y. Sfeir, *J. Phys. Chem. B* **119**, 7644 (2015).
- [4] Jiajun Ren, Qian Peng, Xu Zhang, Yuanping Yi, Zhigang Shuai, *J Phys Chem Lett.* **8**, 2175 (2017)

## Exchange-correlation functionals from density scaling

David J Tozer<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Durham University, South Road, Durham, UK*

Density scaling considerations can be used to determine unconventional DFT exchange-correlation functionals, with desirable characteristics such as approximate satisfaction of Koopmans' theorem (including negative anion HOMO energies) and exact asymptotic exchange-correlation potentials [1]. We shall describe our most recent work in this area.

- [1] J. G. Gledhill and D. J. Tozer, *J. Chem. Phys.* **143**, 024104 (2015).

## Self-interaction Corrected Energy Functional Applied to Molecules and Solids

Hannes Jónsson<sup>1,2,3</sup>

<sup>1</sup>*Science Institute and Faculty of Physical Sciences, University of Iceland, Reykjavík, Iceland*

<sup>2</sup>*Department of Chemistry, Brown University, USA*

<sup>3</sup>*Department of Applied Physics, Aalto University, Finland*

Localized electronic states and weakly bound electrons extending far from atom nuclei are examples where practical implementations of Kohn-Sham density functional theory (DFT) such as GGA, meta-GGA and hybrid functionals tend to fail. A fully variational and self-consistent implementation of the Perdew-Zunger self-interaction correction (PZ-SIC) using complex optimal orbitals [1] has been applied to several such systems and found to give good results. Calculations of dipole bound anion [2], Rydberg excited states of molecules and molecular clusters [3], localized charge state in a diamine cation [4] and electronic holes in oxide crystals [5] will be presented. The computational effort of the PZ-SIC calculations scales with system size in the same way as DFT/GGA calculations but the prefactor is large since an effective potential needs to be evaluated for each orbital (calculations that could, however, be carried out in parallel) and optimal orbitals need to be found in terms of the Kohn-Sham orbitals. PZ-SIC is an example of an extended functional form where the energy depends explicitly on the orbital densities, not just the total electron density. While significant improvements are obtained with PZ-SIC compared with practical implementations of Kohn-Sham DFT, problems can also be introduced such as incorrect symmetry breaking [6]. The orbital density dependent functional form could, however, be exploited more generally to develop a self-interaction free functional rather than as a correction to Kohn-Sham functionals, thereby providing a mean field theory for optimal orbitals and orbital energies.

- [1] S. Lehtola and H. Jónsson, *J. Chem. Theory Comput.* **10**, 5324 (2014); S. Lehtola, E. Ö. Jónsson, and H. Jónsson, *J. Chem. Theory Comput.* **12**, 4296 (2016).
- [2] Y. Zhang, P.M. Weber and H. Jónsson, *J. Phys. Chem. Letters* **7**, 2068 (2016).
- [3] H. Gudmundsdóttir, Y. Zhang, P.M. Weber and H. Jónsson, *J. Chem. Phys.* **141**, 234308 (2014).
- [4] X. Cheng, Y. Zhang, E. Jónsson, H. Jónsson and P.M. Weber, *Nature Communications* **7**, 11013 (2016).
- [5] H. Gudmundsdóttir, E. Ö. Jónsson and H. Jónsson, *New Journal of Physics* **17**, 083006 (2015).
- [6] S. Lehtola, M. Head-Gordon and H. Jónsson, *J. Chem. Theory Comput.* **12**, 3195 (2016).

## Combining density-functional theory and many-body methods

Julien Toulouse<sup>1</sup>

<sup>1</sup>*Laboratoire de Chimie Théorique, Université Pierre et Marie Curie, Sorbonne Universités, CNRS, Paris, France*

Nowadays, a major strategy for improving approximations in density-functional theory (DFT) is to combine DFT with many-body methods such as many-body perturbation theory. Range separation of the electron-electron interaction provides a practical way of performing such a combination by using a (semi)local-density approximation for the short-range part and an explicit many-body approximation for the long-range part. It combines the best of both worlds: an accurate and compact description of short-range interactions by DFT approximations and an accurate description of long-range nonlocal interactions by many-body approximations, while avoiding any double counting of electron correlations.

After giving an overview of such approaches, I will present some recent advances concerning:

- Range-separated hybrid methods for describing ground-state correlations in molecular and solid-state systems, based on second-order perturbation theory and random-phase approximations [1, 2, 3, 4];
- Range-separated hybrid methods for calculating excitation energies in molecular systems, based a long-range frequency-dependent second-order Bethe-Salpeter correlation kernel [5].

- [1] B. Mussard, P. Reinhardt, J. G. Angyan, J. Toulouse, *J. Chem. Phys.* **142**, 154123 (2015).
- [2] G. Sansone, B. Civalleri, D. Usvyat, J. Toulouse, K. Sharkas, L. Maschio, *J. Chem. Phys.* **143**, 102811 (2015).
- [3] S. Smiga, O. Franck, B. Mussard, A. Buksztel, I. Grabowski, E. Luppi, J. Toulouse, *J. Chem. Phys.* **145**, 144102 (2016).
- [4] B. Mussard, J. Toulouse, *Mol. Phys.* **115**, 161 (2017).
- [5] E. Rebolini, J. Toulouse, *J. Chem. Phys.* **144**, 094107 (2016).

## Dispersion interactions from the exchange-hole dipole moment

**Erin R. Johnson<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, Dalhousie University, 6274 Coburg Road, Halifax, Canada*

The exchange-hole dipole moment (XDM) method is a density-functional model of London dispersion based upon second-order perturbation theory. The XDM dispersion coefficients are non-empirical and depend directly on the electron density and related properties. XDM offers simultaneous high accuracy for a diverse range of chemical systems, such as dispersion-bound complexes, hydrogen-bonding, halogen-bonding, metallophilic interactions, molecular crystals, layered materials, and physisorption and chemisorption on metal surfaces. The model's success is due to variation of the atomic dispersion coefficients with chemical environment. Recent applications of XDM will be presented.

## Factorizations of the exchange-correlation hole

Matthias Ernzerhof

*Department of Chemistry, University of Montreal, Canada*

The exchange-correlation hole  $\rho_{xc}(\mathbf{r}, \mathbf{r}+\mathbf{u})$  is a key notion in density functional theory and most functionals for the exchange-correlation energy rely on known properties of  $\rho_{xc}(\mathbf{r}, \mathbf{r}+\mathbf{u})$ . The hole  $\rho_{xc}(\mathbf{r}, \mathbf{r}+\mathbf{u})$  describes the reduction in electron density at point  $\mathbf{r}+\mathbf{u}$  due to the presence of an electron at the reference point  $\mathbf{r}$ . We employ [1,2] a factorization approach to model  $\rho_{xc}(\mathbf{r}, \mathbf{r}+\mathbf{u})$  where  $\rho_{xc}(\mathbf{r}, \mathbf{r}+\mathbf{u}) = f_c(\mathbf{r}, \mathbf{r}+\mathbf{u}) \rho_x(\mathbf{r}, \mathbf{r}+\mathbf{u})$ . The correlation factor  $f_c(\mathbf{r}, \mathbf{r}+\mathbf{u})$  turns  $\rho_x(\mathbf{r}, \mathbf{r}+\mathbf{u})$  into the exchange-correlation hole. Using exact constraints, we develop representations for  $f_c(\mathbf{r}, \mathbf{r}+\mathbf{u})$  that address problems such as self-interaction and strong correlation. The correlation factor reduces to one in cases where exchange-correlation reduces to exchange. A means to gain insight about  $\rho_{xc}(\mathbf{r}, \mathbf{r}+\mathbf{u})$  and  $f_c(\mathbf{r}, \mathbf{r}+\mathbf{u})$  is the adiabatic connection (AC). The AC relates  $\rho_{xc}(\mathbf{r}, \mathbf{r}+\mathbf{u})$  to ground-state wave functions that depend on the coupling constant  $\lambda$ , which scales the electron-electron repulsion. While only  $\lambda$  values between 0 and 1 are relevant for  $\rho_{xc}(\mathbf{r}, \mathbf{r}+\mathbf{u})$ , larger  $\lambda$ -values are useful for the construction of interpolations for the AC. In particular, we focus on the strong-correlation ( $\lambda \rightarrow \infty$ ) limit and develop approximations [3,4] to the exchange-correlation hole in this limit. Starting from the electron density  $\rho(\mathbf{r}+\mathbf{u})$  as a function of the reference point  $\mathbf{r}$  and the electron-electron separation  $\mathbf{u}$ , exchange-correlation factors  $f_{xc}(\mathbf{r}, \mathbf{r}+\mathbf{u})$  are considered that convert  $\rho(\mathbf{r}+\mathbf{u})$  into the exchange-correlation hole of the strong-correlation (SC) limit, i.e.,  $\rho_{xc}^{SC}(\mathbf{r}, \mathbf{r}+\mathbf{u}) = f_{xc}^{SC}(\mathbf{r}, \mathbf{r}+\mathbf{u}) \rho(\mathbf{r}+\mathbf{u})$ . The resulting exchange-correlation energy for the SC limit is then used to construct [3,4] various AC interpolations and hybrid schemes.

- [1] J. Přecechtělová, H. Bahmann, M. Kaupp, M. Ernzerhof *J. Chem. Phys. Communication* **141**, 111102 (2014).
- [2] J. Přecechtělová, H. Bahmann, M. Kaupp, M. Ernzerhof *J. Chem. Phys.* **143**, 144102 (2015).
- [3] Y. Zhou, H. Bahmann, M. Ernzerhof, *J. Chem. Phys.* **143**, 124103 (2015).
- [4] H. Bahmann, Y. Zhou, M. Ernzerhof, *J. Chem. Phys.* **145**, 124104 (2016).

## Multi-scale methods for electron and exciton transfer in biological and organic materials

Marcus Elstner

*Institute of Physical Chemistry, KIT, Karlsruhe, Germany*

In the last years, we have developed a computational methodology to simulate charge transfer processes in complex systems. Due to the large system size, which has to be treated quantum mechanically, we have developed a coarse-grained quantum/classical methodology, which allows to describe the dynamics of the electronic system coupled to the dynamics of environment, e.g. the protein in water solvent. Charge-transfer (CT) parameters are computed using a fragment orbital approach applying the approximate Density Functional method SCC-DFTB. Environmental effects are captured using a combined quantum mechanics/molecular mechanics (QM/MM) coupling scheme and dynamical effects are included by evaluating these CT parameters along extensive classical molecular dynamics (MD) simulations. Using this methodology, the time course of the charge can be followed by propagating the hole wave function using the time dependent Schrödinger equation for the Tight Binding Hamiltonian, which can also be used to compute the transmission and current through e.g. DNA nano-wires. The photo-activation of E. coli Photolyase involves, after photoexcitation of the chromophore and energy transfer to FAD, a long range hole transfer along a chain of Trp residues. Since this process could not be modelled using Marcus theory with parameters computed with classical equilibrium MD simulations, we used fully coupled non-adiabatic (Ehrenfest/surface hopping) quantum mechanics/molecular mechanics (QM/MM) simulations. The most recent extension concerns applications to charge and exciton dynamics in organic materials

- [1] T. Kubař and M. Elstner, *Phys. Chem. Chem. Phys.* **15**, 5794 (2013)
- [2] T. Kubař, R. Gutiérrez, U. Kleinekathöfer, G. Cuniberti, M. Elstner, *physica status solidi* **250**, 2277 (2013)
- [3] G. Lüdemann, I. A. Solov'yov, T. Kubař, M. Elstner, *J. Am. Chem. Soc.* **137**, 1147 (2015)
- [4] B. Popescu et al., *Phys. Rev. Lett.* **109**, 17680 (2012)
- [5] A. Heck, J. Kranz and M. Elstner. *J. Chem. Theory Comput.* **12**, 3087 (2016)
- [6] J. Kranz, M. Elstner. *J. Chem. Theor. Comput.* **12**, 4209 (2016)



## Sulfenic acid or sulfenate? A matter of protein environment and water access in oxidized Cysteine sites of physiological relevance

**E. Laura Coitiño, Jenner Bonanata and Stephanie Portillo**

*Laboratorio de Química Teórica y Computacional, Instituto de Química Biológica,  
Facultad de Ciencias, Universidad de la República (Udelar), Iguá 4225, Montevideo  
11800, Uruguay*

Sulfenic acids (RSOH) are transient intermediates, key in the oxidation of protein cysteines [1]. Mainly formed by reaction of thiols with  $2e^-$  oxidants through  $S_N2$  type mechanisms with post-transition state proton transfer [2,3], they can further react, acting both as nucleophiles or electrophiles. Low-molecular-weight (LMW) RSOHs can promptly react with thiols to yield disulfides (RSSR') or condensate to form thiosulfonates (RS(=O)SR'), too unstable to be isolated in most of the cases. Whereas in some proteins such a fate is prevented by stabilization of the CysSOHs (or the ionized form, sulfenate) by the local environment around the oxidized Cys, they still can undergo irreversible transformation to sulfinic acids by reacting with oxidants, such as it happens for *human serum albumin* (HSA) Cys34-SOH with  $H_2O_2$ , or a further reversible oxidation to RSSR', as in *peroxiredoxin 5* (PRDX5) catalytic cycle, in which a Cys47-SOH reacts with a second Cys151 located  $\sim 14$  Å apart in the same monomer, requiring at some point a local unfolding from a fully-folded enzyme active site. Mechanisms, kinetics of these processes, and pKa of Cys residues in different oxidation states and modulation of their properties by hydrogen-bonded networks (eventually including water molecules) have been studied by us and others for these two proteins of physiological relevance [1,2]. Here we present the most recent advances and insights on these issues that, in consistency with experiments, we obtained by applying a combination of computational methods covering different time and space scales, including conventional and accelerated MD, constant pH MD, QM and additive and/or subtractive QM/MM methods.

- [1] Roos, G., Messens, J. *Free Radical Biol. Med.* **51**, 314 (2011).
- [2] Portillo, S. Ferrer-Sueta, G., Coitiño, E.L. *et al.* *Biochemistry* **53**, 6113 (2014).
- [3] Bonanata, J., Álvarez, B., Coitiño E.L. *et al.* *Free Radical Biol. Med.* **108**, 952 (2017).

## **Solvation and solvent-mediated driving forces: Spatially resolved information from detailed atomistic trajectories**

**Matthias Heyden<sup>1</sup>**

*<sup>1</sup>Theoretical Chemistry, Max-Planck-Institut für Kohlenforschung / Cluster of Excellence RESOLV, Kaiser-Wilhelm-Platz 1, Mülheim an der Ruhr, Germany*

Thermodynamic driving forces of biomolecular processes, i.e. changes in free energy, are the sum of multiple contributions. These include changes in the internal energy of flexible molecules, conformational entropies and solvation free energies. The individual contributions are large in magnitude and often of opposite sign, resulting in significant compensations of favorable and unfavorable terms.

To provide a molecular understanding of the working mechanisms of enzymes or to develop high affinity ligands as potential drugs, we require a detailed microscopic understanding of the underlying driving forces and free energy changes. Here, we utilize atomistic molecular dynamics simulations to investigate in detail important contributions to the free energy, in particular solvation free energies, enthalpies and entropies.

We propose a method that allows us to obtain spatially resolved contributions to the solvation free energy, which utilizes the spectrum of intermolecular vibrations in the solvent to obtain entropic information. We test the approach for small molecules solvated in water for which we reproduce experimental data. In addition, we identify distinct species of hydration water molecules near characteristic functional groups based on their vibrational signatures.

We then apply the method to entire proteins, which allows us to characterize the thermodynamic properties of water solvating complex biomolecular surfaces. Further, we analyze the contribution of the solvation free energy to the thermodynamic driving force of a conformational transition, highlighting the importance of compensating effects as well as exact and approximate cancellations. We then suggest new applications of spatially resolved solvation free energies in multi-scale modelling approaches for complex biomolecular systems.

## Deciphering Molecular Mechanisms of Energy-Converting Proteins from Simulations Across Scales

Ville R. I. Kaila<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Technical University Munich, Lichtenbergstraße 4, 85747 Garching, Germany*

Biological energy conversion is driven by remarkable proteins that capture and convert chemical and light energy into other energy forms. In this talk, I will show how multi-scale quantum and classical molecular simulations can be used to obtain a molecular-level understanding of the structure, energetics and dynamics of energy-capturing proteins, and to characterize their spectroscopic properties in different intermediate states. By combining large-scale classical molecular dynamics simulations with quantum chemical cluster models and hybrid quantum mechanics-classical mechanics (QM/MM) calculations, we have studied the function of respiratory and photosynthetic enzymes, as well the mechanisms of light-capture in many photobiological systems. We find that coupled electrostatic-, conformational-, and hydration changes provide essential functional elements in these systems.

- [1] A. Di Luca, A. P. Gamiz-Hernandez, V.R.I. Kaila, *submitted*.
- [2] C.-M. Suomivuori, A. P. Gamiz-Hernandez, D. Sundholm, V. R. I. Kaila, *Proc. Natl. Acad. Sci. USA* (2017) (in press)
- [3] V. Sharma, G. Belevich, A.P. Gamiz-Hernandez, T. Rog, I. Vattulainen, M.L. Verkhovskaya, M. Wikström, G. Hummer, V.R.I. Kaila, *Proc. Natl. Acad. Sci. USA* **112**, 11571 (2015).
- [3] S. Supekar, A.P. Gamiz-Hernandez, V.R.I. Kaila, *Angew. Chemie Intl. Ed.* **55**, 11940 (2016)
- [5] A.P. Gamiz-Hernandez, I.A. Neycheva, R. Send, D. Sundholm, V.R. I. Kaila, *Angew. Chemie. Intl. Ed.* **54**, 11564 (2015)

## Efficient approximation of configurational entropy changes upon binding to biomolecules

Ido Ben-Shalom<sup>1</sup>, Holger Gohlke<sup>1</sup>

<sup>1</sup>*Institute for Pharmaceutical and Medicinal Chemistry, Heinrich Heine University  
Düsseldorf, Universitätsstr. 1, 40225 Düsseldorf, Germany*

A major uncertainty in binding free energy estimates for protein-ligand complexes by methods such as MM-PB(GB)SA or docking scores results from neglecting or approximating changes in the configurational entropies ( $\Delta S_{\text{config.}}$ ) of the solutes. In MM/PB(GB)SA-type calculations,  $\Delta S_{\text{config.}}$  has usually been estimated in the rigid rotor, harmonic oscillator approximation. Here, we present the development of two computationally efficient methods to approximate  $\Delta S_{\text{config.}}$  I) in terms of the reduction in translational and rotational freedom of the ligand upon protein-ligand binding ( $\Delta S_{\text{R/T}}$ ),(1) starting from the flexible molecule approach,(2) and II) in terms of efficiently approximating vibrational entropy changes ( $\Delta S_{\text{vib}}$ ) upon binding to biomolecules(3) based on rigidity theory.(4, 5) Our results suggest that our approaches are valuable, computationally more efficient complements to existing rigorous methods for estimating changes in binding free energy across structurally (weakly) related series of ligands binding to one target.

- [1] I. Y. Ben-Shalom, S. Pfeiffer-Marek, K.-H. Baringhaus, H. Gohlke, *J. Chem. Inf. Model.* **57**, 170 (2017).
- [2] H. X. Zhou, M. K. Gilson, *Chem. Rev.* **109**, 4092 (2009).
- [3] H. Gohlke, I. Ben-Shalom, H. Kopitz, S. Pfeiffer-Marek, K.-H. Baringhaus, *J. Chem. Theor. Comput.* **13**, 1495 (2017).
- [4] C. Pfleger, P. C. Rathi, D. L. Klein, S. Radestock, H. Gohlke, *J. Chem. Inf. Model.* **53**, 1007 (2013).
- [5] S. M. A. Hermans, C. Pfleger, C. Nutschel, C. A. Hanke, H. Gohlke, *WIREs - Comp. Mol. Sci.* **7**, e1311 (2017).

## Theoretical determination of properties of helium for new temperature and pressure standards

Bogumił Jeziorski<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Waraw, Poland*

Next year the General Conference on Weights and Measures will ratify the redefinition of basic SI units [1]. Specifically the new kilogram will be defined by fixing the numerical value of the Planck constant and the new kelvin by fixing the Boltzmann constant. The exact values of these constants, not decided yet, will be close to the best values measured thus far using the old SI units. The new definitions of pascal and kelvin, will call for new, more accurate primary pressure and temperature standards [2]. In this talk I will present very accurate calculations of the polarizability, the two-body interaction potential, and thermophysical properties of helium that were employed to obtain the current most precise value of the Boltzmann constant and that will be used to define a new pressure standard and to improve primary temperature standards. The high accuracy demanded by the metrological application requires determination of the relativistic, quantum electrodynamics, and nonadiabatic coupling effects with reliable error control and uncertainty estimates. Recent results of such calculations of the dynamic polarizability [3, 4] and the pair potential [5, 6] of helium will be presented and discussed.

- [1] J. Fischer and J. Ulrich, *Nature Phys.* **12**, 4 (2016).
- [2] M. R. Moldover, W. L. Tew and H. W. Yoon, *Nature Phys.* **12**, 7 (2016).
- [3] K. Piszczatowski, M. Puchalski, J. Komasa, B. Jeziorski and K. Szalewicz, *Phys. Rev. Lett.* **114**, 173004 (2015).
- [4] M. Puchalski, K. Piszczatowski, J. Komasa, B. Jeziorski and K. Szalewicz, *Phys. Rev. A* **93**, 032515 (2016).
- [5] M. Przybytek, B. Jeziorski, W. Cencek, J. Komasa, J. Mehl and K. Szalewicz, *Phys. Rev. Lett.* **108**, 183201 (2012).
- [6] M. Przybytek, W. Cencek, B. Jeziorski and K. Szalewicz, <http://arxiv.org/abs/1706.05687>.

## Spontaneous generation of radicals and design of anion sponges through Beryllium bonds

Manuel Yáñez<sup>1</sup>, Inés Corral<sup>1</sup>, Oriana Brea<sup>1</sup>, Otilia Mó<sup>1</sup>, Ibon Alkorta<sup>2</sup>, José Elguero<sup>2</sup>

<sup>1</sup>Departamento de Química, Facultad de Ciencias, Módulo 13, and Institute of Advanced Chemical Sciences (IadChem) Universidad Autónoma de Madrid, 28049 Madrid, Spain

<sup>2</sup>Instituto de Química Médica, C/Juan de la Cierva, 3, CSIC, 28006-Madrid, Spain

The non-covalent interactions named Beryllium bonds were described for the first time some years ago [1]. They arise from the interaction of BeXY molecules, behaving as Lewis acids, with conventional Lewis bases. The rather stable complexes formed are the result of dramatic electron density distortions of both interacting units. In this communication we will show, through the use of high-level *ab initio* and density functional calculations, that the electron density redistribution associated to the formation of  $X_2\text{Be}:Y-R$  ( $X=\text{H}, \text{Cl}$ ;  $Y=\text{F}, \text{OH}, \text{NH}_2$ ;  $R=\text{CH}_3, \text{NH}_2, \text{OH}, \text{F}, \text{SiH}_3, \text{PH}_2, \text{SH}, \text{Cl}, \text{NO}$ ) complexes is so large that leads to the exergonic and spontaneous formation of radicals through the homolytic  $Y-R$  bond fission [2]. We have also showed that even though the Be-Be bond is extremely weak in  $\text{Be}_2$  dimers, the electron attachment to 1,8-diBeX-naphthalene derivatives leads to rather strong Be-Be one-electron sigma bonds, reflected in a dramatic shortening of the Be-Be distance with respect to the corresponding neutral molecule [3]. A similar effect is behind the behavior of 1,8-diBeXnaphthalene ( $X=\text{H}, \text{F}, \text{Cl}, \text{CN}, \text{CF}_3, \text{C}(\text{CF}_3)_3$ ) derivatives as *anion sponges* [4] (see Figure 1c) very much as 1,8-bis(dimethylamino) naphthalene derivatives behave as proton sponges.

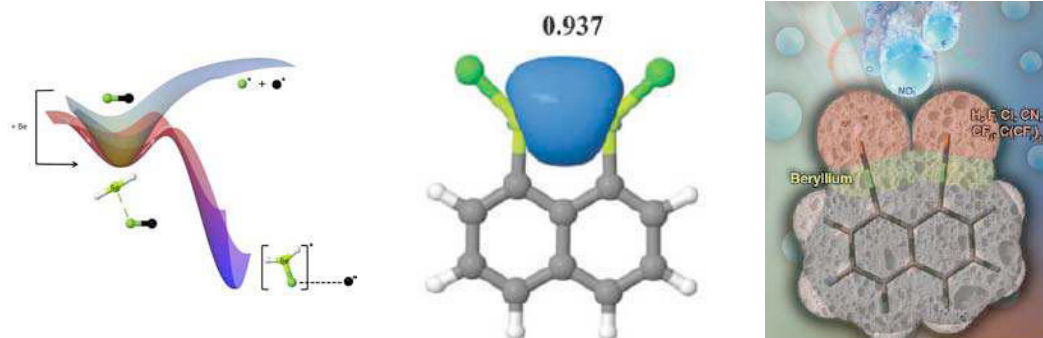


Figure 1. (a) Potential energy curves associated to the exergonic formation of radicals from  $\text{BeH}_2\text{FR}$  complexes. (b) one-electron localized MO and its population for 1,8-diBeCl-naphthalene radical anion. (c) 1,8-diBeX-naphthalene derivatives acting as anion sponges.

[1] P. Sanz, M. Yáñez, O. Mó, I. Alkorta, and J. Elguero *J. Chem. Theor. Comp.* **5**, 2763 (2009)

[2] O. Brea, I. Alkorta, O. Mó, M. Yáñez, J. Elguero, I. Corral *Angew. Int. Chem. Ed.*, **55**, 8736 (2016).

[3] O. Brea, O. Mó, M. Yáñez, I. Alkorta, J. Elguero *Chem. Comm.*, **52**, 9656 (2016)

[4] O. Brea, I. Corral, O. Mó, M. Yáñez, I. Alkorta, J. Elguero *Chem. Eur. J.*, **22**, 18322 (2016)

## Improvements of Instanton Theory to Simulate Atom Tunneling in Astrochemical Reactions

Sean R. McConnell<sup>1</sup>, Thanja Lamberts<sup>1</sup>, Lei Song<sup>1</sup>, Sonia Álvarez-Barcia<sup>1</sup>,  
Jan Meisner<sup>1</sup>, Andreas Löhle<sup>1</sup>, April M. Cooper<sup>1</sup>, Alexander Denzel<sup>1</sup>,  
Johannes Kästner<sup>1</sup>

<sup>1</sup>*Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55,  
Stuttgart, Germany, kaestner@theochem.uni-stuttgart.de*

Instanton theory, based on Feynman path integrals, is increasingly used for accurate prediction of reaction rate constants. We present methodological improvements in several aspects: its accuracy close to the crossover temperature and its limit below that temperature, its convergence properties with the number of images, its temperature-dependence for bimolecular rate constants at low temperature, as well as its dependence on the quality of the potential [1]. Some of these aspects were improved on by using a microcanonical formulation of instanton theory [2]. We applied instanton theory to several reactions of astrochemical interest [3, 4]. Atom tunneling allows reactions to proceed at the cryogenic temperatures of the interstellar medium despite a reaction barrier. These help to explain the formation of water and of the first building blocks of life.

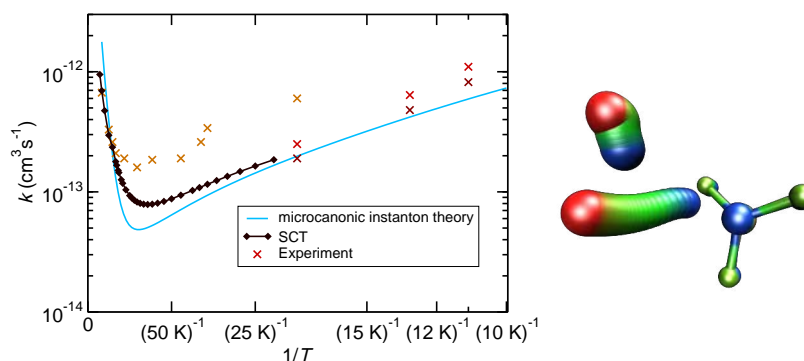


Fig.: Rate constants and instanton path for the reaction  $\text{NH}_3^+ + \text{H}_2 \rightarrow \text{NH}_4^+ + \text{H}$  [5].

- [1] J. Meisner and J. Kästner. *Angew. Chem. Int. Ed.*, **55**, 5400–5413 (2016).
- [2] S. R. McConnell, A. Löhle, and J. Kästner. *J. Chem. Phys.*, **146**, 074105 (2017).
- [3] L. Song and J. Kästner. *Phys. Chem. Chem. Phys.*, **18**, 29278–29285 (2016).
- [4] T. Lamberts, P. K. Samanta, A. Köhn, and J. Kästner. *Phys. Chem. Chem. Phys.*, **18**, 33021–33030 (2016).
- [5] S. Álvarez-Barcia, M.-S. Russ, J. Meisner, and J. Kästner. *Faraday Disc.*, **195**, 69–80 (2016).

## Borophenes, Borospherenes, Boranes, 3D-Boron Allotropes and Boron-Rich Solids.

**Naiwrit Karmodak and Eluvathingal D. Jemmis**

*Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-  
560012, India*

**Abstract:** Structural complexity is the hall mark of the chemistry of boron. Recently observed 2D Boron monolayers (borophenes) is no exception.<sup>[1,2]</sup> These are shown to have differing number of hexagonal holes.<sup>[3]</sup> An electron counting strategy shows the inevitability of hexagonal holes in borophene.<sup>[4]</sup> The number (hole density, HD) and distribution of hexagonal holes decide the binding energy per boron in the monolayer borophenes. The relationship between binding energy and the HD changes dramatically when the borophene is on Ag (111) surface. The requirement of holes in borospherenes (boron fullerenes) follow from these.<sup>[5]</sup> The HD and distribution of holes echo the distribution of the vacancies and extra occupancies in the complex  $\beta$ -rhombohedral boron.<sup>[6]</sup> The presentation will attempt to bring inter-relationship among boranes, borospherenes, borophenes and beta-rhombohedral boron.

### References:

- [1] A. J. Mannix, et al., *Science* **350**, 1513 (2015).
- [2] (a) B. Feng, et al., *Nat Chem* **8**, 563 (2016). (b) Z. Qing, et al., *J. Phys. Condens. Matter* **29**, 095002 (2017).
- [3] (a) H. Tang and S. Ismail-Beigi, *Phys. Rev. Lett.* **99**, 115501 (2007). (b) X. Wu, J. Dai, Y. Zhao, Z. Zhuo, J. Yang, and X. C. Zeng, *ACS Nano* **6**, 7443 (2012).
- [4] N. Karmodak and E. D. Jemmis, *Angew. Chem., Int. Ed.*, (2017). DOI: 10.1002/anie.201610584.
- [5] (a) H.-J. Zhai, et al., *Nat Chem* **6**, 727 (2014). (b) N. Karmodak and E. D. Jemmis, *Chemistry–An Asian Journal* **11**, 3350 (2016).
- [6] (a) E. D. Jemmis and M. M. Balakrishnarajan, *J. Am. Chem. Soc.* **123**, 4324 (2001). (b) E. D. Jemmis and D. L. Prasad, *J. Solid State Chem.* **179**, 2768 (2006). (c) Q. An, K. M. Reddy, K. Y. Xie, K. J. Hemker, and W. A. Goddard, *Phys. Rev. Lett.* **117**, 085501 (2016). (d) N. Karmodak and E. D. Jemmis, *Phys. Rev. B* **95**, 165128 (2017).



## On the accuracy of Coupled-Cluster-type methods describing excited states

**Péter G. Szalay<sup>1</sup>, Attila Tajti<sup>1</sup>, Balázs Partos<sup>1</sup>, Devin A. Matthews<sup>2</sup>,  
John F. Stanton<sup>3</sup>**

<sup>1</sup>*ELTE Eötvös Loránd University, Budapest, Hungary*

<sup>2</sup>*University of Texas at Austin, Austin, USA*

<sup>3</sup>*University of Florida, Gainesville, Florida, USA*

There are a large number of benchmark papers which investigate the performance of excited state methods by comparing vertical excitation energies to reference values. The reference values are taken from various sources, with their quality depending on the size of the molecule. Often, these tests concentrate on valence states only and do not include basis functions which are necessary to describe Rydberg states, which can bias the conclusions.

The fundamental question, however, is, whether tests including just excitation energies provide enough information on accuracy. In applications, one often considers the (full or local) potential energy surface or properties obtained from it. For example, to compare the excitation spectrum with experimental observation, vibrational effects need to be included in the simulation in even the simplest cases. Even more obvious is the need for the potential energy surface if one is interested in the processes taking place after the excitation. The accuracy of vertical excitation energies alone does not give reliable information about the quality of the associated potential energy surface. Thus, in order to investigate the performance of various methods on excited state surfaces, benchmarks need to go beyond the comparison of vertical excitation energies.

In this contribution, we will extend the scope of excited state benchmark calculations to include the above aspects. First, we present a most systematic survey of vertical excitation energies, where we a) use high level (single) reference values including iterative triple excitations; b) include and separately discuss valence and Rydberg states; and c) discuss the behavior of the results with molecular size, bonding patterns, excitation type, etc. Second, we report benchmark results on quantities which represent the quality of the excited state surfaces like equilibrium geometries, Franck-Condon forces, and shape of the steepest decent curves.

The methods we compare represent approximations, as well as extensions with respect to the “standard” CCSD level (EOM-CCSD). In the first category we include popular methods like CIS(D), CC2-LR, ADC(2), and other, less often used rigorous second order methods (EOM-CCSD(2) or PEOM-MBPT(2)). As for the latter methods, we include both iterative (CC3-LR, EOM-CCSDT-3) and non-iterative (EOM-CCSD(T), EOM-CCSD( $\tilde{T}$ ), CCSD(T)(a)\*, CCSDR3-LR) variants.

The general conclusion is that these methods perform very differently for the various properties. Although one can obtain good results with second order methods – in particular for the vertical excitation energies of valence states – there are only certain triples methods which can be trusted in general.

## Recent Developments in Random Phase Approximation Methods

**Filipp Furche, Vamsee K. Voora, Sree Ganesh Balasubramani, Guo P. Chen,  
Matthew M. Agee, Mikko J. Muuronen**

*University of California, Irvine, Department of Chemistry, 1102 Natural Sciences II, Irvine,  
CA 92697-2025, USA*

Random phase approximation (RPA) methods for computing the ground-state correlation energy of many-electron systems have evolved from a semi-analytical technique for model Hamiltonians to a powerful tool for *ab initio* electronic structure calculations in chemistry and materials science [1]. I will review recent developments in four areas: (i) Accuracy and robustness of RPA methods, (ii) molecular properties, (iii) interpretation tools for electron correlation, (iv) efficient algorithms. Particular emphasis will be placed on a new orbital optimization scheme which dramatically reduces density driven error inherent in semi-local density functional calculations without requiring optimized effective potentials. The performance of RPA methods will be illustrated for a broad variety of systems, including small molecules, negative ions, transition states of organic reaction mechanisms, small-gap *d*- and *f*-element compounds, and weakly bound complexes. I will close with a comparison of RPA methods to other electronic structure methods such as semi-local density functional theory, Green's function methods, and single-reference perturbation and coupled cluster theory.

This material is based upon work supported by the National Science Foundation under CHE-1464828.

- [1] G. P. Chen, V. K. Voora, M. M. Agee, S. Ganesh Balasubramani, F. Furche, *Annu. Rev. Phys. Chem.* **68**, 421–445 (2017).

## Vertical Excitation Energies from the Adiabatic Connection.

**Axel D. Becke**

*Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada*

We have recently suggested [1] a simple time-independent approach to the computation of vertical excitation energies through the "adiabatic connection" of Kohn-Sham density-functional theory. In tests on accurate reference data of the TBE-2 organic chromophore set of Thiel and coworkers, the method matches time-dependent B3LYP in quality. Latest developments, and future technical challenges, will be discussed.

- [1] A.D. Becke, *J. Chem. Phys.* **145**, 194107 (2016).

## Reliable DFT results with density correction

Eunji Sim<sup>1</sup>

<sup>1</sup> Department of Chemistry, Yonsei University, Seoul 03722, Korea

E-mail: esim@yonsei.ac.kr

There remain challenges where density functional theory (DFT) suffers from the self-interaction error. We show that the energy error of any variational density functional calculation can be decomposed into errors contributed from the approximate functional and that from the self-consistent Kohn-Sham density [1]. In vast majority of DFT calculations, the functional error dominates; however, we have found several abnormal cases where the density-driven error dominates. In particular, any self-interaction error can be decomposed this way and some of them turned out to be density-driven. We suggest a simple cure for these abnormal calculations, density corrected density functional theory (DC-DFT). DC-DFT is a non-variational DFT which uses more accurate density than the self-consistent approximate density. One of the simplest ways to implement the method is to use the Hartree-Fock density, i.e., HF-DFT, which has been already known to give remarkably accurate results in some cases. We also found that a small HOMO-LUMO gap in DFT calculations leads to large density-driven errors and, thus, may be used as an indicator of abnormal calculations. We discuss examples including simple two electron atom energies [1], electron affinities of small molecules [2], dissociation curves [3], and preferred geometries of ions and radicals in solution [4], transition metal complexes, and more. In addition, the importance of being self-consistent in DFT is discussed.[5]

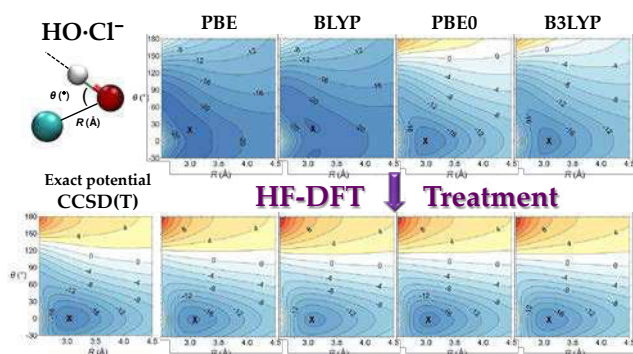


Fig. 1 Improvement using HF-DFT: Potential Energy Surface of HOCl-.

(top panel) self-consistent DFT results and (bottom panel) exact and HF-DFT results

- [1] M.-C. Kim, E. Sim, K. Burke, *Phys. Rev. Lett.* **111**, 073003 (2013).
- [2] M.-C. Kim, E. Sim, K. Burke, *J. Chem. Phys.* **134**, 171103 (2011).
- [3] M.-C. Kim, H. Park, S. Son, E. Sim, K. Burke, *J. Phys. Chem. Lett.* **6**, 3802 (2015).
- [4] M.-C. Kim, E. Sim, K. Burke, *J. Chem. Phys.* **140**, 18A528 (2014).
- [5] A. Wasserman, J. Nafziger, K. Jiang, M.-C. Kim, E. Sim, and K. Burke, *Annu. Rev. Phys. Chem.* **68**, 25 (2017).

## Density-functional methods with the accuracy and wide applicability of high-level multireference approaches

Andreas Görling<sup>1</sup>, Jannis Erhard<sup>1</sup>, Patrick Bleiziffer<sup>1</sup>, Egor Trushin<sup>1</sup>, Simon Kalass<sup>1</sup>

<sup>1</sup>*Lehrstuhl für Theoretische Chemie, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany*

Kohn-Sham (KS) methods based on the adiabatic-connection fluctuation-dissipation (ACFD) theorem can overcome limitations of conventional KS methods based on the local density or generalized gradient approximations. Most ACFD approaches invoke the random phase approximation, i.e., take into account only the Hartree kernel in the construction of the required response functions via time-dependent density-functional theory. Recently, ACFD methods were introduced that consider the exchange kernel in addition to the Hartree kernel. [1, 2] Here in a further step a power series approximation for the correlation kernel of time-dependent density-functional theory is presented. [3] Using this approximation in the ACFD theorem leads to a new family of KS methods. The new methods yield reaction energies of molecules with an unprecedented accuracy equaling that of coupled-cluster methods. Moreover, the new methods enable a treatment of static (strong) correlation with an accuracy of high-level multireference configuration interaction methods but are single-reference methods allowing for a black-box-like handling of static correlation. The new methods exhibit a better scaling of the computational effort with the system size than rivaling wave-function-based electronic structure methods. Furthermore, the new methods do not suffer from the problem of singularities in the response functions plaguing previous ACFD methods [4] and therefore are applicable to any type of electronic system, ranging from dissociating molecules to the homogeneous electron gas.

- [1] P. Bleiziffer, A. Heßelmann, A. Görling, *J. Chem. Phys.* **136**, 134102 (2012).
- [2] P. Bleiziffer, M. Krug, A. Görling, *J. Chem. Phys.* **142**, 244108 (2015).
- [3] J. Erhard, P. Bleiziffer, A. Görling, *Phys. Rev. Lett.* **117**, 143002 (2016).
- [4] P. Bleiziffer, D. Schmidt, A. Görling, *J. Chem. Phys.* **141**, 204107 (2014).

## Variational Principle for Partitioning Molecules into Atomic Contributions

**Paul W. Ayers<sup>1</sup> and Farnaz Heidar-Zadeh<sup>1</sup>**

*<sup>1</sup>Department of Chemistry & Chemical Biology; 1280 Main Street West; Hamilton, Ontario, Canada L8S 4M1*

The “stockholder” atomic partitioning proposed by Hirshfeld divides molecules into atom-in-molecule (AIM) pieces that maximally resemble reference atoms, which are traditionally determined in an *ad hoc* fashion. However, the *best atomic reference state* can be determined variationally. This variational Hirshfeld approach has desirable mathematical properties, is computationally robust, and gives results that agree with chemical intuition. In this talk, the chemical philosophy and mathematical framework of variational Hirshfeld partitioning will be presented, along with the results of computational tests.

Unlike other competing methods that require significant “design choices” and parameterization, the variational Hirshfeld method is so conceptually and mathematically simple it can be completely described in a single sentence: minimize the sum of the extended Kullback-Leibler divergences between the densities of the AIMs and the reference proatoms with respect to the AIM densities and the parameters that define the proatoms, subject to the constraint that the sum of the AIMs’ densities is equal to the molecular density. (The proatom densities are a weighted average of the spherically-averaged electron densities of the isolated atoms and ions, possibly including low-lying excited states.) Any change to this simple protocol impairs the method. E.g., changing the definition of the proatom densities results in a nonconvex optimization that is difficult to perform; changing the extended Kullback-Leibler divergence for a different choice leads to methods that are not size-consistent.

## **Oligosilanes: Intuitive Understanding of $\sigma$ Delocalization in Loose and Localization in Tight Helical Conformations**

**Milena Jovanovic<sup>1,2</sup>, Josef Michl<sup>1,2</sup>**

<sup>1</sup>*Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309, United States*

<sup>2</sup>*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, 16610 Prague 6, Czech Republic*

Conformational effects on  $\sigma$ -electron delocalization in permethylated uniformly helical linear oligosilanes (all- $\omega$ -Si<sub>*n*</sub>R<sub>2*n*+2</sub>) are addressed by Hartree-Fock and time-dependent density functional theory for backbone dihedral angles  $\omega = 55 - 180^\circ$ . The extent of  $\sigma$  delocalization is judged by the partition ratio of the highest occupied molecular orbital and is reflected in the dependence of its shape and energy and of UV absorption spectra on *n*. The results reveal a transition at  $\omega = \sim 90^\circ$  from the " $\sigma$ -delocalized" limit at  $\omega = 180^\circ$  toward and close to the physically non-realizable " $\sigma$ -localized" tight-helix limit  $\omega = 0$ . The distinction is also obtained in the Hückel Ladder H and C models of  $\sigma$  delocalization. An easy intuitive way to understand the origin of the two contrasting limits is to first view the linear chain as two subchains with alternating primary and vicinal interactions ( $\sigma$ -hyperconjugation), one consisting of the odd and the other of the even  $\sigma(\text{SiSi})$  bonds, and then allow the two subchains to interact by geminal interactions ( $\sigma$  conjugation).

# Aspects of Chemical Bonding

Gernot Frenking

*Fachbereich Chemie der Philipps-Universität, Hans-Meerwein-Strasse, D-35043 Marburg,  
Germany*

The lecture discusses the electronic structure of molecules which feature bonds that may be discussed in terms of dative bonding, covalent bonding and ionic bonding.



## Are one-electron bonds any different from standard two-electrons covalent bonds?

David Willian Oliveira de Sousa, Marco Antonio Chaer Nascimento

*Instituto de Química, Universidade Federal do Rio de Janeiro, Cidade Universitária, CT Bloco A  
Sala 41, Rio de Janeiro, RJ 21941-909, Brazil*

The nature of the chemical bond is perhaps the central subject in theoretical chemistry. Our understanding of the behavior of molecules developed amazingly in the last century, mostly with the rise of quantum mechanics (QM) and with QM-based theories such as valence bond and molecular orbital. Such theories are very successful in describing molecular properties, but they are not able to explain the origin of the chemical bond. This problem was first addressed by Ruedenberg [1], who showed that covalent bonds result from quantum interference between one-electron states. The generality of this result and its quantification for a large variety of molecules was made possible through the recent development of the Generalized Product Function Energy Partitioning method (GPF-EP) [2], which allows the partition of the electronic density and energy in their interference and quasi-classical (non-interference) contributions for each bond of a molecule, separately. This Interference Energy Analysis (IEA) has been applied to a large variety of molecules with single, double and triple bonds, with different degrees of polarity, linear or branched, cyclic or not, conjugated and aromatics, to verify the role played by quantum interference. In all cases, the conclusion was **exactly the same**: for each bond of the molecules considered the main contribution to its stability comes from the interference term.

One-electron two-center (2c1e) bonds are the simplest kind of chemical bonds. Yet they are often viewed as odd or unconventional cases of bonding. **But, are they any different from the conventional (2c2e) bonds?** If so, what differences can we expect on the nature of (2c1e) relative to electron-pair bonds? In this talk we present the extension of the GPF-EP method [3] to describe bonds involving  $N$  electrons in  $M$  orbitals ( $N < M$ ), show its application to several (2c1e) bonds and compare the results with the respective analogous molecules exhibiting the “conventional” two-electron bond. For all cases the GPF results show that interference is the dominant effect for the one-electron bonds and, therefore, (2c1e) bonds should not be considered as special, since they also result from quantum interference. These results together with the ones already obtained for (2c,2e) bonds normally classified as pure covalent, polar or ionic, clearly indicate that there is no conceptual difference among them and that quantum interference provides a way for the unification of the chemical bond concept (CNPq, FAPERJ, CAPES).

[1] Ruedenberg, K. *Rev. Mod. Phys.* **1962**, 34 (2), 326–376.

[2] Cardozo, T. M.; Nascimento, M. A. C. *J. Chem. Phys.* **2009**, 130 (10), 104102; *ibid.*, *J. Phys. Chem. A* **2009**, 113 (45), 12541–12548; Cardozo, T. M.; Nascimento Freitas, G.; Nascimento, M. A. C. *J. Phys. Chem. A* **2010**, 114 (33), 8798–8805; Fantuzzi, F.; Cardozo, T. M.; Nascimento, M. A. C. *Phys. Chem. Chem. Phys.* **2012**, 14 (16), 5479–5488; Vieira, F. S.; Fantuzzi, F.; Cardozo, T. M.; Nascimento, M. A. C. *J. Phys. Chem. A* **2013**, 117 (19), 4025–4034; Cardozo, T. M.; Fantuzzi, F.; Nascimento, M. A. C. *Phys. Chem. Chem. Phys.* **2014**, 11024–11030; Fantuzzi, F.; Nascimento, M. A. C. *J. Chem. Theory Comput.* **2014**, 10 (6), 2322–2332; Fantuzzi, F.; Cardozo, T. M.; Nascimento, M. A. C. *J. Phys. Chem. A* **2015**, 119 (21), 5335–5343; Sousa, D. W. O. de; Nascimento, M. A. C. *J. Chem. Theory Comput.* **2016**, 12 (5), 2234–2241; Fantuzzi, F.; Cardozo, T. M.; Nascimento, M. A. C. *ChemPhysChem* **2016**, 17 (2), 288–295; Fantuzzi, F.; de Sousa, D. W. O.; Chaer Nascimento, M. A. *Comput. Theor. Chem.* **2017** (in press); Fantuzzi, F.; Nascimento, M. A. C. *Phys. Chem. Chem. Phys.* (submitted). **2017**; Nascimento, *J. Braz. Chem. Soc.* **2008**, 19 (2), 245–256.

[3] Sousa, D. W. O. de, M.Sc. Thesis (Instituto de Química da UFRJ, Brazil, 2016)

**A new model for reference densities - really getting rid of interactions**  
**Julia Contreras-García<sup>1,2</sup>, C. Lefebvre<sup>3</sup>, H. Khartabil<sup>3</sup>, J-C. Boisson<sup>4</sup>, E. Hénon<sup>3</sup>**

<sup>1</sup> *Sorbonnes Universités, UPMC Univ. Paris 06, UMR CNRS 7616, Laboratoire de Chimie Théorique, Paris, France*

<sup>2</sup> *CNRS UMR 7616 Laboratoire de Chimie Théorique, Paris, France*

<sup>3</sup> *ICMR UMR CNRS 7312, URCA, Moulin de la Housse, Reims, France*

<sup>4</sup> *CReSTIC EA 3804, URCA, Moulin de la Housse, Reims, France*

Constructing reference densities has always been a central topic to understanding interactions. Within crystallographic analysis, it has been quite common to compare the final electron density to the sum of spherically averaged atomic densities. However, it is well known, that this density (also known as promolecular density) already contains a lot of interaction information. For example, the promolecular density already shows critical points which are similar in nature and properties to the ones of the final system [1].

First, we will show a new reference model, the independent gradient model (IGM), where electron densities are summed up, just like in the promolecular approach, but the gradients are not allowed to interfere thanks to the use of absolute values within non interacting regions/atoms [2]. In a second part, we will show that this model can also be developed for relaxed densities which are thus not a mere sum of atomic densities. And still a proper atomic partition can be proposed for gradient based indexes. In other words, partitions based on the gradient (such as Atoms in Molecules) can find an atomic partition with no interactions if the separation is focused on the gradient and not the density itself.

This new model provides a better reference for analyses based on density gradients, such as Atoms in Molecules or the Non-Covalent Interaction index. This new model provides an extremely good reference for obtaining intermolecular properties and defining in an objective manner interacting fragments, which always becomes a hassle in energetic partitions.

[1] Z. Alimohammadi Keyvani, S. Shahbazian, M. Zahedi, *Chem. Eur. J.* **22**, 5003 (2016)

[2] C. Lefebvre, G. Rubez, H. Khartabil, J.-C. Boisson, J. Contreras-García, E. Hénon (submitted)

**Insight into hydrogen-bonded clusters and noncovalent interactions from changes in atomic energies****Russell J. Boyd***Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada*

This presentation will focus on the analysis of internal stabilization of molecular complexes in terms of Bader's atomic energies, which are uniquely defined by zero-flux surfaces of the electron density distribution. The analysis will be shown to lead to insight into cooperative and anticooperative effects in a variety of systems including small water clusters, water wires and guanine complexes formed from a single-stranded telomere sequence. The extension to beryllium bonds, and other types of noncovalent interactions, will be briefly discussed.

## A Fully Polarizable Embedding Model for Molecular Spectroscopy of Aqueous Solutions

Chiara Cappelli<sup>1</sup>

<sup>1</sup>*Scuola Normale Superiore, Piazza dei Cavalieri, 7 I-56126 Pisa, Italy*

The computational modeling of molecular spectra of aqueous solutions is particularly challenging. In fact, it requires at the same time an accurate modeling of the response of the solute to the external radiation field and a reliable account of the effects of the surrounding environment, which can hugely modify the solute's spectral features as a result of specific/directional interactions [1].

A recently developed Quantum-Mechanical (QM)/polarizable molecular mechanics (MM)/polarizable continuum model (PCM) [2] embedding approach has shown extraordinary capabilities, yielding calculated spectra in excellent agreement with experiments.

An overview of the theoretical fundamentals of this methods, which combines a fluctuating charge (FQ) approach to the MM polarization with the PCM is given, and specific issues related to the calculation of spectral responses [3] are discussed in the context of selected applications [4].

[1] F. Egidi, C. Cappelli "Elsevier Reference Module in Chemistry, Molecular Sciences and Chemical Engineering", DOI:10.1016/B978-0-12-409547-2.10881-9 (2015).

[2] C. Cappelli, *Int. J. Quantum Chem.* **116**, 1532 (2016).

[3] (a) F. Lipparini, C. Cappelli, V. Barone, *J. Chem. Theory Comput.*, **8**, 4153 (2012); (b) F. Lipparini, C. Cappelli, N. De Mitri, G. Scalmani, V. Barone, *J. Chem. Theory Comput.* **8**, 4270 (2012); (c) F. Lipparini, C. Cappelli, V. Barone, *J. Chem. Phys.* **138**, 234108 (2013); (d) M. Caricato, F. Lipparini, G. Scalmani, C. Cappelli, V. Barone *J. Chem. Theory Comput.* **9**, 3035 (2013); (e) I. Carnimeo, C. Cappelli, V. Barone, *J. Comput. Chem.* **36**, 2271 (2015).

[4] (a) F. Lipparini, F. Egidi, C. Cappelli, V. Barone, *J. Chem. Theory Comput.* **9**, 1880 (2013); (b) F. Egidi, I. Carnimeo, C. Cappelli, *Opt. Mater. Express* **5**, 196 (2015); (c) F. Egidi, R. Russo, I. Carnimeo, A. D'Urso, G. Mancini, C. Cappelli, *J. Phys. Chem. A* **119**, 5396 (2015); (d) T. Giovannini, M. Olszowka, C. Cappelli, *J. Chem. Theory Comput.* **12**, 5483 (2016).

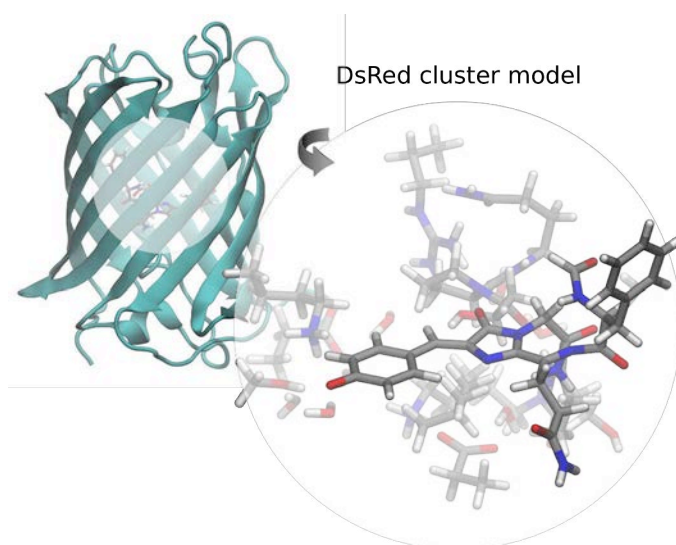
## Excited States in Complex Systems through Polarizable (Density) Embedding

**Jacob Kongsted**

*Department of Physics, Chemistry and Pharmacy  
University of Southern Denmark  
Campusvej 55, 5230 Odense M, Denmark  
kongsted@sdu.dk*

In this talk I will introduce and review the polarizable embedding (PE) and polarizable density embedding (PDE) methods [1,2,3,4,5]. These computational models have recently been developed with the aim of enabling calculations of excited states and general molecular response properties for large and complex systems. The PE/PDE models build on the concepts from mixed quantum mechanics / molecular mechanics (QM/MM) schemes. Thus they represent focused computational models in which different parts of a large molecular system are described using different levels of approximations. A key concept associated with the PE/PDE models is the introduction of quantum mechanical response theory in combination with polarizable force fields. This allows for calculation and simulation of excited states and general molecular properties, i.e. properties relevant for optical, magnetic and mixed optical-magnetic spectroscopies. We will discuss some recent applications of the PE/PDE models aimed at elucidating optical properties of heterogeneous molecular systems highlighting the general flexibility and accuracy of this computational model.

- [1] J.M. Olsen, K. Aidas, J. Kongsted, *JCTC*, **6**, 3721 (2010)
- [2] T. Schwabe, M.T.P. Beerepoot, J.M.H. Olsen, J. Kongsted, *PCCP*, **17**, 2582 (2015)
- [3] N.H. List, H.J.A. Jensen, J. Kongsted, *PCCP*, **18**, 10070 (2016)
- [4] J.M.H. Olsen, C. Steinmann, K. Ruud, J. Kongsted, *JPC A*, **119**, 5344 (2015)
- [5] N.H. List, J.M.H. Olsen, J. Kongsted, *PCCP*, **18**, 20234 (2016)



*A molecular representation of the DsRed fluorescent protein highlighting the chromophore responsible for the optical properties of this protein.*

## **Polarizable embedding and beyond: Modeling photoactive proteins with the Effective Fragment Potential method**

**Lyudmila V. Slipchenko<sup>1</sup>**

*<sup>1</sup>Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN 47906, USA*

Accurate description of solute-solvent interactions is a key for understanding photochemical processes in biological systems. The effective fragment potential (EFP) is a polarizable model providing rigorous description of non-covalent interactions from first principles. When coupled to a QM region, hybrid QM/EFP methods belong to polarizable embedding schemes. Recently, we extended the EFP method to modeling flexible macromolecules and polymers. Additionally, we expanded coupling between QM and EFP Hamiltonians to include short-range van der Waals terms – exchange-repulsion and dispersion. We apply the new scheme to analyze photoprocesses in photoactive and photosynthetic proteins. Specifically, we decompose effects of polarization, electrostatics, charge-penetration and short-range terms on electronic properties of pigments and demonstrate importance of a balanced description of solute-solvent interactions.

## **Multiscale embedding methods for accurate quantum chemistry of complex systems**

**Frederick R Manby<sup>1</sup>**

<sup>1</sup>*Centre for Computational Chemistry, School of Chemistry, University of Bristol, Bristol BS8 1TS, UK*

Predictive computational modelling of many chemical processes is often hampered not by the lack of methods for reliable calculation, but by the fact that the complexity and size of the problem makes such calculations prohibitively expensive to run. Three lines of research around the world target this issue, by: (1) improving the accuracy of such computationally efficient schemes; (2) improving the efficiency of accurate methods; (3) combining high-accuracy and low-cost methods in multiscale schemes. We have worked extensively in this last category, and here I will present some of our recent progress in this area, and discuss some of the pressing challenges that lie ahead.

# Exploitation of Solar Energy

Mikkelsen, Kurt V. <sup>A</sup>

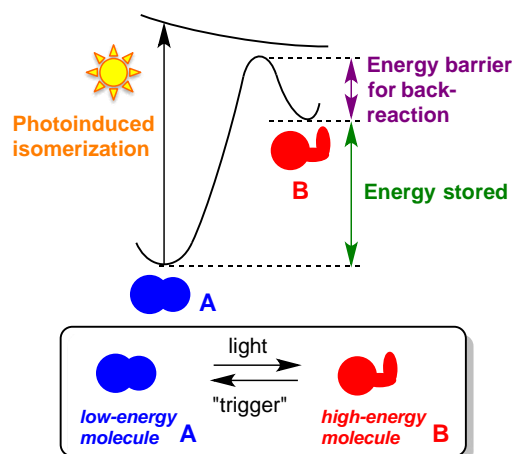
*A) Department of Chemistry, University of Copenhagen, Copenhagen, Denmark*

Contact: [kmi@chem.ku.dk](mailto:kmi@chem.ku.dk)

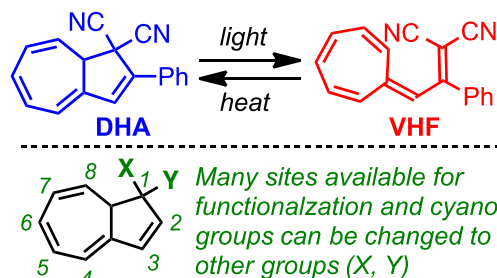
## Purpose of the Project

The Sun delivers within an hour to Earth an amount of energy similar to that consumed by all humans in one year. One major challenge for society is to be able to store solar energy. Our fundamental hypothesis is that we can store energy in chemical bonds via light-induced isomerization reactions of photoactive molecules as illustrated in Fig. 1. Upon irradiation, molecule A is converted to the high-energy photo-isomer B, which upon a certain trigger will return to A and release the absorbed energy as heat. This corresponds to a closed-energy cycle of light-harvesting, energy storage and release, with no emission of CO<sub>2</sub>. The overall purpose of this project is to develop suitable organic molecules for such cycles based on fundamental structure-property relationships (SPRs).

We will focus on the dihydroazulene (DHA) – vinylheptafulvene (VHF) couple (Fig. 2), being attractive as only the DHA to VHF reaction is photoinduced.



**Fig. 1:** Energy storage using



**Fig. 2:** DHA-VHF couple and numbering.

**KEYWORDS:** capture, storage



## **Visualizing the contributions of virtual states to two-photon absorption cross-sections: Natural transition orbitals of perturbed transition density**

**Anna I. Krylov and Kaushik D. Nanda**

*Department of Chemistry, University of Southern California, Los Angeles, CA 90089*

Observables such as two-photon absorption transition moments cannot be computed from the wave functions of the initial and final states alone because of their non-linear nature. Rather, they depend on the entire manifold of the excited states, follows from the familiar sum-over-state expressions of second- and higher-order properties. Consequently, the interpretation of the computed non-linear optical properties in terms of molecular orbitals is not straightforward and usually relies on approximate few-state models. Here, we show that the 2PA transitions can be visualized using perturbed one-particle transition density matrices, which are defined as transition density matrices between the zero-order and first-order perturbed states. We also extend the concept of natural transition orbitals to 2PA transitions. We illustrate the utility of this new tool, which provides a rigorous black-box alternative to traditional qualitative few-state analysis, by considering 2PA transitions in ethylene, trans-stilbene, and pNA.

## Two-Component Non-Collinear Time-Dependent Density Functional Theory for Electronic Dynamics and Excited State Calculations

Xiaosong Li

*Department of Chemistry, University of Washington  
Seattle, WA, USA 98195*

We present a real-time propagation method<sup>1</sup> as well as a linear response formalism<sup>2</sup> for the description of the electronic excitations of a non-collinear reference defined via Kohn-Sham spin density functional methods. A set of auxiliary variables, defined using the density and non-collinear magnetization density vector, allows the generalization of spin density functional kernels commonly used in collinear DFT to non-collinear cases, including local density, GGA, meta-GGA and hybrid functionals. Working equations and derivations of functional second derivatives with respect to the non-collinear density, required in the linear response non-collinear TDDFT formalism, are also presented in this work. This formalism takes all components of the spin magnetization into account independent of the type of reference state (open or closed shell). As a result, the method introduced here is able to afford a non-zero local  $xc$  torque on the spin magnetization, while still satisfying the zero-torque theorem globally. The formalism is applied to a few test cases using the variational exact-two-component (X2C) reference including spin-orbit coupling to illustrate the capabilities of the method. We also applied the real-time X2C-TDDFT method to several Group 12 atoms as well as heavy-element hydrides, comparing with the extensive theoretical and experimental studies on this system, which demonstrates the correctness of our approach.

- [1] J. J. Goings, J. Kasper, F. Egidi, S. Sun, X. Li, "Real Time Propagation of the Exact Two Component Time-Dependent Density Functional Theory," *J. Chem. Phys.*, 2016, *145*, 104107.
- [2] F. Egidi, S. Sun, J. J. Goings, G. Scalmani, M. J. Frisch, X. Li, "Two-Component Non-Collinear Time-Dependent Spin Density Functional Theory for Excited State Calculations," *J. Chem. Theory Comput.*, 2017, **DOI:** 10.1021/acs.jctc.7b00104

## **The Algebraic Diagrammatic Construction - a versatile approach to excited electronic states, ionization potentials and electron affinities**

**Andreas Dreuw**

*Interdisciplinary Center for Scientific Computing, Ruprecht-Karls University, Im  
Neuenheimer Feld 205, 69120 Heidelberg City, Germany*

The algebraic diagrammatic construction (ADC) scheme provides a series of ab initio methods for the calculation of excited, ionized or electron-attached states based on perturbation theory. In recent years, the second-order ADC(2) scheme has attracted attention in the computational chemistry community due to its reliable accuracy and reasonable computational effort in the calculation of predominantly singly-excited states. Owing to their size-consistency, ADC methods are suited for the investigation of large molecules. Their Hermitian structure in combination with the availability of the intermediate state representation (ISR) allows for straightforward computation of excited state properties.

In this talk, I will summarize our recent developments in the framework of ADC, which have all been implemented within the `adcmann` module as part of the Q-Chem program package. These developments comprise ADC(3) for direct computation of excitation energies, ionization potentials and electron affinities of closed and open-shell molecules. The excitation ADC methods have also been adapted to exploit the spin-flip idea to study also ground-state multi-reference molecules, bond-breaking and conical intersections. For the treatment of core-excited states, the core-valence separation (CVS) approximation has also been applied to ADC making efficient CVS-ADC(2) and CVS-ADC(3) programs available. Nuclear excited state gradients are now also available at ADC(2) and ADC(3) level of theory. Environment models like polarizable continuum models and frozen-density embedding have also recently been realized. In addition to the calculation of excited state energies and properties, also an extensive set of density analysis tools are available ranging from standard population analysis tools up to advanced transition density matrix analyses.

## Theoretical Studies of the Interaction of Uracil with Low Energy Electrons

Spiridoula Matsika, Mark A. Fennimore, Tolga N. V. Karsili

Department of Chemistry, Temple University, 1901 N.13th Street, Philadelphia, PA, USA

Ionizing radiation in cells generates secondary low energy electrons (LEE) which can induce biomolecular damage when incident upon a particular biomolecule. Notable biomolecules include those contained within double-stranded DNA and RNA helices, which upon exposure to LEE, may form reactive intermediate products that show detriment to their specific structures and functions. Such damaging processes are understood to proceed via dissociative electron attachment (DEA). Attachment of an electron to nucleobases leads to metastable anion states, resonances, which require special treatment of their electronic structure. Using anion resonance stabilization methods, coupled to state-of-the-art electronic structure methods (coupled cluster theory and multireference perturbation theory) we have investigated shape and Feshbach resonances in uracil, and the role they play in DEA [1, 2]. Non-adiabatic effects and conical intersections were found to play a key role in DEA.

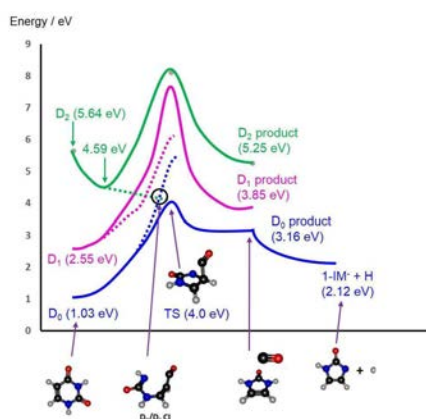


Figure 1: Schematic representation of the overall reaction paths showing the sequential elimination of CO and H from uracil<sup>-</sup> when LEE with energies around 5-6 eV attach to uracil.

- [1] Mark A. Fennimore and Spiridoula Matsika, *Phys. Chem. Chem. Phys.*, **18**, 30536 - 30545, (2016)
- [2] Mark A. Fennimore, Tolga N. V. Karsili, and Spiridoula Matsika, *Phys. Chem. Chem. Phys.*, submitted, (2017)

## First-Principles Exciton Models, with Application to Singlet Fission

John M. Herbert<sup>1</sup>, Adrian F. Morrison<sup>1</sup>

<sup>1</sup>*Department of Chemistry and Biochemistry, The Ohio State University, 100 W. 18th Ave., Columbus, OH, USA*

We have developed a variety of reduced-cost, highly parallelizable electronic structure models for describing collective excitations in molecular liquids, crystals, and aggregates [1, 2, 3, 4]. Some of these represent low-cost approximations to the Casida equations in time-dependent density functional theory [3, 4], while another represents an *ab initio* implementation of the Frenkel-Davydov *ansatz* [1, 2], in which a collective excitation is expanded in a direct-product basis of monomer excitations. The monomer wave functions and the couplings between them can be computed in a trivially-parallelizable fashion, and calculations equivalent to more than 55,000 basis functions have been performed in a few days on only a few hundred processors [2]. Basis functions involving intramolecular electron transfer can be included, such that in the context of singlet fission the model can be used to understand the role (if any) of charge-transfer excitons [5]. Analytic derivative couplings have recently been derived and implemented for this *ab initio* Frenkel-Davydov model [6], and can be used to identify the vibrational modes that promote intermolecular energy transfer. The derivative couplings are equivalent to exciton/phonon couplings that appear as parameters in vibronic model Hamiltonians of the “Holstein-Peierls” type, and we have parameterized such a model to describe the singlet fission process in crystalline tetracene [5, 6]. Dissipative quantum dynamics simulations using this Hamiltonian demonstrate that vibronic coherence can explain why singlet fission is fast in efficient in tetracene, despite ostensibly unfavorable electronic energetics [5]. Triplet exciton mobility parameters have also been computed from first principles [6].

- [1] A. F. Morrison, Z.-Q. You, and J. M. Herbert, *J. Chem. Theory Comput.* **10**, 5366 (2014).
- [2] A. F. Morrison and J. M. Herbert, *J. Phys. Chem. Lett.* **6**, 4390 (2015).
- [3] J. Liu and J. M. Herbert, *J. Chem. Phys.* **143**, 034106 (2015).
- [4] J. Liu and J. M. Herbert, *J. Chem. Theory Comput.* **12**, 157 (2016).
- [5] A. F. Morrison and J. M. Herbert, *J. Phys. Chem. Lett.* **8**, 1442 (2017).
- [6] A. F. Morrison and J. M. Herbert, *J. Chem. Phys.* (in press).

**Quantitative Molecular Orbital Theory**

**Rodney J. Bartlett<sup>1</sup>, Duminda Ranasinghe<sup>2</sup>, Youngchoon Park<sup>3</sup>, Prahash Verma<sup>4</sup>, Yifan Jin<sup>5</sup>,  
Ajith Perera<sup>5</sup>**

*<sup>1-5</sup>Quantum Theory Project, University of Florida, PO Box 118435, Gainesville, FL 32611*

This talk addresses our efforts toward an exact correlated orbital theory. One component of such an approach is to enforce an ionization theorem for each orbital in a Kohn-Sham theory as an exact condition. This enables a minimally parameterized KS-DFT method that works very well for core ionization and core excitation problems. Further considerations provide solutions for charge-transfer excitations and demonstrate that the IP-condition also ameliorates the self-interaction error in KS-DFT.

This work is sponsored by the US AFOSR and the HASI Program of the DoD High Performance Computer Modernization Program.

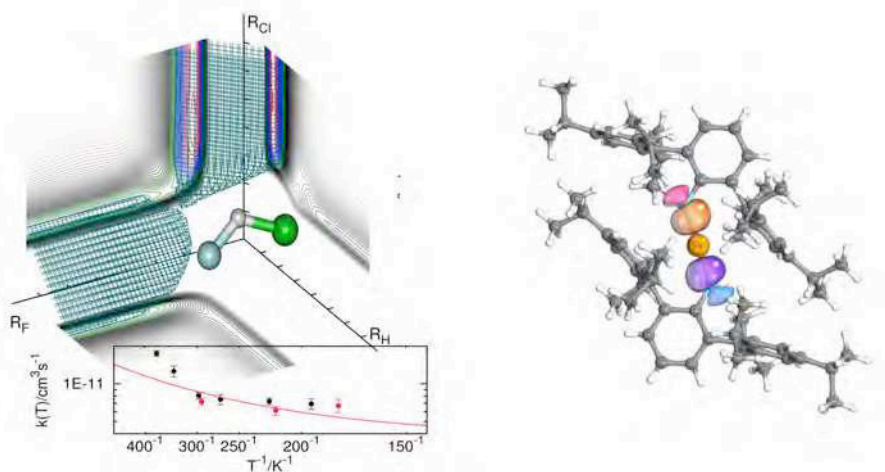
## Applications of internally contracted multireference coupled-cluster theory

Andreas Köhn

*Institut für Theoretische Chemie, Universität Stuttgart,  
Pfaffenwaldring 55, D-70569 Stuttgart, Germany*

Internally contracted multireference coupled-cluster (icMRCC) theory holds the promise to extend the high accuracy of single-reference coupled-cluster methods, in particular that of CCSD(T), to systems with strong correlation and complex open-shell electronic structure [1]. Of course, this promise needs to be underpinned by applications to real problems!

In this contribution, I will show how icMRCC computations can be used for high accuracy computations, either as stand-alone method or as a supplement to standard coupled-cluster approaches [2]. The prospect for more efficient variants of the method and for its use in embedding approaches will also be discussed.



[1] Originally proposed by: A. Banerjee, J. Simons, *Int. J. Quantum Chem.* **19**, 207 (1981); *J. Chem. Phys.* **76**, 4548 (1982); Newer work: M. Hanauer, A. Köhn, *J. Chem. Phys.* **134**, 204111; F. A. Evangelista, M. Hanauer, A. Köhn, J. Gauss, *J. Chem. Phys.* **136**, 204108 (2012); M. Hanauer, A. Köhn, *J. Chem. Phys.* **136**, 204107 (2012); W. Liu, M. Hanauer, A. Köhn, *Chem. Phys. Lett* **565**, 122 (2013); Y. A. Aoto, A. Köhn, *J. Chem. Phys.* **144**, 074103 (2016)

[2] Y. A. Aoto, A. Köhn, *Phys. Chem. Chem. Phys.* **18**, 30241-30253 (2016); T. Lamberts, P.K. Samanta, A. Köhn, J. Kästner, *Phys. Chem. Chem. Phys.* **18**, 33021-33030 (2016)

## Advances in Electronic Structure Methods for Strongly Correlated Systems and Condensed Phase Systems

Shuhua Li

<sup>1</sup>*School of Chemistry and Chemical Engineering, Institute of Theoretical and Computational Chemistry, Nanjing University, Nanjing, 210023, P. R. China*

**Abstract:** In this talk, I will report our recent advances in developing electronic structure methods for strongly correlated systems, large molecules and condensed phase systems. For strongly correlated systems, we have developed two new electronic structure methods: block-correlated second-order perturbation theory with the GVB reference (GVB-BCPT2) and a hybrid approach by combining GVB-BCPT2 with a variational method such as the CASCI or DMRG method.<sup>1,2</sup> In the hybrid method, the inter-block correlation within the active space is described variationally, while the remaining inter-block correlation is treated by the GVB-BCPT2 approach. The GVB-BCPT2 approach can provide reasonably accurate descriptions for simultaneous dissociations of many single bonds in some systems, while the hybrid one can provide comparable results with CASPT2 for multi-bond dissociation processes, which are much better than the GVB-BCPT2 results. The hybrid method can be used to treat strongly correlated systems with large active spaces, which are beyond the capability of CASPT2. For large molecules, we have further improved the generalized energy-based fragmentation (GEBF) approach.<sup>3,4</sup> This approach has been employed to obtain accurate relative energies of different conformers, optimized structures, vibrational spectra, and NMR properties for many complex systems of chemical interest.<sup>4-6</sup> We have also extended the GEBF approach to molecular crystals with periodic boundary conditions.<sup>7</sup> The energy derivatives of the PBC-GEBF approach for geometry optimizations<sup>7</sup> and vibrational frequencies of molecular crystals<sup>8</sup> have been implemented. Illustrative applications demonstrate that the PBC-GEBF method with advanced electron correlation methods is capable of providing accurate descriptions on the lattice energies, structures, and vibrational spectra for various types of molecular or ionic liquid crystals.<sup>8</sup>

- [1] Xu E.; Li S. *J. Chem. Phys.* **139**, 17411 (2013).
- [2] Xu E.; Zhao D; Li S. *J. Chem. Theory Comput.* **11**, 4634 (2015).
- [3] W. Li, S. Li, Y. Jiang *J. Phys. Chem. A* **111**, 2193 (2007).
- [4] Li S.; Li W.; Ma J. *Acc. Chem. Res.* **47**, 2712 (2014).
- [5] Yuan D.; Shen X.; Li W.; Li S. *Phys. Chem. Chem. Phys.* **18**, 16491 (2016).
- [6] Yuan D. *et al.* *J. Chem. Theory Comput.* DOI: 10.1021/acs.jctc.7b00284 (2017).
- [7] Fang T.; Li W.; Gu F.; Li S. *J. Chem. Theory Comput.* **11**, 91 (2015).
- [8] Fang T.; Li Y.; Li S. *WIREs Comput. Mol. Sci.* **7**:e1297 (2017).



## DMRG-externally-corrected local pair natural orbital based coupled cluster method

**Libor Veis<sup>1</sup>, Ondřej Demel<sup>1</sup>, Andrej Antalík<sup>1</sup>, Jiří Brabec<sup>1</sup>, Örs Legeza<sup>2</sup>,  
Frank Neese<sup>3</sup>, Jiří Pittner<sup>1</sup>**

<sup>1</sup> *J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Dolejškova 3, 18223 Prague 8, Czech Republic*

<sup>2</sup> *Strongly Correlated Systems "Lendület" Research group, Wigner Research Centre for Physics, H-1525, Budapest, Hungary*

<sup>3</sup> *Max Planck Institut für Chemische Energiekonversion, Stiftstr. 34-36, D-45470 Mülheim an der Ruhr, Germany*

In the last decade, the quantum chemical version of the density matrix renormalization group (DMRG) method has established itself as the method of choice for calculations of strongly correlated molecular systems. Despite its favourable scaling, it is in practice not suitable for computations of dynamic correlation. We present a new method for accurate "post-DMRG" treatment of dynamic correlation based on the tailored coupled cluster (CC) theory [2] in which the DMRG method is responsible for the proper description of non-dynamic correlation, whereas dynamic correlation is incorporated through the framework of the CC theory [3]. We illustrate the potential of this method on prominent multireference systems, in particular N<sub>2</sub> and Cr<sub>2</sub> molecules.

In order to overcome the computational scaling bottleneck of traditional CC methods, we have developed an implementation of the DMRG - tailored coupled cluster method based on the local pair natural orbital formalism (LPNO) [4]. LPNO-CC methods can recover 99.8% of the correlation energy at the same CC truncation level computed in canonical orbitals, at a dramatically reduced computational cost, also in the multireference context [5]. We illustrate the capabilities of our implementation on the oxo-Mn(Salen) molecule and phthalocyanine-iron complex, for which we have performed the first "post-DMRG" computations in order to shed light on the energy ordering of the lowest spin states.

- [1] White S. R., *Phys. Rev. Lett.* **69**, 2863 (1992).
- [2] Kinoshita T., Hino O., Bartlett R. J., *J. Chem. Phys.* **123**, 074106 (2005).
- [3] Veis L., Antalík A., Brabec J., Neese F., Legeza Ö, Pittner J., *J. Phys. Chem. Lett.* **7**, 4072 (2016).
- [4] Riplinger C., Neese F, *J. Chem. Phys.* **138**, 034106, (2013).
- [5] Demel O., Pittner J., Neese F, *J. Chem. Theor. Comp.* **11**, 3104 (2015).

## Tensor decomposition and coupled cluster theory

**Ove Christiansen<sup>1</sup>, Ian H. Godtlielsen<sup>1</sup>, Niels K. Madsen<sup>1</sup>, Gunnar Schmitz<sup>1</sup>,  
Mads Bøttger Hansen<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, Aarhus University, Denmark*

Wave functions in quantum chemistry employs a particular format and an associated number of parameters. Often these parameters can be seen as sets of multiway arrays, tensors. In this talk I will discuss tensor decomposition of wave function parameters.

The primary example will be vibrational coupled cluster (VCC) theory. Vibrational coupled cluster theory is concerned with calculation of anharmonic vibrational wave functions for molecules. Here the construction of a cost-efficient wave-function parameterization is important for accuracy and wide applicability. I will discuss challenges and new work aimed at developing efficient implementations for systems with many atoms integrating tensor decomposition. Both the non-linear ground state coupled cluster equations and the eigenvalue equations of coupled cluster response theory can be solved using iterative methods giving directly result vectors in stacked tensorial form. [1, 2, 3]

The canonical tensor decomposition (CP, Candecomp/Parafac) provides compression of data and a computational convenient representation, but also comes with some potential problematic features. Numerical results show that there is significant perspective in applying tensor decomposition in the context of anharmonic vibrational wave functions. It will be demonstrated that tensor decomposition opens for adjusting the computational effort spent on a particular coupling between modes according to the significance of that particular coupling.

The calculations illustrate how the multiplicative separability of the coupled cluster ansatz with respect to non-interacting degrees of freedom goes well together with a tensor decomposition approach. I will furthermore describe the opposite perspective: how the coupled cluster wave function can be understood as its own type of decomposition satisfying some separability conditions.

Finally I will discuss perspectives in extending these ideas to electronic wave functions, where the first problem is obtaining two-electron repulsion integral in decomposed format.[4]

- [1] I. H. Godtlielsen, B. Thomsen, and O. Christiansen *J. Phys. Chem. A*, **117**, 7267 (2013).
- [2] I. H. Godtlielsen, M. Bøttger Hansen, and O. Christiansen.  
*J. Chem. Phys.* **142**, 024105 (2015).
- [3] N. K. Madsen, I. H. Godtlielsen, and O. Christiansen *J. Chem. Phys.* **146**, 134110 (2017).
- [4] G. Schmitz, N.K. Madsen and O. Christiansen *J. Chem. Phys.* **146**, 134112 (2017).

## Nanosecond-Timescale Conformational Dynamics of Enzymes, and its Impact on Reaction Rates

Pedro Alexandrino Fernandes<sup>1</sup>

<sup>1</sup> UCIBIO@REQUIMTE/Faculty of Sciences, University of Porto, Rua do Campo Alegre, S/N 4169-007 Porto, Portugal; e-mail: pafernan@fc.up.pt

This talk will start by addressing the developments in several fields of computational proteomics and enzymology that are taking place within our group. The talk will then focus on the calculation of enzyme reaction mechanisms with QM/MM techniques [1-3], emphasizing the methodological aspects that, in our view, have the most impact in the predicted enzyme reaction mechanisms and respective energetics [4]. The role of enzyme flexibility on the activation free energies will be discussed as well, in the context of multiple geometry optimizations of large QM layers described with high theoretical levels. The influence of nanosecond and sub-nanosecond timescale conformational fluctuations on the reaction rate will be discussed in detail [5].

### Acknowledgments:

This work received financial support from the European Union (FEDER funds POCI/01/0145/FEDER/00 7728 and NORTE/01/0145/FEDER/000024) and National Funds (FCT/MEC, Fundação para a Ciência e Tecnologia and Ministério da Educação e Ciência) under the Partnership Agreement PT2020 UID/MULTI/04378/2013, and grants INCENTIVO/EQB/LA0006/2014.

- [1] R. P. P. Neves, P. A. Fernandes, M. J. Ramos, Mechanistic insights on the reduction of glutathione disulfide by protein disulfide isomerase, *PNAS*, in press.
- [2] A. Ribeiro, M. J. Ramos, P. A. Fernandes, *J. Am. Chem. Soc.*, **134**, 13436 (2012).
- [3] N. M. F. S. A. Cerqueira, P. Gonzalez; P. A. Fernandes, J. Moura, M. J. Ramos, *Acc. Chem. Res.*, **48**, 2875 (2015).
- [4] S. F. Sousa, A. J. M. Ribeiro, R. P. P. Neves, N. F. Brás, N. M. F. S. A. Cerqueira, P. A. Fernandes, M. J. Ramos, *WIREs Comput. Molec. Sci.*, doi: 10.1002/wcms.1281 (2016,)
- [5] A. Ribeiro, D. Santos-Martins, N. Russo, M. J. Ramos, P. A. Fernandes *ACS Cat.*, **5**, 5617 (2015).

## Computer simulations of chemical reactions in solution

*Jun Zhang<sup>1</sup>, Yi Qin Gao<sup>1,2\*</sup>*

<sup>1</sup>Institute of Theoretical and Computational Chemistry, College of Chemistry and Molecular Engineering, <sup>2</sup>BIOPIC, Peking University, Beijing 100871, China

\*Email: gaoyq@pku.edu.cn

### ABSTRACT

We developed a sampling strategy for rare events to generate chemical reaction trajectories using which a statistical investigation can be performed on the thermodynamics, kinetics, dynamics and mechanisms of the chemical reactions in solution. Free of predefined CVs or RCs, the post-analysis of reaction mechanisms can be performed. As an example, the reaction coordinate(s) of a (retro-)Claisen rearrangement in bulk water was variationally optimized based on a Bayesian learning algorithm as well as a machine learning method. It was found that the hydrogen-bonding of water molecule to the charge-enriched site of the reactant state changes the dynamics of reaction. A characteristic shrinkage of the solvent shell during the chemical transition was identified, suggesting a necessary energy transferring process during the thermal activated chemical reaction, reminiscent of the “cage-effect”. The transition path time of the reaction and the rate constants for the forward and backward reaction were calculated independent of RCs, and we were able to self-consistently connect the kinetics to the thermodynamics. The diffusion coefficient over the energy barrier was also determined according to Kramers’ theory, showing the limitation of canonical transition state theory in dealing with the condensed phase reactions.

## Simulating photo-excited dynamics of biological complexes: Overcoming present challenges with interpolated potentials

Young Min Rhee

*Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST),  
Daejeon 34141, Korea*

Photo-excited dynamics plays essential roles in many complex systems of biological importance. Yet, theoretically following the dynamics presents various challenges in terms of both cost and reliability. In this presentation, we will overview how these issues can be overcome with the use of interpolation technique for building the multi-state potential models of involved chromophore units. The technique, which is termed as interpolation mechanics / interpolation mechanics (IM/MM), indeed is a useful tool that achieves the reliability of more conventional QM/MM at the speed of molecular mechanics [1, 2]. With this technique, statistically meaningful analysis of dynamics can be performed, which may open doors to new discoveries. For demonstrations, we will see two branches of its applications: chromophore twisting dynamics in green fluorescent protein (GFP) [3] and exciton transfer dynamics of the photosynthetic Fenna-Matthews-Olson (FMO) complex. With GFP, we will see that steric congestion by the protein barrel is not an important factor contrary to commonly accepted belief. Rather, electrostatics is the key factor as advocated by some theoreticians in the past. With FMO, we will observe that the IM/MM potential provides reliable chromophore vibrations [4] and is useful toward elucidating the role of coupling between electronic and vibrational degrees of freedom. The presentation will be concluded with a clip of atom-detailed molecular movie that the IM/MM simulations provided, as a representation of the unique capability that theory / computation can have for understanding complex chemistry.

- [1] J. W. Park, Y. M. Rhee, *ChemPhysChem* **15**, 3183 (2014).
- [2] Y. M. Rhee, J. W. Park, *Int. J. Quantum Chem.* **116**, 573 (2016).
- [3] J. W. Park, Y. M. Rhee, *J. Am. Chem. Soc.* **138**, 13619 (2016).
- [4] C. W. Kim, Y. M. Rhee, *J. Chem. Theory Comput.* **12**, 5235 (2016).

## How Native and Alien Metal Cations Bind ATP

**Todor Dudev<sup>1</sup>, Cédric Grauffel<sup>2</sup>, Carmay Lim<sup>2,3</sup>**

<sup>1</sup> *Faculty of Chemistry and Pharmacy, Sofia University, Sofia 1164, Bulgaria*

<sup>2</sup> *Institute of Biomedical Sciences, Academia Sinica, Taipei 11529, Taiwan*

<sup>3</sup> *Department of Chemistry, National Tsing Hua University, Hsinchu 300, Taiwan*

Adenosine triphosphate (ATP), the major energy currency of the cell, exists in solution mostly as ATP-Mg. Recent experiments suggest that  $\text{Mg}^{2+}$  interacts with the highly charged ATP triphosphate group and  $\text{Li}^+$  can co-bind with the native  $\text{Mg}^{2+}$  to form ATP-Mg-Li and modulate the neuronal purine receptor response. How the negatively charged ATP triphosphate group binds  $\text{Mg}^{2+}$  and  $\text{Li}^+$  (i.e., which phosphate group(s) bind  $\text{Mg}^{2+}/\text{Li}^+$ ) or how the ATP solution conformation depends on the type of metal cation and the metal-binding mode was unknown. We have revealed the preferred ATP-binding mode of  $\text{Mg}^{2+}/\text{Li}^+$  alone and combined. We have also revealed how the metal cation type and its binding mode affect the ATP conformation and properties. Our findings help elucidate the mechanism of lithium's therapeutic action [1].

[1] Todor Dudev, Cédric Grauffel, & Carmay Lim, *Sci. Rep.* **7**, 42377 (2017).

## A Multiscale Computational Investigation of SILP Catalysis: The Water-Gas Shift Reaction

**Robert Stepić,<sup>1,3</sup> Nataša Vučemilović-Alagić,<sup>1,2,3</sup> Daniel Berger,<sup>1,4</sup> Christian Wick,<sup>2</sup> Jens Harting,<sup>4,5</sup> Ana-Sunčana Smith<sup>1,2,3</sup> and David M. Smith<sup>2,3</sup>**

<sup>1</sup> PULS Group, Friedrich-Alexander-Universität (FAU), Erlangen, Germany

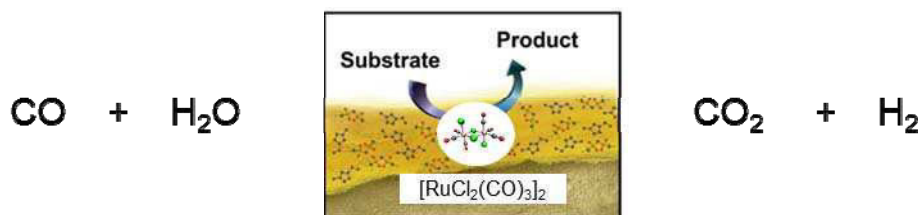
<sup>2</sup> CLS Group, Division of Physical Chemistry, Ruđer Bošković Institute, Zagreb, Croatia

<sup>3</sup> Cluster of Excellence: Engineering of Advanced Materials, FAU, Erlangen, Germany

<sup>4</sup> Forschungszentrum Jülich, Helmholtz Institute ERN, Nürnberg, Germany

<sup>5</sup> Department of Applied Physics, Eindhoven University of Technology, Netherlands

The Water Gas-Shift reaction (WGSR) is a process which results in the conversion of CO and H<sub>2</sub>O into H<sub>2</sub> and CO<sub>2</sub>, usually in presence of a catalytic material. The abundance of water, the toxicity of carbon monoxide and the importance of hydrogen as potential fuel are just some of the factors that have attracted the interest of the industrial and scientific communities to this reaction [1].



In this study, we apply a range of computational techniques to investigate the WGSR catalysed by a ruthenium-based catalyst ([RuCl<sub>2</sub>(CO)<sub>3</sub>]), known for its high efficiency in the supported ionic liquid phase (SILP) [2,3]. More specifically, we present an investigation of the catalytic mechanism using an appropriate density functional theory treatment [4]. This approach is complemented by fully atomistic molecular dynamics simulations of the ionic liquid on an alumina support. The ultimate goal of the research is to bridge the gap between multiple scales and provide a theoretical prediction of output, and optimization, of these important catalytic systems.

[1] C. Ratnasamy, J. P. Wagner, *Cat. Rev.: Sci. Eng.* **51**, 325 (2009).

[2] S. Werner, N. Szesni, A. Bittermann, M. J. Schneider, P. Härter, M. Haumann, P. Wasserscheid, *Appl. Catal. A* **377**, 70 (2010).

[3] S. Werner, N. Szesni, M. Kaiser, R. W. Fischer, M. Haumann, P. Wasserscheid, *ChemCatChem* **2**, 1399 (2010).

[4] M. Sobota, S. Schernich, H. Schulz, W. Hieringer, N. Paape, P. Wasserscheid, A. Görling, M. Laurin, J. Libuda, *Phys. Chem. Chem. Phys.* **14**, 10603 (2012).

## Theory for the Entropy of Liquid Mixtures of Flexible Molecules

**Richard H. Henchman<sup>1,2</sup> and Jonathan Higham<sup>1,2,3</sup>**

<sup>1</sup>*School of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom*

<sup>2</sup>*Manchester Institute of Biotechnology, The University of Manchester, 131 Princess Street, Manchester, M1 7DN, United Kingdom*

<sup>3</sup>*Human Genetics Unit and Institute of Genetics & Molecular Medicine, The University of Edinburgh, Western General Hospital, Crewe Road South, Edinburgh, EH4 2XU, United Kingdom.*

A fundamental thermodynamic property of any system is its entropy. The difficulty of calculating entropy, however, restricts its widespread use in understanding structure and stability. Most studies resort to qualitative, partial structural measures or differences in Gibbs energy or entropy. Building on previous work for liquids [1,2,3,4] and isolated flexible molecules [5], we present new theory to calculate the entropy from a trajectory generated in a molecular dynamics simulation for the important case of liquid mixtures of flexible molecules. The vibrational entropic term is derived from the covariance matrix of forces and torques for subsets of atoms of each molecule. The mixture and conformational entropic term is derived from the probabilities of molecular coordination states defined using the parameter-free RAD algorithm [6]. The theory is tested on a range of simple liquids and organic liquids and results are compared with values from perturbation theory.

[1] R. H. Henchman, *J. Chem. Phys.*, **119**, 400, 2003.

[2] R. H. Henchman, *J. Chem. Phys.*, **126**, 064504, 2007.

[3] R. H. Henchman, S. J. Irudayam, *J. Phys. Chem. B*, **114**, 16792, 2010.

[4] J. A. Green, S. J. Irudayam, R. H. Henchman, *J. Chem. Thermodyn.*, **43**, 868, 2011.

[5] U. Hensen, F. Grater, R. H. Henchman, *J. Chem. Theory Comput.*, **10**, 4777, 2014.

[6] J. Higham, R. H. Henchman, *J. Chem. Phys.*, **145**, 084108, 2016.



## Entropy and enzyme catalysis

**Johan Åqvist<sup>1</sup>**

*<sup>1</sup>Department of Cell & Molecular Biology, Uppsala University, Uppsala, Sweden*

The speed of chemical reactions in water and in enzymes varies with temperature, depending on how the free energy of activation is partitioned into enthalpy and entropy. In enzymes, this partitioning is also optimized as a consequence of the organism's adaptation to the environment. We will show how the temperature dependence of chemical reaction rates can be obtained from brute force computer simulations. Such calculations shed new light on entropic effects in enzyme catalysis and on how protein structures have evolved in differently adapted species.

## Understanding metalloenzyme catalysis with QM/MM free energy simulations

Qiang Cui<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of Wisconsin, Madison, 1101 University Avenue,  
Madison, WI 53706*

I'll discuss challenges associated with understanding enzyme catalysis using hybrid QM/MM simulations, especially metalloenzymes that feature a dynamic active site and/or a high degree of solvent accessibility. Relevant examples include molecular motors, DNA repair enzymes and enzymes with a high degree of catalytic promiscuity. I'll discuss recent developments in the density functional tight binding (DFTB) model[1] and its integration with efficient sampling techniques (e.g., the thermal string approach) as well as with high-level QM/MM methods for more quantitative free energy computations[2]. The developments are illustrated with several recent applications to metalloenzymes such as alkaline phosphatase[3, 4] and myosin[5].

- [1] A. S. Christensen, T. Kubar, Q. Cui and M. Elstner, *Chem. Rev.*, **116**, 5301-5337 (2016).
- [2] X. Lu, D. Fang, S. Ito, Y. Okamoto, V. Ovchinnikov and Q. Cui, *Mol. Simul. Special Issue on "Free Energy Simulations"*, **42**, 1056-1078 (2016).
- [3] D. Roston, D. Demapan and Q. Cui, *J. Am. Chem. Soc.*, **138**, 7386-7394 (2016).
- [4] D. Roston, Q. Cui, *J. Am. Chem. Soc.*, **138**, 11946-11957 (2016).
- [5] X. Lu, V. Ovchinnikov and Q. Cui, *Biochem.*, **56**, 1482-1497 (2017).

## Cell Penetration and Membrane Fusion: Two Sides of the Same Coin

**Pavel Jungwirth**

*Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, Flemingovo nám. 2, 16610 Prague 6, Czech Republic, e-mail: pavel.jungwirth@uochb.cas.cz*

Cell penetrating peptides have a unique potential for targeted drug delivery, therefore, mechanistic understanding of their membrane action has been sought since their discovery over 20 years ago. While ATP-driven endocytosis is known to play a major role in their internalization, there has been also ample evidence for the importance of passive translocation for which the direct mechanism, where the peptide is thought to directly pass through the membrane via a temporary pore, has been widely advocated. In this talk, I will question this view and demonstrate that arginine-rich cell penetrating peptides instead enter vesicles by inducing multilamellarity and fusion, analogously to the action of calcium ions. The molecular picture of this penetration mode, which differs qualitatively from the previously proposed direct mechanism, is provided by molecular dynamics simulations. In addition, the kinetics of vesicle agglomeration and fusion by nonaarginine, nonalysine, and calcium ions are documented in real time by fluorescence techniques and the induction of multilamellar phases is revealed both via electron microscopy and fluorescence spectroscopy. We thus show that the newly identified passive cell penetration mechanism is analogous to vesicle fusion induced by calcium ions, demonstrating that the two processes are of a common mechanistic origin.

## Molecular simulations of lipid membrane sensing and remodeling dynamics

Gerhard Hummer<sup>1,2</sup>

<sup>1</sup>*Department of Theoretical Biophysics Max Planck Institute of Biophysics, 60438 Frankfurt am Main*

<sup>2</sup>*Institute of Biophysics, Goethe University Frankfurt, 60438 Frankfurt am Main*

Living cells need to exert tight control over their lipid membranes, to maintain their internal structure, to guard their outside boundary, to establish potential and concentration gradients as their energy source, or to transmit signals between their compartments and to the outside. As a consequence, elaborate machineries have evolved that allow cells to sense and regulate both shapes and physical characteristics of their lipid membranes. The molecular modeling of these machineries faces enormous challenges because of their complexity, size, and dynamic nature. To address these challenges, we combine atomistic and coarse-grained simulation approaches. In my talk, I will describe different mechanisms used by eukaryotic cells to sense and regulate the fluidity of their lipid membranes, as deduced in part from molecular dynamics simulations [1,2]. In addition, large-scale membrane remodeling processes will be explored, including membrane fusion mediated by carbon nanotubes [3].

[1] R. Covino, S. Ballweg, C. Stordeur, J. B. Michaelis, K. Puth, F. Wernig, A. Bahrami, A. M. Ernst, G. Hummer, R. Ernst, *Mol. Cell* **63**, 49 (2016).

[2] K. Halbleib, K. Pesek, R. Covino, H. F. Hofbauer, D. Wunnicke, I. Hänelt, G. Hummer, R. Ernst, *Mol. Cell*, in press (2017).

[3] R. M. Bhaskara, S. Linker, M. Vögele, J. Köfinger, G. Hummer, *ACS Nano* **12**, 1273 (2017).

## **Towards a Local Coupled Cluster Theory for Solids.**

**Marcel Nooijen, Mike Lecours<sup>1</sup> and Ondrej Demel<sup>2</sup>**

<sup>1</sup>*Department of Chemistry, University of Waterloo, 200 University Ave West, Waterloo, Ontario, N2L 3G1, Canada*

<sup>2</sup>*Acad Sci Czech Republic, J Heyrovsky Inst Phys Chem, Vvi, Dolejskova 3, CR-18223 Prague 8, Czech Republic*

The key towards developing a local Coupled Cluster method for periodic systems is the use of occupied orbitals that are both localized and reflect the periodicity of the system. Two types of orbitals will be introduced for this purpose: i) Enveloping Localized Orbitals (ELOs), which mix in partly virtual character to achieve localization, and ii) Periodic (or Projected) Localized Orbitals (PLOs), which are in general a linear dependent set. Importantly, both sets of orbitals can be obtained from merely a reference density matrix and AO overlap integrals. Moreover, both types of orbitals require some modifications of canonical CC methods to deal with special features of the orbitals. Such ELO and PLO orbitals can also be defined for molecular systems, and they can then be used in the design of a local Coupled Cluster method that exploits molecular symmetry. This is in essence the problem in designing a local correlation method for solids.

The project is in a pioneering stage and we will present the outline of ideas and illustrate the principles using pilot implementations for molecules (not solids), which moreover are not yet efficient. Efficient implementations will be pursued using suitably adjusted code generators.

In addition to the electron correlation problem using CC methods, the problem of Hartree-Fock calculations for solids will be discussed. This includes efficient ways to calculate the Fock matrix using a combination of density fitting and Fourier transform techniques, and a partitioning of the Coulomb interaction in long range and short-range parts. In addition we will pursue the calculation of the HF density matrix without the introduction of a k-point integration over the Brillouin zone. This step (avoiding diagonalization of the Fock matrix) uses a Coupled Cluster singles approach in conjunction with a crude set of PLOs, and uses the same ideas as will be used for CCSD and electron correlation. The possibility of finite temperature calculations, obtaining the density matrix corresponding to a Fermi-Dirac distribution without diagonalization of the Fock matrix is noteworthy, and vital in order to compute metallic systems using the above ideas.

## The relation between the random phase approximation and GW and analytic forces for the RPA

**Georg Kresse<sup>1</sup>, Benjamin Ramberger<sup>1</sup>, Tobias Schäfer<sup>1</sup>, Peitao Liu<sup>1</sup>**

<sup>1</sup>*University of Vienna, Faculty of Physics and Center for Computational Materials Sciences, Sensengasse 8/12, 1090 Vienna, Austria*

The random phase approximation (RPA) to the correlation energy and the related GW approximation are among the most promising methods to obtain accurate correlation energy differences and QP energies from diagrammatic perturbation theory at reasonable computational cost, in particular, for solid state systems. The calculations are, however, usually two to three orders of magnitude more demanding than conventional density functional theory calculations. Here, we show that a cubic system size scaling can be readily obtained reducing the computation time by typically one order of magnitude for large systems [1, 2, 3]. Furthermore, the scaling with respect to the number of k points used to sample the Brillouin zone can be reduced to linear order. In combination, this allows accurate and very well-converged single-point RPA and GW calculations, with a time complexity that is roughly on par to self-consistent Hartree-Fock and hybrid functional calculations. Furthermore, the talk discusses the relation between the RPA correlation energy and the GW approximation. It is shown that the GW selfenergy is the derivative of the RPA correlation energy with respect to the Green's function. The calculated self-energy can be used to compute QP-energies in the GW approximation, any first derivative of the total energy including forces, as well as corrections to the correlation energy from the changes of the charge density when switching from DFT to a many-body body description (GW singles energy contribution) [4]. First applications of RPA forces to systems with mixed covalent and vdW bonding are discussed. These applications include phonons, relaxation of structures, as well as molecular dynamics simulations [5].

- [1] M. Kaltak, J. Klimés, and G. Kresse, *J. Chem. Theory Comput.*, 10, 2498 (2014).
- [2] M. Kaltak, J. Klimés, and G. Kresse, *Phys. Rev. B* 90, 054115 (2014).
- [3] P. Liu, M. Kaltak, J. Klimés, and G. Kresse, *Phys. Rev. B* 94, 165109 (2016).
- [4] J. Klimés, M. Kaltak, E. Maggio, and G. Kresse, *J. Chem. Phys.* 140, 084502 (2015).
- [5] B. Ramberger, T. Schäfer, G. Kresse, *Phys. Rev. Lett.* 118 106403 (2017).

## Electronic Structure Calculations for Correlated Electron Materials: a Dynamical Mean Field Perspective

Silke Biermann<sup>1</sup>

<sup>1</sup>*Centre de Physique Théorique, Ecole Polytechnique, CNRS UMR7644, 91128 Palaiseau, France*

Dynamical mean field theory (DMFT), in conjunction with electronic structure techniques such as density functional theory (DFT), has led to tremendous progress in the description of excited state properties of materials with strong electronic Coulomb correlations. The challenge nowadays consists in refining the interface of electronic structure and many-body theory in order to develop quantitatively accurate schemes.

We will review the current state of the art in the field, and then focus on recent efforts of incorporating dynamical screening effects into a DMFT-based description of correlated materials [1]. Such effects can stem either from higher energy degrees of freedom that have been integrated out or from nonlocal processes that are effectively backfolded into a local description. This can be conveniently done by combined many-body perturbation theory and dynamical mean field theory ("GW+DMFT") techniques [2]. An analysis of the effects of the different corrections to standard DFT+DMFT schemes leads to new insights also into DFT itself [3].

- [1] For reviews see S. Biermann, *J. Phys.: Condens. Matter* **26**, 173202 (2014); A. van Roekeghem *J. El. Spect. Rel. Phen.* **208**, 17 (2016).
- [2] S. Biermann, F. Aryasetiawan, A. Georges, *Phys. Rev. Lett.* **90**, 086402 (2003); T. Ayrál et al., *Phys. Rev. B* **87**, 125149 (2013), *Phys. Rev. Lett.* **109**, 226401 (2012); J. M. Tomczak et al., *Europhys. Lett.* **100** 67001 (2012); *Phys. Rev. B* **90**, 165138 (2014).
- [3] A. van Roekeghem et al., *Phys. Rev. Lett.* **113**, 266403 (2014); *Europhys. Lett.* **108**, 57003 (2014); Hirayama et al., *Phys. Rev. B* in press, available electronically as arXiv:1511.03757; T. Ayrál et al., *Phys. Rev. B* **95**, 245130 (2017); P. Delange et al., *J. Phys. Soc. Jap.*, in press, available electronically as arXiv:1707.00456.

## Affordable High Numerical Accuracy for Large Molecules and Materials from Numeric Atom-Centered Basis Functions

Volker Blum<sup>1</sup>

<sup>1</sup>*Department of Mechanical Engineering and Materials Science and Department of Chemistry, Duke University, Durham, NC 27708, USA*

This talk describes concepts, algorithms, and recent advances of electronic structure theory based on numeric atom-centered orbital (NAO) basis sets, as implemented in the all-electron electronic structure code FHI-aims [1]. This basis set prescription enables seamless simulations from fast qualitative to essentially basis-set converged accuracy [2], on equal footing from light to the heaviest elements, and in an implementation that maintains scalability up to thousands of atoms and up to the highest-performance supercomputers available today.[3,4] Production methods include density-functional theory (DFT) for non-periodic and periodic systems, as well as many-body theory including the random-phase approximation, *GW*, and other high-level approaches. We review recent developments including a new, open-source framework “ELSI” [3], aimed at enabling seamless switching between  $O(N^3)$  and lower-scaling solvers for DFT towards very large systems (10,000 atoms and beyond). We also demonstrate new approaches to affordable basis-set convergence for explicitly correlated methods for charged excitations (*GW*) and for neutral excitations (Bethe-Salpeter Equation). We demonstrate the power of the approach for predicting new inorganic materials for thin-film photovoltaics and for complex, 2D organic-inorganic hybrid perovskites, allowing one to integrate complex organic functionality with inorganic components in a single, crystalline and electronically tunable semiconductor framework.

This work was performed in collaboration with numerous outstanding collaborators in the FHI-aims community, the wider electronic structure community, and the experimental group of David Mitzi, Duke University.

[1] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, M. Scheffler, *Comp. Phys. Commun.* **180**, 2175 (2009).

[2] S. R. Jensen, S. Saha, J. A. Flores-Livas, V. Blum, W. P. Huhn, S. Goedecker, L. Frediani, *J. Phys. Chem. Lett.* **8**, 1449 (2017).

[3] V. W. Yu, F. Corsetti, A. Garcia, W. P. Huhn, M. Jacquelin, W. Jia, B. Lange, L. Lin, J. Lu, W. Mi, A. Seifitokaldani, A. Vazquez-Mayagoitia, C. Yang, H. Yang, V. Blum, arXiv:1705.11191 [physics.comp-ph] (2017).

[4] S. Levchenko, X. Ren, J. Wieferink, R. Johanni, P. Rinke, V. Blum, M. Scheffler, *Comp. Phys. Commun.* **192**, 60 (2015).

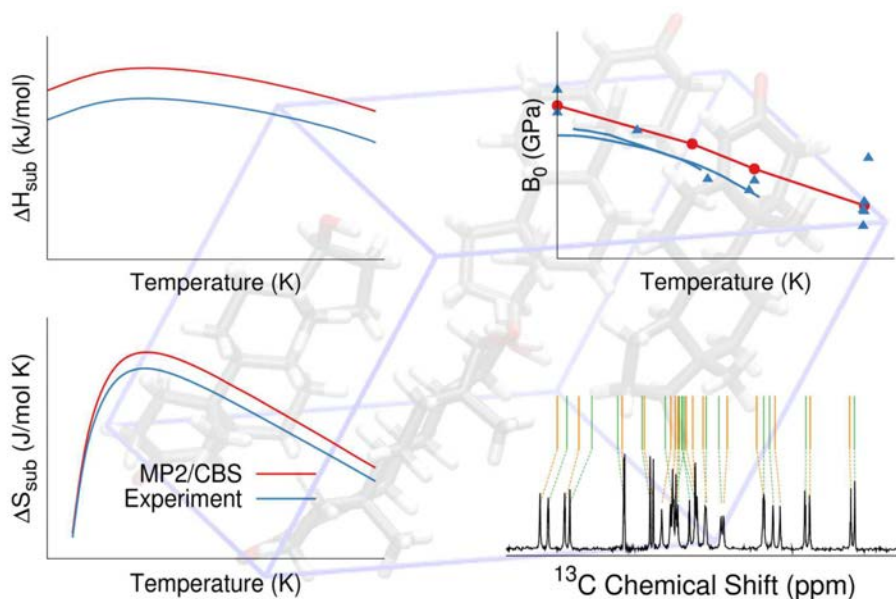


## *Ab initio* Molecular Crystallography: Aiding and Abetting Experiment

Gregory Beran

*Department of Chemistry, University of California Riverside, 501 Big Springs Rd, Riverside, CA 92506, USA*

Molecular crystal structure and function are intimately connected, with different crystal packing motifs often producing materials with dramatically different physical properties. Characterizing these crystal structures is essential in pharmaceuticals and other solid state organic materials applications, but crystal structure determination via traditional x-ray diffraction techniques is not always feasible or sufficient. This talk will highlight ways in which fragment-based electronic structure calculations facilitate experimental crystallography in molecular crystals.[1, 2] Key themes will include (1) achieving higher accuracy nuclear magnetic resonance (NMR) chemical shift predictions, which translates to increased discrimination between correct and incorrect structural assignments for NMR crystallography, and (2) challenging the experimental interpretations of the high-pressure phases of carbon dioxide. These studies require a combination of high-quality structural modeling and accurate prediction of thermochemical, mechanical, and spectroscopic observables in molecular crystals.



[1] G. Beran, J. Hartman, and Y. Heit. *Acc. Chem. Res.* **49**, 2501 (2016).

[2] G. Beran. *Chem. Rev.* **116**, 5567-5613 (2016).

# Many-body Green's function theory: Algebraic recursions, linked- and irreducible-diagram theorems, and general-order algorithms

So Hirata<sup>1</sup>, Alexander E. Doran<sup>1</sup>, Peter J. Knowles<sup>2</sup>, J. V. Ortiz<sup>3</sup>

<sup>1</sup>*Department of Chemistry, University of Illinois at Urbana-Champaign, Illinois, U.S.A.*

<sup>2</sup>*School of Chemistry, Cardiff University, Cardiff, United Kingdom*

<sup>3</sup>*Department of Chemistry and Biochemistry, Auburn University, Alabama, U.S.A.*

We present thorough analytical and numerical characterization of the whole perturbation series of one-particle many-body Green's function (MBGF) theory. Three distinct but equivalent algebraic recursive definitions of the Feynman–Dyson perturbation series of the Green's function and one recursive definition of the perturbation series of the nondiagonal, frequency-dependent Dyson self-energy are derived. On this basis, six general-order algorithms of MBGF ( $\Delta MP_n$ ,  $\lambda$ -variation, diagrammatic, the three recursions) are implemented, all giving the same results except one ( $\Delta MP_n$ ). We prove the linked-diagram theorem for the Green's function and self-energy as well as the irreducible-diagram theorem for the self-energy in the time-independent picture. We rationalize the three diagrammatic rules of MBGF and the differences and similarities between  $\Delta MP_n$  and MBGF. We quantify the impact of the diagonal, frequency-independent, perturbation, and  $\Delta MP_n$  approximations on the self-energy.

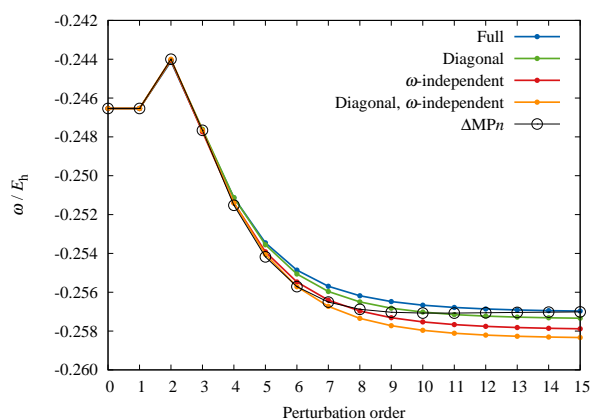


Figure 1: Convergence of the self-energy of HOMO of BH.

## Green's function embedding methods

**Dominika Zgid<sup>1</sup>, T. N. Lan<sup>1</sup>, A. A. Rusakov<sup>1</sup>, A. Shee<sup>1</sup>, A. A. Kananenka<sup>1</sup>,  
A. R. Welden<sup>1</sup>, B. A. Winograd<sup>1</sup>**

*<sup>1</sup>Department of chemistry, Michigan University, 930 N University Ave, Ann Arbor, MI,  
48109, USA*

We present a detailed discussion of self-energy embedding theory (SEET) which is a quantum embedding scheme allowing us to describe a chosen subsystem very accurately while keeping the description of the environment at a lower cost. We apply SEET to molecular examples where commonly our chosen subsystem is made out of a set of strongly correlated orbitals while the weakly correlated orbitals constitute an environment. Such a self-energy separation is very general and to make this procedure applicable to multiple systems a detailed and practical procedure for the evaluation of the system and environment self-energy is necessary. We list all the intricacies for one of the possible procedures while focusing our discussion on many practical implementation aspects such as the choice of best orbital basis, impurity solver, and many steps necessary to reach chemical accuracy. Finally, on a set of carefully chosen molecular and periodic examples, we demonstrate that SEET, which is a controlled, systematically improvable Green's function method can be as accurate as established wavefunction quantum chemistry methods.

## Is BSE/*GW* an effective method for modeling optical spectra of molecules?

Denis Jacquemin<sup>1,2</sup>

<sup>1</sup> CEISAM (UMR CNRS 6230), Université de Nantes, 2, rue de la Houssinière, 44322 Nantes, France

<sup>2</sup> Institut Universitaire de France, 1, Rue Descartes, 75005 Paris, France

Time-Dependent Density Functional Theory (TD-DFT) is the most widely used method to model electronically excited-states [1]. However, as its wavefunction alternatives, it suffers from a specific limitations. As a consequence, other methods able to reproduce excited-state properties at a moderate computational cost are always welcome. Among those approaches, the Bethe-Salpeter (BSE) scheme, an extension of the ground-state *GW* method, offers an appealing alternative to TD-DFT, as it maintains the same scaling with system size. In this talk, the performances of BSE/*GW* for excitations energies of molecules will be presented, considering vertical transitions [2], 0-0 energies [3] and oscillator strengths [4]. It will be shown that a partial self-consistent scheme at the *GW* level leads to a significantly reduced dependency on the starting DFT functional compared to both TD-DFT and BSE/*G<sub>0</sub>W<sub>0</sub>* [2], as well as an accuracy similar to the one of reference wavefunction approaches [5]. Finally, applications on large systems [6] will be discussed.

- [1] D. Jacquemin, C. Adamo, *Chem. Soc. Rev.* **42**, 845 (2013).
- [2] D. Jacquemin, I. Duchemin, X. Blase, *J. Chem. Theory Comput.* **11**, 3290 (2015).
- [3] D. Jacquemin, I. Duchemin, X. Blase, *J. Chem. Theory Comput.* **11**, 5340 (2015).
- [4] D. Jacquemin, I. Duchemin, A. Blondel, X. Blase, *J. Chem. Theory Comput.* **12**, 3969 (2016).
- [5] D. Jacquemin, I. Duchemin, X. Blase, *J. Phys. Chem. Lett.* **8**, 1524 (2016).
- [6] D. Escudero, I. Duchemin, X. Blase, D. Jacquemin, *J. Phys. Chem. Lett.* **8**, 936 (2016).

## Quasi-particles and satellites from a direct approach to the calculation of many-body Green's functions

Lucia Reining<sup>1, 2</sup>

<sup>1</sup>*Laboratoire des Solides Irradiés, École Polytechnique, CNRS, CEA, Université Paris-Saclay, 91128 Palaiseau, France*

<sup>2</sup>*European Theoretical Spectroscopy Facility (ETSF)*

Many-body perturbation theory is a powerful approach to describe many properties of materials. Most often one solves a Dyson equation with a self-energy kernel that is approximated to low order in the interaction, for example, using Hedin's GW approximation [1]. This is the state-of-the art method for bandstructure calculations in a wide range of materials. However, sometimes the GW approximation and related approaches are not sufficient, for example when one is interested in satellite structure beyond the quasi-particle peaks in the spectral function, or in the case of strong coupling, where the quasi-particle picture is no longer adequate. We explore an alternative route to the calculation of interacting electron Green's functions. It is based on a set of functional differential equations [2] relating the one-body Green's function to its functional derivative with respect to an external perturbing potential. This set of equations can be used to generate the perturbation series. The present talk, instead, will show how one can work directly with these differential equations [3,4]. Like in Hedin's equations, we express the problem in terms of the screened Coulomb interaction. The talk will contain an overview of results for a variety of materials. More in particular, it will become clear how important details of the screening can be. Therefore, we will also present a way to obtain screened interactions beyond standard approximations, for example by using results which other methods yield for the homogeneous electron gas.

- [1] L. Hedin, *Phys. Rev.* **139**, A796 (1965).
- [2] L.P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (New York: Benjamin, 1962).
- [3] G. Lani, P. Romaniello, and L. Reining, *New J. Phys.* **14**, 013056 (2012); J.A. Berger et al., *New J. Phys.* **16**, 113025 (2014).
- [4] M. Guzzo et al., *Phys. Rev. Lett.* **107**, 166401 (2011) and *Phys. Rev. B* **89**, 085425 (2014); J. Zhou et al., *J. Chem. Phys.* **143**, 184109 (2015).

## Using the *GW* and Bethe-Salpeter Methods in Molecular Quantum Chemistry

Wim Klopper<sup>1</sup>

<sup>1</sup>*Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), Kaiserstr. 12,  
D-76131 Karlsruhe, Germany*

We have implemented a computational approach based on the Bethe–Salpeter equation (BSE) for the theoretical description of electronically excited states of finite systems (atoms and molecules). The approach is much used in computational solid-state physics and materials science, but not so much in quantum chemistry. In recent years, however, interest in using the approach for molecular systems has increased [1, 2]. Within the framework of the TURBOMOLE program system, we have implemented the BSE approach using a resolution-of-the-identity (RI) approximation for all two-electron electron-repulsion integrals that are required for solving the equation [3]. Symmetry is utilized for the point group  $D_{2h}$  and its subgroups, and the BSE approach can be applied in either a spin-restricted or a spin-unrestricted Kohn–Sham formalism. Triplet as well as singlet excited states of closed-shell atoms and molecules can be treated in the spin-restricted formalism. As a side product, our implementation also allows for the application of the RI approximation to the Hartree–Fock exchange contribution that occurs when a hybrid functional is used in time-dependent density-functional theory.

On input, BSE calculations need (Kohn–Sham) orbitals together with quasiparticle energies obtained from a *GW* calculation. In the present work, we have explored the use of quasiparticle energies obtained from linearized  $G_0W_0$ ,  $x_\alpha$ - $G_0W_0$ , eigenvalue self-consistent *GW* (ev*GW*), and fully quasiparticle self-consistent *GW* (sc*GW*) calculations. The performance of the *GW*/BSE approach is assessed by computing singlet and triplet excitation energies of 28 small organic molecules. CPU timings are reported as well.

- [1] D. Jacquemin, I. Duchemin, X. Blase, *J. Phys. Chem. Lett.* **8**, 1524 (2017).
- [2] T. Rangel, S. M. Hamed, F. Bruneval, J. B. Neaton, *J. Chem. Phys.* **146**, 194108 (2017).
- [3] K. Krause, W. Klopper, *J. Comput. Chem.* **38**, 383 (2017).

## On-the-fly CASPT2 surface hopping dynamics

**Toru Shiozaki<sup>1</sup>**

*<sup>1</sup>Department of Chemistry, Northwestern University*

In this talk, I will present our recent work on analytical nuclear energy gradients and non-adiabatic coupling matrix elements for the fully internally contracted (X)MS-CASPT2 method, which are implemented in BAGEL, a publicly available open-source electronic-structure program package. Numerical examples of on-the-fly non-adiabatic dynamics that we have enabled (photodynamics of adenine and a GFP model chromophore) will be presented.

## Quantum Dynamics on Accurate Electronic Potentials

David P. Tew

*School of Chemistry, University of Bristol, Cantocks Close, Bristol, UK*

A prerequisite for quantum dynamics is an accurate representation of the electronic potential. Two approaches for constructing model potentials from ab initio data will be introduced: one based on Gaussian Process Regression[1] and one based on Elastic Net constrained least squares regression[2]. Applications of the latter to vibrational structure of fluxional molecules[3] and to the prototypical two-state reaction[4]  $\text{FeO}^+ + \text{H}_2 \rightarrow \text{Fe}^+ + \text{H}_2\text{O}$  will be presented.

- [1] P. Alborzpour, D. P. Tew and S. Habershon, *J. Chem. Phys.* **145**, 174112 (2016).
- [2] W. Mizukami, S. Habershon and D. P. Tew, *J. Chem. Phys.* **141**, 144310 (2014).
- [3] D. P. Tew and W. Mizukami, *J. Phys. Chem. A* **120**, 9815–9828 (2016).
- [4] S. Essafi, D. P. Tew and J. N. Harvey, *Angew. Chem. Int. Ed.* **56**, 5790–5794 (2017).



***Ab initio* modeling of inter-molecular electronic transition processes  
in molecular aggregates**

**Yuki Kurashige**

<sup>1</sup> *Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, Japan*

<sup>2</sup> *PRESTO, Japan Science and Technology Agency, Saitama Japan.*

Recent advancements of ultrafast spectroscopies enable experimental measurements of microscopic processes in molecular aggregates and provide insight into the underlying mechanism. Simulation of these experiments in an *ab initio* manner require an accurate but tractable expression of the electronic wavefunction of the molecular aggregates. Here, an efficient low-rank approximation to the full-rank wavefunctions of molecular aggregates is presented. In the method, low-lying states of molecular aggregates are efficiently expanded by a small number of rank-one *n*-particle basis states that are direct products of mono-molecular wavefunctions, each of which is written as a highly-entangled state such as the matrix product state. The complexities raised by the strong intra-molecular entanglement of  $\pi$ -conjugated molecules are, therefore, encapsulated by the MPS and eliminated from the degrees of freedom of the effective Hamiltonian of the molecular aggregates. It is demonstrated that the excitation energies of low-lying excited states of a pair of bacteriochlorophyll units with the CAS(52e, 50o) are accurately reproduced by only five rank-one basis. A theoretical investigation of the coherent and ultrafast fission process in rubrene crystal observed transient absorption spectroscopy will be also presented.

[1] K. Miyata, Y. Kurashige, K. Watanabe, T. Sugimoto, S. Takahashi, S. Tanaka, J. Takeya, T. Yanai, and Y. Matsumoto, *Nature Chem.*, **DOI**: 10.1038/NCHEM.2784.

## Open-shell MC-srDFT -

**a new way to describe high-spin, low-spin, intermediate spin states and more**

**Hans Jørgen Aagaard Jensen**

*Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, DK-5230 Odense M, Denmark (hjj@sdu.dk)*

Reliable and cost-effective modeling of open-shell transition metal complexes and enzymes is still a huge challenge for computational quantum chemistry. In many cases DFT is not sufficiently reliable, and often state-of-the art methods such as CASPT2 and NEVPT2 are computationally too expensive.

I have recently together with Erik Hedegård (Lund University) extended the multi-configuration short-range density functional theory (MC-srDFT) methodology [1-7] to open-shell systems. This extension allows us to target transition metal systems where we aim to handle relative energies of different spin states, core- and valence electronic transitions, as well as magnetic response properties such as EPR and pNMR; all important ingredients for the understanding of (metallo)enzyme mechanisms. I will present the new method and some initial results. I hope to convince you that in the future your first choice should be open-shell MC-srDFT rather than CASPT2 or NEVPT2 for such applications.

[1] On the universality of the long-/short-range separation in multiconfigurational density-functional theory. E. Fromager, J. Toulouse, and H. J. Aa. Jensen, *J. Chem. Phys.* **126**, 074111 (2007).

[2] Merging multireference perturbation and density-functional theories by means of range separation: Potential curves for Be<sub>2</sub>, Mg<sub>2</sub>, and Ca<sub>2</sub>. E. Fromager, R. Cimraglia, and H. J. Aa. Jensen, *Phys. Rev. A* **81**, 024502 (2010).

[3] Multi-configuration time-dependent density-functional theory based on range separation. E. Fromager, S. Knecht, and H. J. Aa. Jensen, *J. Chem. Phys.* **138**, 084101 (2013).

[4] On the universality of the long-/short-range separation in multiconfigurational density-functional theory. E. Fromager, J. Toulouse, and H. J. Aa. Jensen, *J. Chem. Phys.* **126**, 074111 (2007).

[5] Density Matrix Renormalization Group with Efficient Dynamical Electron Correlation Through Range Separation. E. D. Hedegård, S. Knecht, J. Skau Kielberg, H. J. Aa. Jensen, and M. Reiher, *J. Chem. Phys.* **142**, 224108 (2015).

[6] Excitation Spectra of Nucleobases with Multiconfigurational Density Functional Theory. M. Hubert, H. J. Aa. Jensen, and E.D. Hedegård, *J. Phys. Chem. A* **120**, 36–43 (2016).

[7] Investigation of Multiconfigurational short-range Density Functional Theory for Electronic Excitations in Organic Molecules. M. Hubert, E.D. Hedegård, and H. J. Aa. Jensen, *J. Chem. Theory Comput.* **12**, 2203–2213 (2016).

## Stochastic CC( $P;Q$ ) Theory: Converging High-Level Coupled-Cluster Energetics by Monte Carlo Sampling and Moment Expansions

**Piotr Piecuch<sup>1,2</sup>, Jorge Emiliano Deustua<sup>1</sup>, Jun Shen<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, U.S.A.*

<sup>2</sup>*Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824, U.S.A.*

The development of computationally efficient *ab initio* wave function methods, especially those that can provide precise description of bond breaking, biradicals, excited states dominated by two-electron transitions, and other multi-reference situations, continues to be at the center of quantum chemistry. This is particularly true in coupled-cluster (CC) theory, where one can either turn to multi-reference ideas or take advantage of the fact that the single-reference CC methods with a full treatment of higher-than-doubly excited clusters, including CCSDT, CCSDTQ, etc., rapidly converge to the exact, full configuration interaction (FCI), limit, allowing one to incorporate dynamical and non-dynamical correlation effects in a conceptually straightforward manner through particle-hole excitations from a single Slater determinant. The main challenge in this area has been how to incorporate higher-order excitations within the single-reference CC framework without running into prohibitive computational costs of the CCSDT, CCSDTQ, and similar schemes, while avoiding failures of conventional CC approximations of the CCSD(T) type. In this talk, we explore a radically new way of obtaining highly accurate electronic energies, which rapidly converge to those resulting from the high-level CC calculations of the full CCSDT or CCSDTQ type with the ease of a single-reference computation. The key idea is a merger of the CC( $P;Q$ ) formalism [1-4], which enables one to correct energies obtained with conventional as well as unconventional truncations in the cluster and excitation operators for any category of many-electron correlation effects of interest, with the stochastic FCI Quantum Monte Carlo (FCIQMC) [5,6] and CC Monte Carlo (CCMC) [7] methodologies. When applied to CCSDT as the parent approach, the resulting stochastic CC( $P;Q$ ) formalism allows us to reach full CCSDT energetics to within tiny fractions of a millihartree at the small fraction of the computer cost, even when electronic near-degeneracies become substantial, without resorting to active-space concepts utilized in the previously developed [1-4] CC(t;3), CC(t,q;3), and CC(t,q;3,4) methods and practically eliminating the numerical noise present in FCIQMC and CCMC computations.

[1] J. Shen and P. Piecuch, *Chem. Phys.* **401**, 180 (2012).

[2] J. Shen and P. Piecuch, *J. Chem. Phys.* **136**, 144104 (2012).

[3] J. Shen and P. Piecuch, *J. Chem. Theory Comput.* **8**, 4968 (2012).

[4] N.P. Bauman, J. Shen, and P. Piecuch, *Mol. Phys.*, submitted.

[5] G.H. Booth, A.J.W. Thom, and A. Alavi, *J. Chem. Phys.* **131**, 054106 (2009).

[6] D. Cleland, G.H. Booth, and A. Alavi, *J. Chem. Phys.* **132**, 041103 (2010).

[7] A.J.W. Thom, *Phys. Rev. Lett.* **105**, 263004 (2010).



Stockholm 12 Jun 2017

## Response theory techniques to address X-ray spectroscopies

by

Patrick Norman

With the installation of the fourth-generation synchrotron facility MAX IV in Sweden and XFEL facilities around the world, the Knut and Alice Wallenberg Foundation has initiated a concomitant investment in the development of theory and simulation techniques. The resulting Consortium for Theoretical X-ray Sciences (CoTXS) initiative builds on the active collaboration and synergy between seven leading theoretical groups in Sweden with principal investigators P. Norman, I. Abrikosov, R. Lindh, O. Eriksson, L.G.M. Pettersson, Y. Luo, and H. Ågren.

We will present recent advances in response theory, designed to address molecular systems under electronic resonance conditions and referred to as the complex polarization propagator (CPP) approach [1]. In the CPP formulation, electronic relaxation in the core-excited state becomes a matter of electron correlation as illustrated in studies employing the hierarchical sets of coupled cluster (CC) and algebraic diagrammatic construction (ADC) methods. The full propagator formulation of inelastic scattering matrix elements (the Kramer–Heisenberg–Dirac formula) has been derived in the ADC framework, which provides a response theory treatment of resonant inelastic X-ray scattering (RIXS) spectroscopy. The CPP approach is open-ended for extensions toward nonlinear X-ray spectroscopies, such as e.g. X-ray two-photon absorption (XTPA), which are of concern in connection with research at X-ray free electron laser (XFEL) facilities.

[1] Norman, A perspective on nonresonant and resonant electronic response theory for time-dependent molecular properties, *Phys. Chem. Chem. Phys.*, 2011, 13, 2051

## Streamlining Coupled Cluster Response Theory

T. Daniel Crawford<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Virginia Tech, Blacksburg, Virginia, U.S.A.*

The optical properties of chiral molecules are among the most challenging to predict and simulate — even for state-of-the-art quantum chemical methods — because of their delicate dependence on a variety of intrinsic and extrinsic factors, including electron correlation, basis set, vibrational/temperature effects, etc.[1, 2] In numerous studies over the last decade, we have demonstrated the importance of advanced quantum chemical methods such as coupled cluster response theory for the prediction of an array of gas-phase chiroptical properties such as optical rotation angles, circular dichroism rotatory strengths, Raman optical activity scattering intensity differences, and more[3]. The primary disadvantage of such methods, however, is their high-degree polynomial scaling, which limits significantly the size of system to which they may be applied. Furthermore, solvation makes the task even more difficult, not only dramatically expanding the complexity of the simulation, but sometimes altering even the sign of the chiral response. It is thus essential that we reduce the computational demands of the more accurate and reliable quantum chemical methods. In this lecture, we will discuss recent efforts in our group toward this goal, including the exploration of local correlation techniques[4], many-body expansions for the description explicitly solvated systems[5], a variety of implicit solvation models[6], frozen-virtual natural orbitals for reduction of the correlation space[7], and real-time dynamics.

- [1] T. D. Crawford, *Theor. Chem. Acc.* **115**, 227-245 (2006).
- [2] T. D. Crawford, M. C. Tam, and M. L. Abrams, *J. Phys. Chem. A*, **111**, 12057-12068 (2007).
- [3] T. D. Crawford, “High Accuracy Quantum Chemistry and Chiroptical Properties,” in *Comprehensive Chiroptical Spectroscopy*, N. Berova, K. Nakanishi, R. W. Woody, and P. Polavarapu, eds., Wiley, New Jersey, 2012.
- [4] H. R. McAlexander and T. D. Crawford, *J. Chem. Theory Comput.* **12**, 209-222 (2016).
- [5] T. J. Mach and T. D. Crawford, *Theor. Chem. Acc.* **133**, 1449 (2014).
- [6] T. D. Crawford, A. Kumar, K. Hannon, T. J. Mach, H. R. McAlexander, S. Höfener, and L. Visscher, *J. Chem. Theory Comput.* **11**, 5305-5315 (2015).
- [7] A. Kumar and T. D. Crawford, *J. Phys. Chem. A* **121**, 708-716 (2017).

## Towards investigating the optical properties of molecular and ionic crystals using multi-scale approaches

**Benoît Champagne**

*Laboratory of Theoretical Chemistry, University of Namur*

*Rue de Bruxelles, 61, B-5000 Namur, Belgium*

[benoit.champagne@unamur.be](mailto:benoit.champagne@unamur.be)

The presentation assesses the use of multi-scale approaches to describe the optical properties of molecular crystals, emphasizing on different strategies to account for solid state effects. The first challenge is the prediction and interpretation of the linear and nonlinear optical (NLO) responses of compounds ranging from molecular crystals to ionic crystals, and to metal organic frameworks (MOFs), *i.e.* their refractive indices and the second-order NLO susceptibilities (second harmonic generation). The simulations are carried out by combining i) first principles evaluations of the molecular properties using a surrounding of point charges to describe the crystal polarizing field with ii) electrostatic interaction schemes to account for electric field screening – also called local field – effects. Several aspects of these simulations (geometry, DFT *versus* wavefunction, vibrational contributions, crystal field) are discussed at the light of comparisons with experiment [1]. The second challenge aims at improving thermochromism in organic crystals and co-crystals by predicting the properties of these dynamical systems. The corresponding computational investigations are discussed in a systematic way by considering i) the prediction of the crystal structures and of the key geometrical parameters, ii) the evaluation of the relative energy of the different forms of these molecular switches, and iii) the simulation of their optical properties. The salicylideneaniline family has been selected to illustrate these issues, owing to the availability of experimental data on their thermochromic properties [2].

[1] T. Seidler, K. Stadnicka, and B. Champagne, *J. Chem. Theor. Comput.* **10**, 2114-2124 (2014); T. Seidler, A. Krawczuk, B. Champagne, and K. Stadnicka, *J. Phys. Chem. C* **120**, 4481-4494 (2016).

[2] J. Quertinmont, A. Carletta, N. A. Tumanov, T. Leyssens, J. Wouters, and B. Champagne, *J. Phys. Chem. C* **121**, 6898-6908 (2017).

## Developing Theoretical “Beamlines” for Modern Experiments

Sonia Coriani<sup>1</sup>

<sup>1</sup>*DTU Chemistry, Technical University of Denmark, Kemitorvet, Build. 206, DK-2800 Kongens Lyngby, Denmark*

One powerful way to investigate the molecular world is to study its response to electromagnetic fields. Massive investments have been made, during the last two decades, in the advancement of experimental installations for the detection of increasingly sophisticated light-matter interaction, as exemplified by last generation synchrotron and (x-ray) free electron laser facilities. New ways of probing molecules and materials are emerging, addressing a broad range of scientific problems of both fundamental and applied character. These developments are accompanied by an increasing demand for reliable theoretical and computational methodologies, as an essential component to be able to interpret the experimental results and to retrieve precise quantitative chemical information. An overview of our work on the development of such methodologies will be presented, with particular focus on coupled-cluster based methods for core (x-ray) spectroscopy of both ground and excited states [1-8], photoionization processes and photoelectron spectroscopy [9-10], and both coupled cluster and density functional theory protocols for magnetically induced/chiral effects [11-13].

- [1] S. Coriani and H. Koch, *J. Chem. Phys.* **143**, 181103 (2015);
- [2] R.H. Myhre, S. Coriani and H. Koch, *J. Chem. Theory Comput.*, **12**, 2633 (2016)
- [3] S. Coriani, O. Christiansen, T. Fransson, P. Norman, *Phys. Rev. A* **85**, 022507 (2012)
- [4] S. Coriani, T. Fransson, et al., *J. Chem. Theory Comp.* **8**, 1616 (2012)
- [5] J. Kauczor, P. Norman, O. Christiansen, S. Coriani, *J. Chem. Phys.*, **139** (2013) 211102
- [6] N. H. List, S. Coriani, J. Kongsted, O. Christiansen, *J. Chem. Phys.* **141** (2014) 244107
- [7] T. J. A. Wolf, R. H. Myhre, J. P. Cryan, S. Coriani, R. J. Squibb, A. Battistoni, N. Berrah, C. Bostedt, P. Bucksbaum, G. Coslovich, R. Feifel, K. J. Gaffney, J. Grilj, T. J. Martinez, S. Miyabe, S. P. Moeller, M. Mucke, A. Natan, R. Obaid, T. Osipov, O. Plekan, S. Wang, H. Koch, M. Gühr, *Nature Commun.* 2017, in press; arXiv:1610.08498 [physics.chem-ph]
- [8] J. Carbone, R. H. Myhre, H. Koch, L. Cheng, S. Coriani, 2017, in preparation
- [9] B.N.C. Tenorio, M. A. C. Nascimento, S. Coriani, A. Braga Rocha, *J. Chem. Theory Comput.* **12**, 4440 (2016)
- [10] A. Ponzi, P. Decleva, H. Koch, S. Coriani, 2017, in preparation
- [11] F. Santoro, R. Improta, T. Fahleson, J. Kauczor, P. Norman, S. Coriani, *J. Phys. Chem. Lett.* **5**, 180 (2014)
- [12] J. Cukras, J. Kauczor, P. Norman, A. Rizzo, G. L.J.A. Rikken, S. Coriani, *Phys. Chem. Chem. Phys.* **18**, 13267 (2016)
- [13] M. Kaminski, J. Cukras, M. Pecul, A. Rizzo, S. Coriani, *Phys. Chem. Chem. Phys.* **17**, 19079 (2015)

**Electronic nonlinear spectroscopies:  
recent contributions of theory and computational science.**

**Antonio Rizzo<sup>1</sup>**

<sup>1</sup>*Consiglio Nazionale delle Ricerche – CNR, Istituto per i Processi Chimico Fisici  
(IPCF-CNR), Area della Ricerca, I-56126, Pisa, Italy  
E-mail: rizzo@ipcf.cnr.it*

Some of the latest developments in the theoretical and computational studies of nonlinear chiroptical properties and spectroscopies, will be reviewed. Both electric and magnetic field induced second harmonic generation (EFISHG<sup>1</sup> & MFISHG<sup>2</sup>), and the related circular intensity differences (CIDs) in chiral samples, will be discussed. The phenomena, never having been explored experimentally to date, are related to special nonlinear mixed electric and magnetic frequency dependent responses, conveniently computed nowadays employing modern analytic response theory tools. Among the other nonlinear chiroptical spectroscopic properties, all proven to be amenable to *ab initio* simulation resorting to the tools of modern analytical response theory, to be discussed are: excited state electronic circular dichroism,<sup>3</sup> magnetochiral dichroism and birefringence,<sup>4</sup> and circularly polarized phosphorescence.<sup>5</sup> The computational extension to highly accurate, Coupled Cluster models, for the increasingly popular Two-Photon Circular Dichroism (TPCD),<sup>6</sup> will also be presented.

- 
- [1] A. Rizzo, H. Ågren, *Phys. Chem. Chem. Phys.* **15**, 1198, (2013).  
[2] A. Rizzo, G. L. J. A. Rikken, R. Mathevet, *Phys. Chem. Chem. Phys.* **18**, 1846, (2016).  
[3] A. Rizzo, O. Vahtras, *J. Chem. Phys.* **134**, 244109, (2011).  
[4] J. Cukras, J. Kauczor, P. Norman, A. Rizzo, G. L. J. A. Rikken, S. Coriani, *Phys. Chem. Chem. Phys.* **18**, 13267, (2016).  
[5] M. Kaminski, J. Cukras, M. Pecul, A. Rizzo, S. Coriani, *Phys. Chem. Chem. Phys.* **17**, 19079, (2015).  
[6] D. H. Friese, C. Hattig, A. Rizzo, *Phys. Chem. Chem. Phys.* **18**, 13683, (2016).

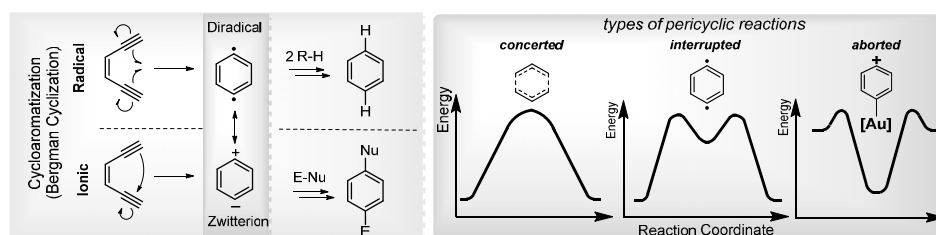


## Reinventing cycloaromatization reactions: the diradical /zwitterion dichotomy.

Igor V. Alabugin, Gabriel Gomes

Department of Chemistry and Biochemistry,  
Florida State University, Tallahassee, Florida 32306, United States

The synergy between bond formation and bond breaking that is typical for pericyclic reactions is lost in their mechanistic cousins, cycloaromatization reactions. In these reactions, exemplified by the Bergman cyclization (BC), two bonds are sacrificed to form a single bond, and the reaction progress is interrupted at the stage of a cyclic intermediate. We will show that this intermediate, p-benzyne, is a chemical chameleon with reactivity ranging between the diradical and zwitterionic extremes. The diradical/zwitterion dichotomy is general and manifests itself in a variety of useful reactivity features.



For example, the catalytic power of Au(I) in BC stems from a combination of two sources: stereoelectronic assistance of C–C bond formation (i.e., “LUMO umpolung”) and crossover from a diradical to a zwitterionic mechanism, that takes advantage of the catalyst’s dual ability to stabilize both negative and positive charges. Not only does the synergy between the bond-forming and charge-delocalizing interactions lead to a dramatic (>hundred-billion-fold) acceleration, but the evolution of the two effects results in continuous reinforcement of the substrate/catalyst interaction along the cyclization path [1]. This cooperativity converts the BC into the first example of an aborted [3,3] sigmatropic shift [2] where the pericyclic “transition state” becomes the most stable species on the reaction hypersurface.

[1] R. P. Feynman, *Phys. Rev.* **56**, 340 (1939). G. P. Gomes, I. V. Alabugin, *J. Am. Chem. Soc.*, **139**, 3406 (2017).

[2] K. Gilmore, M. Manoharan, J. Wu, P. v. R. Schleyer, I. V. Alabugin, *J. Amer. Chem. Soc.* **134**, 10584 (2012).

## DFT study of the Au-C bond formation in gold implanted polyethylene.

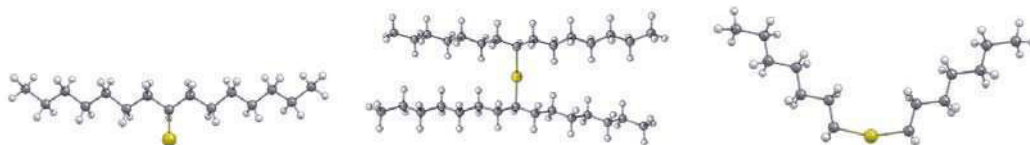
**Andrej Antušek<sup>1</sup>, Martin Blaško<sup>2</sup>, Miroslav Urban<sup>2</sup>, Pavol Noga<sup>1</sup>, Miloš Nenadovič<sup>3</sup>**

<sup>1</sup>*ATRI, Faculty of Materials Science and Technology in Trnava, ATRI, Slovak University of Technology in Bratislava, J. Bottu 25, 917 24 Trnava, Slovak Republic*

<sup>2</sup>*Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Ilkovičova 6, Mlynská dolina, 84215 Bratislava, Slovak Republic*

<sup>3</sup>*INS Vinča, Laboratory of Atomic Physics, Mike Alasa 12-14, Belgrade, Serbia*

We studied processes of the gold implantation to the polyethylene (PE). For the basic insight into PE implanted by Au we used its smaller fragments consisting of 5 to 15 carbon atoms. The Car-Parrinello molecular dynamics was used for the modeling of collisions of  $\text{Au}^+$ , Au and AuH with PE. Based on CCSD(T) benchmarks and previous studies on small  $\text{Au}_n$  – ligand clusters [1] we used the DFT/PBE0 method for calculations of thermodynamic data and IR spectra of possible Au containing PE. Basic motifs are described as H atom of PE substituted by gold, Au serving as a C-Au-C bridge connecting two PE fragments and Au incorporated in the backbone structure of PE:



NBO analysis reveals the covalent character of C-Au bonds with binding energies of about 200 – 320 kJ/mol. Calculated IR spectra helped to assign experimental FTIR spectra of HDPE before and after Au implantation, employing methods described in Ref. [2]. Most significant indication of Au implanted in PE are stretching C-Au vibrations lying around  $500\text{ cm}^{-1}$ , (difficult to measure experimentally) and a broad  $1000 - 1300\text{ cm}^{-1}$  band IR active in PE upon implantation by Au, but not in pure PE.

We thank for the support from Slovak grants APVV-15-0105, VEGA 1/0465/15 and the ERDF –RDO Progr. "Univ. Sci. Park Campus MTF STU - CAMBO" ITMS: 2622022017.

[1] M. Blaško, T. Rajskeý, M. Urban, *Chem. Phys. Letters* **671** 84 (2017).

[2] M. Nenadovič, J. Potočník, M. Mitrič, S. Štrbac, Z. Rakočević, *Mat. Chem. Phys.* **142**, 633 (2013).

## Astructural Molecules

Attila G. Császár<sup>1,2</sup>

<sup>1</sup>*Institute of Chemistry, Eötvös Loránd University,  
H-1117 Budapest, Pázmány Péter sétány 1/A, Hungary*  
<sup>2</sup>*MTA-ELTE Complex Chemical Systems Research Group,  
H-1518 Budapest 112, P.O. Box 32, Hungary*

The notion of molecules and structures is central to our chemical understanding. One useful definition of molecules is that they correspond to minima on potential energy surfaces (PES) and the local PES must support at least one bound rovibrational state. The structure of a molecule is usually considered to be the geometry corresponding to the minimum. If a molecule exists and has a structure, it is also commonly accepted that its internal motions can be separated into vibrations and rotations, motions which usually have very different time and energy scales.

Nevertheless, there are chemical systems where both the notion of a molecule, that of a structure, as well as the separation of rotational and vibrational motion can be questioned. The lecture is centered around molecules where the concept of a structure and the separation of vibrations and rotations seems to break down. Complexes held together by van der Waals forces as well as those characterized by bonds whereby the covalent bonding picture is challenged are prone to exhibit unusual structures and unusual dynamical behavior. Highly excited states of “simple” molecules also exhibit unusual rotational-vibrational characteristics but in these cases it is still useful to keep the concept of a well-defined structure to explain the high-resolution spectrum of the molecule.

For an astructural molecule consideration of a single minimum is insufficient to understand the observed high-resolution spectra, the structure averaged over the vibrational ground state ( $r_0$ ) is significantly different from the equilibrium Born–Oppenheimer one ( $r_e$ ), rotational and vibrational spacings are of the same magnitude, the usual simple tools provided by the rigid rotor harmonic oscillator (RRHO) approximation are unable to yield a reasonable estimate of even the lowest rotational and rovibrational energy levels, and simple perturbative treatments based on the RRHO approximation fail already for the lowest nuclear motion states. Nevertheless, sophisticated tools of the fourth age of quantum chemistry are able to yield a quantitative understanding of the energy level structure and the high-resolution spectra of these astructural molecules and new models can also be developed to aid the qualitative understanding of nuclear motion dynamics of astructural molecules.

## The Role of Acid-Base Equilibria in the Antioxidant and Pro-Oxidant Activity of Phenolic Compounds.

Annia Galano<sup>1</sup>

<sup>1</sup> *Departamento de Química. Universidad Autónoma Metropolitana-Iztapalapa. San Rafael Atlixco 186, Col. Vicentina. Iztapalapa. C. P. 09340. México City, México.*

There is currently no doubt about the serious threat that oxidative stress (OS) represent to human health. Therefore, it is crucial to understand OS in detail, which implies identifying molecules capable of offering protection against it, or promoting it, through chemical routes. Biological systems are very complex, and so is the chemistry involved in OS and its prevention. This chemical stress takes place under diverse environmental conditions, and involve a wide variety of chemical species, as well as simultaneous and competing reactions [1,2]. Considering as many of such factors as possible is then a key aspect to properly model chemical systems related to OS. Some of them are analyzed, and particular attention is paid to the role of the pH, and acid-base equilibria in the protective vs. pro-oxidant effects of phenolic compounds against OS. A kinetics-based methodology is used and validated against experimental data, and trends in reactivity are identified. A rapid approach to estimate the *pK*<sub>a</sub> values is presented, for molecules with different functional groups [3]. Some paradigmatic examples are used to illustrate the main points of the talk. They include molecules with dual antioxidant / pro-oxidant behavior [4], as well as rationally designed molecules intended to be particular efficient as OS protectors [5].

[1] A. Galano, *J. Mex. Chem. Soc.* **59**, 231 (2015).

[2] A. Galano, G. Mazzone, R. Alvarez-Diduk, T. Marino, J. R. Alvarez-Idaboy, N. Russo, *Annu. Rev. Food Sci. Technol.* **7**, 335 (2016).

[3] A. Galano, A. Pérez-González, R. Castañeda-Arriaga, L. Muñoz-Rugeles, G. Mendoza-Sarmiento, et. al., *J. Chem. Inf. Model.* **56**, 1714 (2016).

[4] A. Perez-Gonzalez, J. R. Alvarez-Idaboy, A. Galano, *New J. Chem.* **41**, 3829 (2017).

[5] A. Galano, *Theor. Chem. Acc.* **135**, art. 157 (2016).

## Thermodynamic forces between plant cell wall constituents

**Munir S. Skaf**

*Institute of Chemistry, University of Campinas – UNICAMP – P.O.Box 6154 Campinas,  
SP, 13083-970, Brazil*

Lignocellulosic biomass is a major source of raw materials for the sustainable production of biofuels and valuable chemicals. The essential constituents of plant biomass - cellulose, hemicellulose, and lignin - are organized in highly recalcitrant structures in plant cell walls, such that the depolymerization of the polysaccharide and polyphenolic matrices by enzymatic or chemical processes requires previous thermal or chemical pretreatments of the biomass. In this talk, I report recent studies [1-4] based on the 3D-RISM [5] molecular theory of solvation and MD simulations to investigate the thermodynamic forces between plant cell wall constituents and the role played by the solvent in cellulose aggregation under different thermodynamic conditions.

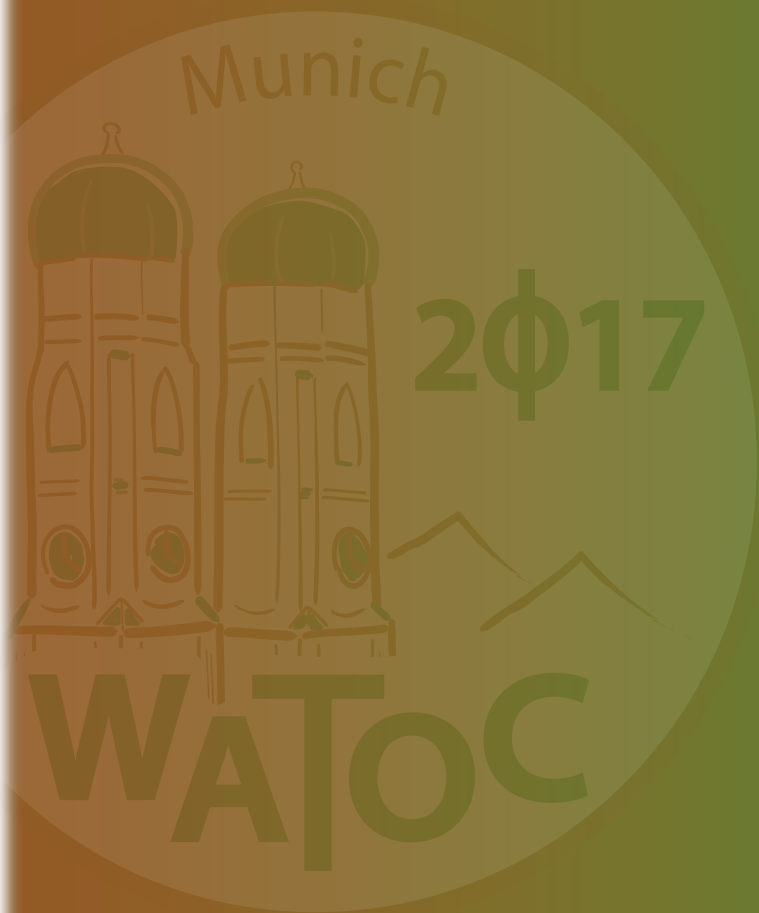
[1] C. S. Pereira, R. L. Silveira, P. Dupree, M. S. Skaf, *Biomacromolecules* **18**, 1311 (2017).

[2] R. L. Silveira, S. R. Stoyanov, A. Kovalenko, M. S. Skaf, *Biomacromolecules* **17**, 2582 (2016).

[3] R. L. Silveira, S. R. Stoyanov, S. Gusarov, M. S. Skaf, A. Kovalenko, *J. Phys. Chem. Lett.* **6**, 206 (2014).

[4] R. L. Silveira, S. R. Stoyanov, S. Gusarov, M. S. Skaf, A. Kovalenko, *J. Am. Chem. Soc.* **135**, 19048 (2013).

[5] E. L. Ratkova, D. S. Palmer, M. V. Fedorov, *Chem. Rev.* **115**, 6312 (2015).



# INDUSTRY SYMPOSIUM



## **The Challenge of Chemical Thermodynamics and Kinetics for Real World Problems**

**Peter Deglmann**

*BASF SE, Digitalization in Research, Carl-Bosch-Str. 38, 67056 Ludwigshafen, Germany*

Whereas for gas phase reactions between small molecules quantum chemical predictions have reached and even bypassed the limit of chemical accuracy (1 kcal/mol), this is typically not the case for reactions in the condensed phase (e.g. in solution or bulk). Thus, in addition to a highly accurate prediction of gas phase reactivity, a reliable calculation of solvation thermodynamics represents a critical issue when applying quantum chemistry to most problems of industrial interest.

Although there are techniques like (ab-initio) molecular dynamics or coupling schemes between quantum chemistry and force field based methods (QM/MM), an explicit treatment of many solvent molecules is often prohibitive if fast answers to questions or a broad screening are required. Therefore, an implicit inclusion of solvent effects is typically preferred.

This presentation discusses for the example of the COSMO-RS solvation model, how Gibbs free energies of reaction and activation are computed in solution; furthermore, the accuracy of this approach is analyzed. Examples of extreme cases are shown where either one or a few explicit solvent molecules are still necessary in order to obtain reasonable results or where it is even required to include the COSMO-RS free energy functional in energy and gradient calculation upon structure optimization. Application examples for the presented workflows out of the area of polymerization chemistry will be given.

## Mechanistic aspects of high temperature reactions of acetonitrile

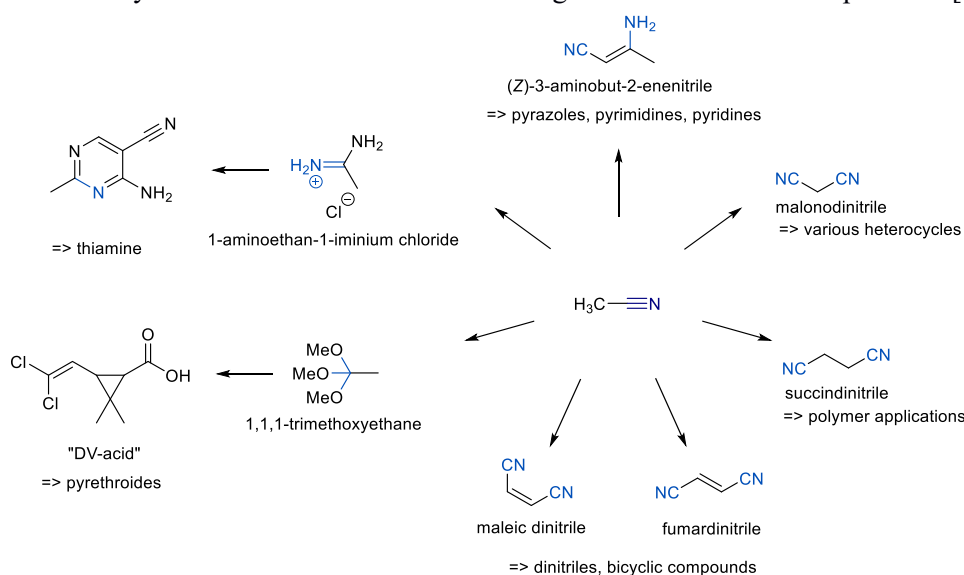
Hanns Jörg Freund<sup>2</sup>, Wolfgang Hieringer<sup>2</sup>, Nichola McCann<sup>1</sup>

Christoph Taeschler<sup>1</sup>, Peter Wasserscheid<sup>2</sup>, Gizem Zoludomir<sup>2</sup>

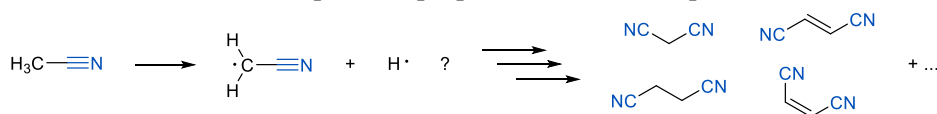
<sup>1</sup>Lonza Ltd, Lonzastrasse, 3930 Visp, Switzerland

<sup>2</sup>Friedrich-Alexander Universität Erlangen-Nürnberg, Schloßplatz 4, 91054 Erlangen, Germany

Nitriles are essential intermediates used in the pharma, food and agrochemical industry as well as in material sciences. Acetonitrile is one basic example of this class of compounds that can not only serve as solvent but also as starting material for numerous products [1].



Some of these products are accessible by high temperature reactions involving acetonitrile. In order to gain more fundamental insights into these types of reactions, experimental and computational results were compared to propose mechanistic aspects.



[1] a) P. Pollak, G. Romeder, F. Hagedorn, H.-P. Gelbke, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, **2000**. b) G. Moine, H.-P. Hohmann, R. Kurth, J. Paust, W. Hähnlein, H. Pauling, B. J. Weimann, B. Kaesler, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, **2000**. c) S. C. DeVito, in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., **2000**.



## Digging deep into binding modes in protein-ligand-complexes by quantum chemistry

**Michael E. Beck<sup>1</sup>**

<sup>1</sup> *Bayer AG, Division Crop Science/ Alfred-Nobel-Str. 50 / 40789 Monheim am Rhein*

Rational design of new active ingredients for pharmaceutical or agricultural use has become routine in industrial research. Almost all virtual screening and other computational high throughput methods are, for reasons of computational efficiency, based on classical mechanics, i.e. force field approaches, or are based on heuristics. Useful as these approaches are, the insights into the actual nature of binding are limited by approximations inherent to the respective approaches. With advances in computing power as well as advances in methodology, methods putting less approximate physics into the equation gain attractiveness.

Applications of quantum theory for understanding ligand protein interactions are today still limited to low throughput, and are thus only rarely used in industrial applications.

Following up on work from an earlier contribution [1], this talk exemplifies, how quantum chemistry can help to dig deeper into the way of how ligands and their protein targets interact. This knowledge further contributes to the understanding of binding modes and thus to rational design. As an example, a class of agrochemicals is discussed, in terms of efficacy, selectivity and specificity.

- [1] M.E. Beck, O. Gutbrod, S. Matthiesen, *Chemphyschem* **16(13)**, 2760 (2015).  
doi: 10.1002/cphc.201500341

**The use of scoring functions for structure-based drug discovery.****Marcel L. Verdonk***Astex Pharmaceuticals, 436 Cambridge Science Park, Milton Road, Cambridge CB4 0QA,  
United Kingdom*

Scoring functions provide an estimate of the quality of a binding pose of a ligand bound to a protein, and have been used in structure-based drug discovery for decades. These functions make significant approximations, but are fast enough to allow interactive visualisation and to drive protein-ligand docking applications. We will give a short historical summary of scoring functions, discuss the key challenges, and provide a perspective on how these functions are used within the pharmaceutical industry. Additionally, we present our own efforts in this field in terms of the development of novel knowledge-based scoring functions and docking algorithms. Finally, we will illustrate how scoring functions, and the applications and infrastructure we have built around them, impact on our fragment-based drug discovery projects.

## Free Energy Calculations in Drug Design

**Thomas Fox**

*Computational Chemistry, Medicinal Chemistry,  
Boehringer Ingelheim Pharma GmbH & Co. KG, 88397 Biberach, Germany*

The free energy of binding of a ligand to its target is an important optimization parameter in drug design, thus, its accurate prediction is highly desirable. Due to methodological advances and increased computer power, thermodynamic integration (TI) calculations can now be used to obtain relative free energies of binding of ligands in a timescale comparable to synthesis.

To make these studies – especially for larger set of ligands – possible, we automated the setup procedure: starting from user defined binding modes, the procedure decides which ligands to connect via a perturbation based on maximum common substructure criteria and produces all necessary parameter and input files for free energy calculations in with the AMBER MD simulation package.

We will present a number of examples to assess the performance and applicability of free energy calculations in a drug design context.

## Industrial Applications of First-Principles Modelling to Obtain Quality Measures for Screening of Catalyst Materials

Glenn Jones

*Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading, Oxfordshire, UK RG49ND*

Over the last two decades first-principles calculations have leveraged algorithm development and increased computational power to enable detailed screening studies of materials candidates to be undertaken. Central to this approach is to identify a quality measure and series of numerical descriptors which characterise the quality of a candidate material. These descriptors vary for the application in question and due to their semi-quantitative nature can often be open to debate. When these simplified descriptor based models are coupled with databases (in the cases presented generated computationally) the power of first principles screening can be unlocked.

This presentation will discuss the background of this approach for catalyst materials screening, where the quality measure is often relative activity or selectivity i.e. properties that rely on a kinetic model that capture the essence of a reaction in question. Secondary quality descriptors can also be introduced that allow, stability or cost (for example) to be probed. Following on from an introduction several examples from past and recent applications within JM will be illustrated. These examples will show, that whilst we cannot say precisely what a new catalysts should be (given all of the experimental parameters involved in the preparation), we can go a long way towards reducing phase space and therefore have a tangible influence on the development of new catalyst materials.

The final part of the presentation will briefly discuss some of the open challenges we are working on. In terms of screening this can involve adding more complexity to the models; this could be in the form of metal support interactions and particle size effects or moving towards a more holistic predictive model, where materials properties, porosity, and reactor design are coupled and optimised together.

### Selected References:

- [1] M. Sarwar, C. Cooper, L. Briquet, A. M. Ukpong, C. B. Perry, G. Jones, Atomic-Scale Modelling and its application to Catalytic Materials Science, Johnson Matthey Technology Review, (2015).
- [2] S. W. Hoh, L. Thomas, G. Jones, D. J. Willock, A density functional study of oxygen vacancy on  $\alpha\text{-Fe}_2\text{O}_3(0001)$  surface and the effect of supported Au nanoparticles. Res. Chem. Intermediat., doi: 10.1007/s11164-015-1984-7 (2015).
- [3] J. Yates, G.H. Spikes and G. Jones Platinum-Carbide Interactions: Core-shells for catalytic use. Physical Chemistry Chemical Physics, **17** (6), 4250 (2015).
- [4] G. Jones, The origin of catalytic activity in sponge Ni catalysts for the hydrogenation of carbonyl compounds, Accepted Catalysis Structure and Reactivity, **1** (2), 78-87, (2015).
- [5] N. Acerbi, S.C.E Tsang, G.Jones, S. Golunski, P.Collier, Rationalisation of interactions in precious metal/ceria catalysts using the d-band center model, Angewandte Chemie International, **52**, 7737-7741 (2013).
- [6] G. Jones, J. Kleis, M. P. Andersson, F. Abild-Pedersen, T. Bligaard, J. K. Nørskov, I. Chorkendorff, J. G. Jakobsen, S. S. Shim, S. Helveg, B. Hinnemann and J. Sehested, First Principles Calculations and Experimental Insight Into Methane Steam Reforming Over Transition Metal Catalysts. Journal of Catalysis, Volume **259**, 147-160 (2008).

## **A Complete Reaction Mechanism for Standard and Fast Selective Catalytic Reduction of Nitrogen Oxides on low coverage VOx/TiO<sub>2</sub>(001) catalysts**

**Logi Arnarson<sup>1,2</sup>, Hanne Falsig<sup>2</sup>, Søren B. Rasmussen<sup>2</sup>, Jeppe V. Lauritsen<sup>1</sup> and Poul Georg Moses<sup>2\*</sup>**

<sup>1</sup>*Interdisciplinary Nanoscience Center, Aarhus University, DK-8000 Aarhus C, Denmark*

<sup>2</sup>*Haldor Topsøe A/S, Haldor Topsøes Allé 1, DK-2800 Kongens Lyngby, Denmark*

Emission of nitrogen oxides (NO<sub>x</sub>) is a serious issue in our society today. During combustion of fossil fuels, air is heated to very high temperatures and NO<sub>x</sub> is formed. NO<sub>x</sub> consists of ~90% NO and ~10% NO<sub>2</sub> which have negative effect on the environment by e.g. smog formation in big cities and acid rain formation. The standard SCR reaction,  $4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$ , and fast SCR reaction,  $2\text{NO} + 2\text{NO}_2 + 4\text{NH}_3 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$ , are key reactions in the current technology for emission control of diesel engines. The most widely used catalyst for the SCR reaction is Vanadium deposited on TiO<sub>2</sub> anatase and promoted with Tungsten (VO<sub>x</sub>/WO<sub>x</sub>/TiO<sub>2</sub>) which reduces NO<sub>x</sub> effectively in the temperature range 200-500°C.

We present a Density Functional Theory (DFT) study of the full catalytic mechanism describing both the Standard and the Fast selective catalytic reduction (SCR) reactions in their correct stoichiometric form on a vanadia titania based catalyst model. It consists of two cycles, NO-activation cycle and Fast SCR cycle that share the same reduction part but use NO+O<sub>2</sub> and NO<sub>2</sub> respectively for the reoxidation. The stoichiometry of the Standard SCR reaction is obtained by coupling the two cycles and the stoichiometry of the Fast SCR reaction is represented by the Fast SCR cycle. We establish structures and energetics for each elementary reaction allowing us to calculate the rate for the two reactions by microkinetic modeling. We find at low temperatures the rate for the Standard SCR reaction is determined by H<sub>2</sub>O formation and desorption as neither NO nor O<sub>2</sub> reacts exothermically with the reduced site prior to H<sub>2</sub>O desorption. On the contrary NO<sub>2</sub> reacts directly with the reduced site resulting in higher rate for the Fast SCR reaction at low temperatures. The rate for the two reactions is the same at higher temperatures as the rate determining step is in the reduction part which is common to both reactions.

## Investigations on SiO<sub>2</sub> glasses to answer the question: “What is a 'good' glass structure?”

M. Letz<sup>1</sup>, C. Scherrer<sup>1,2</sup>

<sup>1</sup>*SCHOTT AG, Hattenbergstr. 10, Mainz 55122, Germany*

<sup>2</sup>*Max Planck Institute for Polymer Research, Ackermannweg 10, Mainz 55128, Germany*

The biggest hurdle to widely use atomic scale techniques on glasses is the lack of knowledge of a representative glass structure. While crystal structures are periodic and unique, glass structures miss long range order and depend on details of the thermal history. It is easy to create a random, disordered structure in a computer simulation, it is also possible to create disordered structures which resemble all observable details of the experimental static structure factor. However; this is not enough for a 'good' glass structure. In the present work [1] we restrict our self to small structures (< 200 atoms) and use as a criterion for a 'good' glass structure the detailed match of the phonon band structure with experimental observation. Based on that we calculate amorphous structures using a combined approach of classic molecular dynamics and ab initio calculations. The use of small systems allows long time equilibration runs and a quench to zero temperature starting from a temperature at which the system shows clearly glassy dynamics on logarithmic time scales in its two-time correlation functions with a structural relaxation up to six orders of magnitude larger than microscopic vibrations. A final relaxation with ab initio methods turns out to be essential to obtain a phonon density of states which matches experimental observations. The low temperature thermodynamics of a solid, for temperatures below the Debye temperature, depend mainly on the thermal occupation of phonon bands. The correct low temperature thermodynamics is shown by calculating the temperature dependent Grüneisen parameters and following from that the temperature dependent thermal expansion. Using two different classical potentials as a starting point the sign change of the thermal expansion of fused silica around 160K is correctly obtained from 9 out of 10 independent simulation runs.

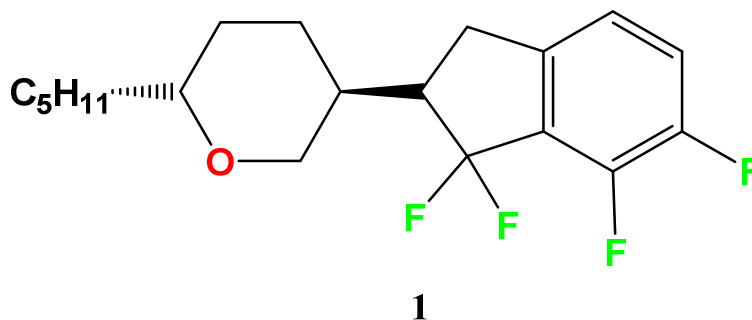
- [1] C. Scherrer, J. Horbach, F. Schmid, M. Letz, *J. Non-Cryst. Sol.* **468**, 82 (2017).

## Increasing the Polarity of Liquid Crystals – Synthesis and Computations

Matthias Bremer<sup>1</sup>

<sup>1</sup>*Merck KGaA, Performance Materials, Liquid Crystals Chemistry Research  
Frankfurterstr. 250, 64293 Darmstadt, Germany*

Abstract: Tetrafluoroindanes **1** that contain a tetrahydropyranyl ring instead of a cyclohexane ring exhibit record polarities combined with relatively low rotational viscosities and acceptable clearing points. The synthetic approach to these molecules will be described together with a computational study on their properties and mechanistic details.



**Automated high-throughput DFT simulations for the development of  
enhanced energy storage and energy conversion materials**

**Thomas Eckl<sup>1</sup>, Anika Marusczyk<sup>1</sup>, Benedikt Ziebarth<sup>1</sup>, Lothar Kunz<sup>1</sup>**

*<sup>1</sup>Corporate Sector Research and Advance Engineering, Robert Bosch GmbH, Robert-  
Bosch-Campus 1, 71272 Renningen, Germany*

The transformation from combustion engines to E-mobility is one of the key challenges within the next years. Providing batteries and fuel cells which allow for a long driving range, which are affordable and save, as well as durable, requires specially designed materials. Screening for new and improved materials by means of an automated simulation infrastructure, huge data bases and machine learning is more and more becoming a standard tool in industrial research. Here we will present the general framework and specific approaches used, as well as examples of new insights gained from our ab-initio DFT simulations.





# CONTRIBUTED TALKS



## Modeling of Two-Dimensional (2D) Materials: Influence of Chemical Modifications

Thaneshwor P. Kaloni<sup>1</sup>, Laura S. Ferch<sup>1</sup>, Michael S. Freund<sup>1,2</sup>, Georg Schreckenbach<sup>1</sup>

<sup>1</sup>Department of Chemistry, University of Manitoba, Winnipeg, MB, Canada.

<sup>2</sup>Department of Chemistry, Florida Institute of Technology, Melbourne, FL, USA.

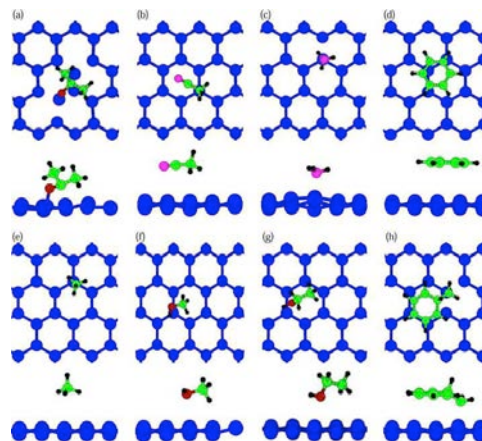
Quantum chemistry methods has reached maturity for a number of applications, allowing the non-specialist to use its tools in a productive manner, while being very much frontier areas with active research and development in other aspects. Amongst the latter is the computational **modeling of materials**. Materials modeling is a frontier area chiefly because of the *complexity* involved that is generally much higher than for more traditional studies on isolated molecules. Thus, it becomes essential to choose computational models that capture the essence of the physics and chemistry of the system of interest, yet remain tractable at an appropriate computational level.

The novel class of **2-dimensional (2D) materials** is placed at the interface of physics, chemistry and materials science. In order to fully exploit these unique materials, it is desirable to be able to *tune their properties*, such as the band gap. Chemistry plays a unique role in this respect, in that *chemical modifications* allow for the desired versatility in modifying properties. [1]

For a variety of 2D materials (silicene, germanene, stanene etc.) the influence on structure and electronic structure/ band structure of the choice of material, electric fields, and chemical substitutions (small organic molecules and heavy metals) have been studied. Both, **periodic boundary conditions** and **cluster models** have been applied. These types of computational models are complementary; each approach has its own unique advantages in characterizing materials.

[1] T. P. Kaloni, G. Schreckenbach, M. S. Freund, U. Schwingenschlögl, *Phys. Status Solidi – Rapid Res. Lett.* **10**, 133 (2016).

[2] T. P. Kaloni, G. Schreckenbach, M. S. Freund, *J. Phys. Chem. C* **118**, 23361 (2014).



Organic molecules adsorbed onto silicene, top and side views. (Optimized structures; periodic calculations.) [2]

## Local Correlation for Crystalline Solids: Dual Basis Sets by Projection in the Reciprocal Space.

**Lorenzo Maschio<sup>1</sup>**

<sup>1</sup> *Chemistry Department, University of Torino, Via P. Giuria 5, Torino, Italy;  
e-mail: lorenzo.maschio@unito.it*

In the quantum-chemical treatment of crystalline solids, methods based on local atom-centered (gaussian) functions have certain advantages with respect to the plane wave approach, such as a more efficient screening of exchange integrals and consequently faster code for Hartree-Fock and hybrid functionals.

However, the problem of choosing a basis set is a major one, as: (i) molecular basis sets cannot be adopted as such, since they can give rise to linear dependencies and severe numerical instabilities in the infinite Ewald summations; (ii) standardized basis sets for solids do not exist, also because of the difficulty posed by the many different chemical situations possible in solids, as the same atomic species can be involved in ionic, covalent or metallic bonding situations. Such problems become even more severe when electron correlation methods are to be used, as large basis sets with diffuse functions are required.

In this contribution I will present a newly developed dual basis set scheme which allows to handle basis sets up to augmented quintuple-zeta at the post-HF level for crystalline solids. The approach is based on the extension to periodic systems of the dual basis set approach of Liang and Head-Gordon[1]. In essence, the SCF and localization are performed in a small basis and then the result is projected in a larger basis, where the correlation calculation is performed. The small basis is not required to be a subset of the large one, and no diagonalization of the Fock matrix in the large basis is needed. The only constraint is that the small basis is good enough (*e.g.* triple-zeta) to represent the occupied manifold. The method has been implemented in the CRYSCOR[2,3] program, which enables local correlation methods [4] for nonconducting crystalline solids.[5]

[1] W. Liang, M. Head-Gordon, *J. Phys. Chem. A*, **108**, 3206-3210 (2004).

[2] L. Maschio, D. Usvyat, C. Pisani, F. Manby, S. Casassa, M. Schütz, *Phys. Rev. B*, **76**, 075101 (2007).

[3] L. Maschio, *J. Chem. Theory Comput.* **7**, 2818-2830 (2011).

[4] M. Schütz, G. Hetzer, H.-J. Werner, *J. Chem. Phys.* **111**, 5691 (1999).

[5] M. Schütz, L. Maschio, A. Karttunen, D. Usvyat, *J. Phys. Chem. Lett.* **121**, 9312–9324 (2017).

## Density functional theory for periodic systems using density fitting and continuous fast multipole method.

**Marek Sierka<sup>1</sup>, Asbjörn Burow<sup>2</sup>, Roman Łazarski<sup>1</sup>, Lukáš Grajciar<sup>1</sup>**

<sup>1</sup>*Otto Schott Institute of Materials Research, Friedrich Schiller University of Jena,  
Löbdergraben 32, D-07743 Jena, Germany*

<sup>2</sup>*Department of Chemistry, University of Munich (LMU), Butenandtstrasse 7, D-81377  
Munich, Germany*

An implementation of Kohn–Sham density functional theory using Gaussian-type orbitals as basis functions is reported that treats molecular and periodic systems of any dimensionality on an equal footing. Its key component is a combination of density fitting/resolution of identity (DF) approximation and continuous fast multipole method (CFMM) applied for the electronic Coulomb term [1,2]. The inherent limitations of DF, i.e., significant memory demand and  $O(N^3)$  scaling with the system size are circumvented using a low-memory iterative density fitting (LMIDF) method [3]. It is based on a combination of CFMM and a preconditioned conjugate gradient solver applied for an iterative solution of the DF problem. Computational efficiency and favorable scaling behavior of our implementation approaching  $O(N)$  for the formation of the Kohn–Sham matrix and calculation of energy gradients is demonstrated for various molecular and periodic systems, with the largest one containing several thousands of atoms.

[1] R. Łazarski, A. Burow, M. Sierka, L. Grajciar, *J. Comput. Chem.* **37**, 2518 (2016).

[2] R. Łazarski, A. Burow, M. Sierka, *J. Chem. Theory Comput.* **11**, 3029 (2015).

[3] L. Grajciar, *J. Comput. Chem.* **36**, 1521 (2015).

**Adsorption of Glycerol and Dihydroxyacetone on CaO and MgO Surfaces****J. B. L. Martins<sup>1</sup>, A. L. Almeida<sup>2</sup>, Ademair D. M. Neto<sup>1</sup>, Junio C. F. Silva<sup>1</sup>**

<sup>1</sup>*Universidade de Brasília (UnB), Instituto de Química, CP 04478, Brasília, DF, 70904-970, Brazil*

<sup>2</sup>*Universidade do Estado da Bahia (UNEB), Departamento de Ciências Exatas e da Terra, Estrada das Barreiras, s/n, Cabula, Salvador, BA, 41195-001, Brazil*

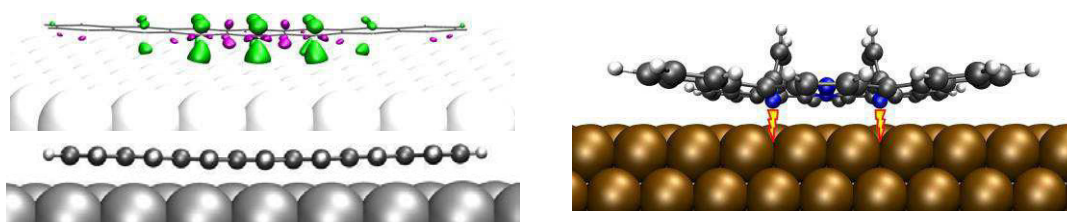
Glycerol, propanetriol, is one of the byproducts of biodiesel production. Due to the production of this polyalcohol exceeds its demand, strategies and alternatives of use of glycerol have been studied. Among these alternatives is the reform of glycerol with water vapor. Ab initio calculations of large cluster models have been performed in order to study glycerol and dihydroxyacetone adsorption at the three-fold coordinated adsorption site on pure MgO(001) and CaO surfaces. The geometric parameters of the adsorbed glycerol and dihydroxyacetone molecules were optimized to analyze binding energies, charge transfer, and the geometry through bonding distances, angles and dihedral. We have used Mulliken population analysis, electrostatic and natural atomic charge methods in order to evaluate charge distribution and transfer. The descriptors used are the electron populations of different types, and the number of the unpaired electrons of atom in ground state. The investigations on the model systems, for the adsorption of glycerol on MgO surface, showed that the striking directionality and affinity toward electron density donors. An NBO analysis indicates that the second-order orbital interaction plays an important role in stabilizing the directional bond.

## Electronic Structure of Molecules at Metal Surfaces: Recent Results on Adsorbed Organic Molecules and Coordination Compounds

Wolfgang Hieringer

*Theoretical Chemistry, University of Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany*

Molecules adsorbed on atomically well-defined single-crystal metal surfaces are important building blocks for the bottom-up fabrication of functional nanostructures. In particular, adsorbed transition metal coordination compounds can exhibit interesting electronic properties at metal substrates. We use quantum chemical methods to analyze the electronic structure and spectroscopic properties of “large” organic molecules as well as coordination compounds on metal surfaces. In this contribution, we discuss recent examples of large oligophenylene rings [1] and acenes [2,3] as well as porphyrins [4,5] that are demonstrated to undergo unexpected electronic interactions with metal substrates.



In particular, we show that dispersion-corrected density functional theory calculations predict an unprecedented “inverted” structure of free-base porphyrin on a copper surface that is stabilized by a combination of electronic and van der Waals dispersion effects. [5] The metal surface is also shown to have a pronounced effect on the reactivity of the central metal in related coordination compounds.

- [1] M. Chen, J. Shang, Y. Wang, K. Wu, J. Kuttner, G. Hilt, W. Hieringer, J. M. Gottfried, *ACS Nano* **11**, 134 (2017).
- [2] N. Schmidt, J. Wenzel, A. Dreuw, R. H. Fink, W. Hieringer, *J. Chem. Phys.* **145**, 234307 (2016).
- [3] M. Zugermeier, M. Gruber, M. Schmid, B. P. Klein, L. Ruppenthal, P. Müller, R. Einholz, W. Hieringer, R. Berndt, H. F. Bettinger, J. M. Gottfried, *submitted*.
- [4] W. Hieringer, K. Flechtner, A. Kretschmann, K. Seufert, W. Auwärter, J. V. Barth, A. Görling, H.-P. Steinrück, J. M. Gottfried, *J. Am. Chem. Soc.* **133**, 6206 (2011).
- [5] M. Lepper, J. Köbl, T. Schmitt, M. Gurrath, A. de Siervo, M. A. Schneider, H.-P. Steinrück, B. Meyer, H. Marbach, W. Hieringer, *submitted*.

## Explaining organic chemistry at surfaces with energy decomposition analysis

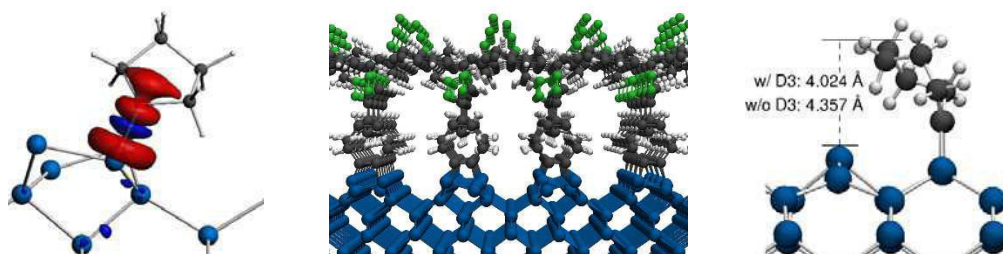
Lisa Pecher, Ralf Tonner

*Fachbereich Chemie and Material Sciences Center, Philipps-Universität Marburg,  
Hans-Meerwein-Straße 4, 35032 Marburg, Germany*

Hybrid organic-inorganic interfaces are of current interest to the scientific community due to their large application range (e.g. OLEDs) but also for the unsolved questions regarding the details of charge transfer processes. An accurate description of interface structure, energetics and reactivity in the construction of these materials is therefore required.[1] Selected challenges for theory in this field are the understanding of (i) adsorption dynamics, (ii) surface bonding and (iii) on-surface reactivity of organic molecules.

We transferred the well-established energy decomposition analysis (EDA) method[2] from molecular systems to extended systems in the framework of density functional theory (pEDA)[3] to address these questions for organic functionalization of silicon surfaces.

By exploiting the advantages of both plane wave based approaches and local basis sets, we could shed light on the questions outlined above. The pEDA could resolve the question regarding the balance in surface bonding (physisorption/chemisorption) for the precursor state of ethene on Si(001), which is a prototype system for unsaturated organic adsorbates.[4] This investigation helped us to reveal the adsorption dynamics of cyclooctyne - a highly relevant interface building block where accurate description of dispersion interactions is required to explain the experimental observations.[5] The understanding for the on-surface reactivity of tetrahydrofuran, a model system for functionalized interface building blocks, could then ultimately be found in textbook organic chemistry after careful pEDA analysis.[6]



*Surface bonding (left) and dispersion-induced bending (right) as two approaches to understand hybrid organic-inorganic interfaces (middle).*

- [1] a) G. Mette, M. Dürr, R. Bartholomäus, U. Koert, U. Höfer, *Chem. Phys. Lett.* **556**, 70 (2013); b) B. Shong, T. E. Sandoval, A. M. Crow, S. F. Bent, *J. Phys. Chem. Lett.* **6**, 1037 (2015); c) G. Mette, M. Reutzel, R. Bartholomäus, S. Laref, R. Tonner, M. Dürr, U. Koert, U. Höfer, *ChemPhysChem* **15**, 3725 (2014); d) M. Reutzel, N. Münster, M. A. Lipponer, C. Langer, U. Höfer, U. Koert, M. Dürr, *J. Phys. Chem. C* **120**, 26284 (2016). [2] a) K. Morokuma, *J. Chem. Phys.* **55**, 1236 (1971); b) T. Ziegler, A. Rauk, *Inorg. Chem.*, **18**, 1558 (1979); F. M. Bickelhaupt, E. J. Baerends, in *Rev. Comput. Chem.*, Vol. 15 (Eds.: K. B. Lipkowitz, D. B. Boyd), Wiley-VCH, (2000). [3] M. Raupach, R. Tonner, *J. Chem. Phys.* **142**, 194105 (2015); [4] J. Pecher, R. Tonner, *ChemPhysChem* **18**, 34 (2017); [5] J. Pecher, C. Schober, R. Tonner, *Chem. - Eur. J.* **23**, 5459 (2017); [6] L. Pecher, S. Laref, M. Raupach, R. Tonner, in preparation.



## Crystal structure prediction of inorganic-organic coordination polymers

Antti J. Karttunen<sup>1</sup>, J. Heiska<sup>1</sup>, M. Nisula<sup>1</sup>, J. Linnerna<sup>1</sup>, M. Karppinen<sup>1</sup>

<sup>1</sup>*Department of Chemistry and Materials Science, Aalto University, Finland*

Atomic/molecular layer deposition (ALD/MLD) offers a highly controllable way to synthesize crystalline inorganic-organic coordination polymer (CP) thin films.[1] The fabricated materials could also be considered as metal-organic framework (MOF) thin films and they show a layered structure with inorganic-organic interfaces. We have recently investigated lithium aryloxide CP thin films fabricated by ALD/MLD (dilithium 1,4-benzenediolate,  $\text{Li}_2[\text{p-C}_6\text{H}_4\text{O}_2]$ ).[2] The atomic-level structure of the CP thin films was solved by combining X-Ray diffraction and infrared spectroscopic studies with Density Functional Theory (DFT) calculations. In this case, a related bulk crystal structure facilitated the structure solution of the CP thin film. Using 2-aminoterephthalic acid (TPA- $\text{NH}_2$ ) as the organic building block also results in a crystalline CP thin film. However, no previous structural information from related bulk materials is available and the structure must be solved from scratch. We used the USPEX evolutionary crystal prediction approach together with DFT calculations to predict the atomic-level structure.[3] When we define the inorganic-organic CP as a pseudo-molecular structure with rigid building blocks, the USPEX structure search works in a highly efficient manner.

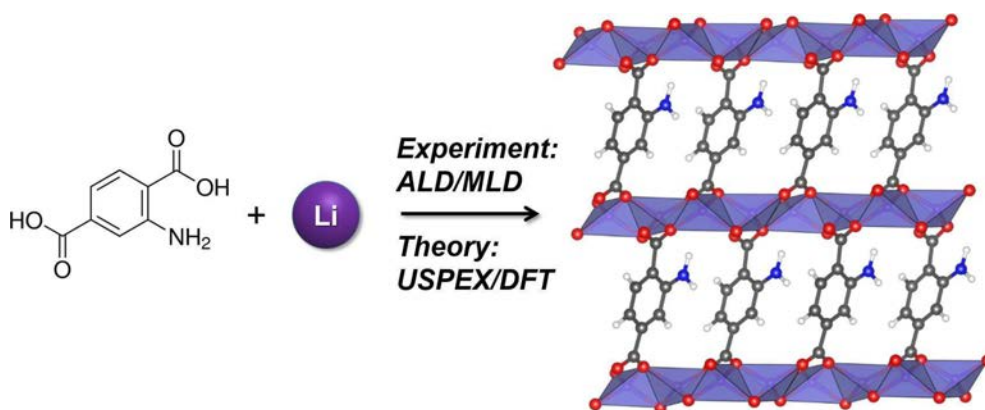


Figure 1: The predicted structure of  $\text{Li}_2\text{-TP-NH}_2$  coordination polymer (USPEX/DFT)

- [1] E. Ahvenniemi, M. Karppinen, *Chem. Mater.* **56**, 6260 (2016).
- [2] M. Nisula, J. Linnerna, A. J. Karttunen, M. Karppinen, *Chem. Eur. J.* **23**, 2988 (2017).
- [3] A. R. Oganov, A. O. Lyakhov, M. Valle, *Acc. Chem. Res.* **44**, 227 (2011)



## Transition Metal Doped Magnetic Zn<sub>12</sub>S<sub>12</sub> Nanoparticles

Iker Ortiz de Luzuriaga<sup>1</sup>, and Jon M. Matxain<sup>1</sup>

<sup>1</sup>*Kimika Fakultatea, Euskal Herriko Unibertsitatea/University of the Basque Country (UPV/EHU) and Donostia International Physics Center (DIPC), PK 1072, 20080, Donostia, Euskadi.*

Nanoparticles of semiconducting materials are gaining attention due to their electronic, optical and catalytic properties. In this work, we focus on small hollow ZnS nanoclusters, concretely, on Zn<sub>12</sub>S<sub>12</sub>, characterized previously both theoretically [1] and experimentally [2]. The cavity inside the structure allows for the design of endohedral compounds resembling those of C<sub>60</sub>. Transition metal doped compounds are very sound compounds due to their magnetic properties. However, previous studies [3, 4] predicted that the first-row [TM@Zn<sub>12</sub>S<sub>12</sub>](#) endohedral compounds were unstable compared to the surface compounds, where the TM atom was located at the surface of the compound. The transition states connecting both structure families were calculated, and the estimated half-life of these compounds were seen to be very small for experimental detection.

However, in the mentioned previous works dispersion effects were not taken into account. In order to check for the influence of dispersion, several functionals were tested and compared to MP2, which is known to account for these effects. All these calculations were carried out using the def2-TZVPP basis set and a smaller DZP quality basis set combined with the SKBJ core potentials. PBE functional, using the empirical D3BJ term for dispersion, combined with the small basis set, compared pretty good with MP2/def2-TZVPP results, and were further used in this study. We recalculated the relative stability of the endohedral compounds vs the surface ones, and recalculated the barriers separating both minima, using the new methodology. Surprisingly, dispersion plays a very important role for such metals with the 4s3d shell half-filled or completely filled. From the magnetic point of view, the endohedral Cr(<sup>7</sup>S)[@Zn<sub>12</sub>S<sub>12</sub>](#) compound was the most interesting case, since the endohedral compound was predicted to be the most stable one with a barrier towards the surface compound of roughly 20 kcal/mol. Further Ab Initio Born-Oppenheimer Molecular Dynamics simulations at 300K confirmed this stability. According to these results, we believe that these materials could be experimentally detectable, and would be very interesting compounds for applications such as spintronics.

### Bibliography

- [1] S. Hamad, C. R. A. Catlow, E. Spano, J. M. Matxain, J. M. Ugalde, *J. Phys. Chem. B*, **109**, 2703-2709 (2005).
- [2] A. Burnin, E. Sanville, J. J. BelBruno, *J. Phys. Chem. A*, **109**, 5026-5030 (2005).
- [3] E. Jimenez-Izal, J. M. Matxain, M. Piris, J. M. Ugalde, *J. Phys. Chem. C*, 2011, **115**, 7829-7835 (2011).
- [4] E. Jimenez-Izal, J. M. Matxain, M. Piris, J. M. Ugalde, *Comput.*, **1**, 31-45 (2013).

## The name is bond - Hydrogen bond

Thomas D. Kühne<sup>1,2</sup>

<sup>1</sup>*Dynamics of Condensed Matter, Department of Chemistry, University of Paderborn,  
Warburger Str. 100, D-33098 Paderborn, Germany*

A new energy decomposition analysis method for periodic systems based on absolutely localized molecular orbitals is presented [1, 2]. In combination with an accurate and efficient technique to compute nuclear quantum effects and the previously developed second generation Car-Parrinello molecular dynamics approach [3, 4, 5], this not only allows for quantum molecular dynamics simulations on previously inaccessible time and length scales, but also provide unprecedented insights into the nature of hydrogen bonding between water molecules. The effectiveness of this new combined approach is demonstrated on liquid water, ice and the water/air interface [6]. Our simulations reveal that although a water molecule forms, on average, two strong donor and two strong acceptor bonds, there is a significant asymmetry in the energy of these contacts. We demonstrate that this asymmetry is a result of small instantaneous distortions of hydrogen bonds and show that the distinct features of vibrational and X-ray absorption spectra originate from molecules with high instantaneous asymmetry [7, 8]. Moreover, we found a striking correlation between the covalency of a hydrogen bond and the anisotropy of the proton magnetic shielding tensor, which enables to experimentally determine the strength and charge transfer of hydrogen bonding by NMR [9].

- [1] T. D. Kühne and R. Z. Khaliullin, *Nature Comm.* 4, 1450 (2013).
- [2] R. Z. Khaliullin and T. D. Kühne, *Phys. Chem. Chem. Phys.* 15, 15746 (2013).
- [3] T. D. Kühne and M. Krack and F. Mohamed and M. Parrinello, *Phys. Rev. Lett.* 98, 066401 (2007).
- [4] T. D. Kühne, *WIREs Comput. Mol. Sci.* 4, 391 (2014).
- [5] C. John and T. Spura and S. Habershon and T. D. Kühne, *Phys. Rev. E* 93, 043305 (2016).
- [6] J. Kessler and H. Elgabarty and T. Spura and K. Karhan and P. Partovi-Azar and T. D. Kühne, *J. Phys. Chem. B* 119, 10079 (2015).
- [7] R. Z. Khaliullin and T. D. Kühne, *J. Am. Chem. Soc.* 136, 3395 (2014).
- [8] C. Zhang and R. Z. Khaliullin and D. Bovi and L. Guidoni and T. D. Kühne, *J. Chem. Phys. Lett.* 4, 3245 (2013).
- [9] H. Elgabarty and R. Z. Khaliullin and T. D. Kühne, *Nature Commun.* 6, 8318 (2015).

## High-throughput screening of drug-membrane thermodynamics

**Roberto Menichetti<sup>1</sup>, Kiran H. Kanekal<sup>1</sup>, Kurt Kremer<sup>1</sup>, Tristan Bereau<sup>1</sup>**

<sup>1</sup>*Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany*

The partitioning of small molecules in cell membranes—a key parameter for pharmaceutical applications—typically relies on experimentally-available bulk partitioning coefficients. Computer simulations provide a structural resolution of the insertion thermodynamics via the potential of mean force, but require significant sampling at the atomistic level. Here, we introduce high-throughput coarse-grained molecular dynamics simulations to screen thermodynamic properties. This application of physics-based models in a large-scale study of small molecules establishes linear relationships between partitioning coefficients and key features of the potential of mean force. This allows us to predict the structure of the insertion from bulk experimental measurements for more than 400,000 compounds. The potential of mean force hereby becomes an easily accessible quantity—already recognized for its high predictability of certain properties, e.g., passive permeation. Further, we demonstrate how coarse graining helps reduce the size of chemical space, enabling a hierarchical approach to screening small molecules.

## New insights into nitrogenase: QM/MM broken-symmetry DFT studies of FeMoco and model compounds

Ragnar Bjornsson<sup>1</sup>, Barði Benediktsson<sup>1</sup>, Albert Þ. Þórhallsson<sup>1</sup>

<sup>1</sup>Science Institute-University of Iceland, Dunhagi 3, 107 Reykjavík, Iceland

Nitrogenase is one of the most fascinating enzymes in Nature, being responsible for all biological nitrogen reduction. Despite decades of research it remains the enzyme in bioinorganic chemistry whose mechanism is the most poorly understood. The MoFe protein of nitrogenase contains 2 metal-sulfur clusters: the P-cluster that receives electrons from the Fe protein and shuttles them to FeMoco, an iron-molybdenum-sulfur cluster where N<sub>2</sub> reduction takes place. The resting state of FeMoco (E<sub>0</sub>) has been characterized by crystallography, multiple spectroscopic techniques (XAS, Mössbauer, EPR) and theory (BS-DFT) and its molecular structure can be considered complete while the complex electronic structure, involving 8-metal spin coupling, delocalized electrons and weak metal-metal bonding, is not completely understood yet[1, 2, 3]. Much less is known about the other redox states (E<sub>1</sub>-E<sub>7</sub>) where no crystal structure is available and only limited spectroscopic data but hydrides have been proposed to be present in the early redox states. Theory can contribute a lot to this field although it is vital to compare computations to experimental data, given the imperfect theoretical tools being used and new experimental data on this system is greatly needed.

We have recently created QM/MM models of FeMoco and the P-cluster within a local version of Chemshell in order to go beyond the standard cluster modelling and properly incorporate protein environmental effects. The CHARMM36 forcefield has been used to describe the MM region while broken-symmetry DFT calculations using the TPSSh functional are used to describe the QM region using ORCA. The QM region has been systematically expanded and the convergence of the FeMoco geometry and redox potentials has been analyzed. Analysis of the resting state geometry of the FeMoco cluster reveals how it changes with different spin isomers that leads us to suggest one spin isomer is favored over others: an unusual case of spin coupling being observed in the molecular structure. Additionally we have taken first steps towards characterization of the E<sub>1</sub> and E<sub>2</sub> states and put forward new models for these states that are in agreement with the experimental data available.

Finally we present reaction mechanisms of structural model compounds of FeMoco that show catalysis of many of the same substrates as nitrogenase. The insight gained into these substrates may have relevance for the yet unknown mechanism of nitrogenase [2].

[1] R. Bjornsson, F. A. Lima, T. Spatzal, T. Weyhermüller, P. Glatzel, E. Bill, O. Einsle, F. Neese, S. DeBeer, *Chem. Sci.* **5**, 3096 (2014).

[2] R. Bjornsson, F. Neese, R. R. Schrock, O. Einsle, S. DeBeer, *J. Biol. Inorg. Chem.* **20**, 447 (2015).

[3] R. Bjornsson, F. Neese, S. DeBeer, *Inorg. Chem.* **56**, 1470 (2017).

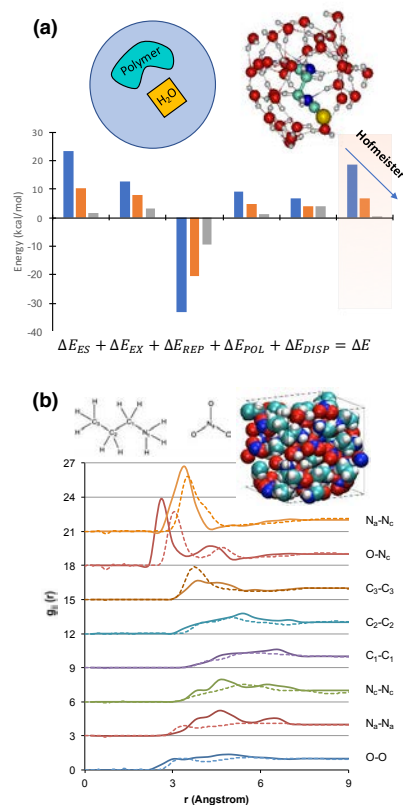
# Quantum Chemical Insights into Polymer Solvation and Hofmeister Effects in Aqueous and Non-Aqueous Environments

Ryan Stefanovic<sup>1</sup>, Kas Gregory<sup>1</sup>, Alister J. Page<sup>1</sup>

<sup>1</sup>Newcastle Institute for Energy and Resources, The University of Newcastle, Callaghan, Australia

We present quantum chemical simulations showing how inorganic salts influence the structure and solvation of polymers in ionic liquids (ILs) and water. Such specific ion or “Hofmeister” effects were established in the 1880s. Despite intense research, our understanding of their origins remains poor. We provide fundamental insights into the origins of specific ion effects, for both aqueous and non-aqueous solvents. We discuss two specific cases:

- (1) **Poly(N-isopropylacrylamide) (PNIPAM) in water/salt mixtures.** We show that the well-known “Hofmeister series” correlates with the relative strengths of the polymer-ion and ion-solvent interactions, and depend primarily on polarization effects (Figure 1a). We also show that trends in specific ion effects are observed without any solvent whatsoever.
- (2) **Polyethylene oxide (PEO) in IL/salt mixtures.** ILs such as propylammonium nitrate are “nanostructured” – the bulk structure features well-defined polar and non-polar domains that arise from the segregation of the ionic and neutral components of the constituent ions (Figure 1b). We show how added salts lead to a change in bulk IL nanostructure, and how, in turn, this change in solvent nanostructure influences the IL-polymer interactions and dissolved polymer structure [1-2].



**Figure 1.** (a) LMOEDA analysis (M06-2X/aug-cc-pVTZ) reveals energetic origins of Hofmeister effects in water. (b) DFTB3-D/MD simulations show nanostructure in ILs and influence of dissolved salts.

[1] M. A. Addicoat, et al, *J. Chem. Theor. Comp.*, **10**, 4633 (2014).

[2] A. J. Page, et al., *Nanoscale*, **6**, 8100 (2014).

## The Past, Present, and Future of Q2MM

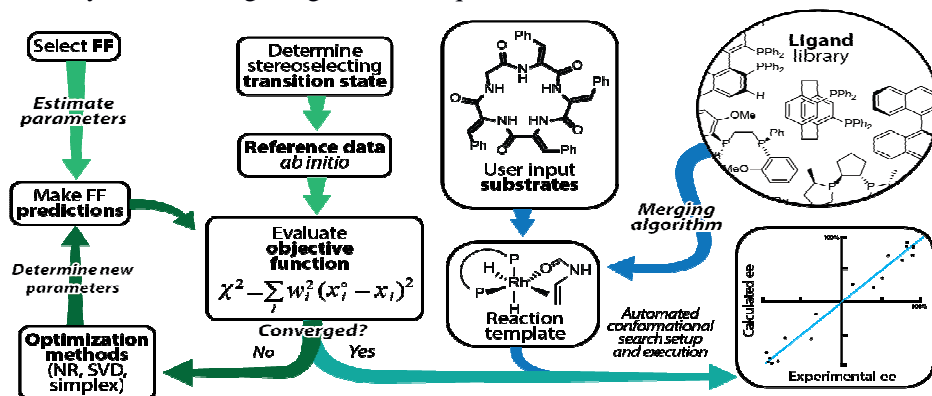
Olaf Wiest<sup>1</sup>, Eric Hansen<sup>1</sup>, Taylor Quinn<sup>1</sup>, Brandon Haines<sup>1</sup>, Jiping Lei<sup>2</sup>,  
Xuhui Huang<sup>2</sup>, Per-Ola Norrby<sup>3</sup>

<sup>1</sup>Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA

<sup>2</sup>Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

<sup>4</sup>Pharmaceutical Sciences, AstraZeneca, Pepparedsleden 1, SE-431 83 Mölndal, Sweden

The further develop of the Quantum Guided Molecular Mechanics (Q2MM) method [1] is presented. Q2MM allows the rapid parameterization of accurate and reaction specific transition state force fields (TSFF) using the approach shown in Fig. 1, left. These TSFFs can be used for fast virtual screening of ligands in enantioselective catalysis (Fig 1, right). The Q2MM and virtual screening codes as well as the TSFFs are available to the community free of charge at [github.com/q2mm](https://github.com/q2mm)



**Figure 1:** Flow scheme for generation of TSFF by Q2MM and application to virtual screening of ligands for enantioselective catalysis.

Application of Q2MM to biomolecular systems such as HMG CoA Reductase (HMGR, Fig 2) is an attractive alternative to QM/MM approaches because it enables long time scale simulations at the transition state, allowing the protein to sample the conformational space and providing insights into the large-scale protein movement that contribute to catalysis



[1] Hansen, E.; Rosales, A.R.; Tutkowski, B.M.; Norrby, P.O.; Wiest, O. *Acc. Chem. Res.*, **49**, 996 (2016).

**Figure 2:** 20  $\mu$ s simulation of hydride transfer TS of HMGR

## Hybrid Molecular Dynamics - hydrodynamics modelling of liquid solutions: whole virus at atomistic resolution

**Dmitry Nerukh<sup>1</sup>, Sergey Karabasov<sup>2</sup>, Elvira Tarasova<sup>3</sup>, Ivan Korotkin<sup>2</sup>,  
Vladimir Farafonov<sup>4</sup>**

<sup>1</sup>*Systems Analytics Research Institute, Aston University, Birmingham, B4 7ET, UK*

<sup>2</sup>*Sch. of Eng. and Mater. Science, Queen Mary University of London, London, E1 4NS, UK*

<sup>3</sup>*Baltic Federal University, A. Nevskogo str. 14, Kaliningrad, 236041, Russian Federation*

<sup>4</sup>*Dept. of Physical Chemistry, Kharkiv University, Svobody Sq. 4, Kharkiv, 61022, Ukraine*

Our novel methodology for modelling liquid molecular systems at very different space and time scales simultaneously with consistent transition between the scales is described. Regions of atomistic representation of the liquid of arbitrary shape and time evolution coexist with fluctuating hydrodynamics environment which in turn is coupled to macroscopic hydrodynamics at larger scales. In the model, the hydrodynamics description is used as an effective boundary condition to close the molecular dynamics solution without resorting to standard periodic boundary conditions. A nominally two-phase liquid model is considered as a representation of the same chemical substance. The ‘phases’ are immersed into each other as ‘fine grains’, the surface tension effects are irrelevant, and both ‘phases’ simultaneously occupy the same control volume. The partial concentrations of the MD ‘phase’ and the hydrodynamics ‘phase’ are equal to  $s$  and  $1-s$ , respectively, where  $s$  is a parameter of the model  $0 \leq s \leq 1$ .  $s$  is a user-defined function of space and time which controls how much atomistic information is required in a particular region of the simulation domain. The approach is implemented in a popular Molecular Dynamics package GROMACS.

As an example, a virus PCV2 is modelled at all-atom resolution for the protein shell of the virus, surrounded by a layer of atomistic water (any model of water such as TIP3P, SPC, etc can be used) that gradually changes to hydrodynamic continuum away from the virus. We analyse the connection between the number of ions inside an empty capsid of PCV2 virus and its stability. We compare the crystallographic structures of the capsids with unresolved N-termini and without them at physiological conditions and show that the structure is preserved. We find that the chloride ions play a key role in the stability of the capsid. A low number of chloride ions results in loss of the native icosahedral symmetry, while an optimal number of chloride ions creates a neutralising layer next to the positively charged inner surface of the capsid. Understanding the dependence of the capsid stability on the distribution of the ions will help clarify the details of the viral life cycle that is ultimately connected to the role of packaged viral genome inside the capsid.

## Reduced point charge models of proteins - Influence of protein-solvent interactions

**Laurence Leherte, Daniel P. Vercauteren**

*Laboratoire de Physico-Chimie Informatique, Unité de Chimie Physique Théorique et Structurale, Department of Chemistry, Namur MEDicine & Drug Innovation Center (NAMEDIC), University of Namur, Rue de Bruxelles 61, B-5000 Namur, Belgium*

We investigate the influence of various solvent models on the structural stability and the protein-water interface of three Ubiquitin complexes (PDB access codes: 1Q0W, 2MBB, 2G3Q) modelled using Amber99sb with two different point charge distributions. A previously developed reduced point charge model (RPCM) [1], where each amino acid residue is described by a limited number of point charges, is tested and compared to its all-atom (AA) version. The complexes are solvated in TIP4P-Ew or TIP3P water molecules, involving either a correction of the Lennard-Jones protein-O<sub>water</sub> interaction parameters [2] or the coarse-grain SIRAH water description [3]. Molecular Dynamics (MD) simulation conditions are first refined for complex 1Q0W, whose ligand is a single helix structure that has the ability to bend due to a low  $\alpha$ -propensity region occurring in its amino acid sequence. Results are further confirmed by MD simulations carried out on complexes 2MBB and 2G3Q.

MD results show that the best agreements between the RPCM and AA models are obtained when using (i) the TIP4P-Ew water force field (FF) with a correction factor  $\gamma = 0.7$  or (ii) the hybrid TIP3P/SIRAH FF with a sufficiently large box size and a molecule/bead ratio of 1.2 to 1.4. At the RPCM level, a decrease in  $\gamma$  or the inclusion of SIRAH particles allows to weaken the protein-solvent interactions. It results in a slight collapse of the protein structure and a less dense hydration shell, thus involving a decrease in the protein-water and water-water H-bonds. The dynamics of the surface protein atoms and of the water shell molecules is also slightly refrained, thus allowing to generate stable RPCM trajectories, at a reduced computational cost. Conversely, solvation conditions such as the uncorrected TIP4P-Ew FF and the TIP3P FF at  $\gamma = 1.1$  proposed by Best *et al.* [2] favor the unfolding of protein RPCMs.

- [1] L. Leherte, *Mol. Simul.* **42**, 289 (2016).
- [2] R.B. Best, W. Zheng, J. Mittal, *J. Chem. Theory Comput.* **10**, 5113 (2014).
- [3] L. Darré, A. Tek, M. Baaden, S. Pantano, *J. Chem. Theory Comput.* **8**, 3880 (2012).

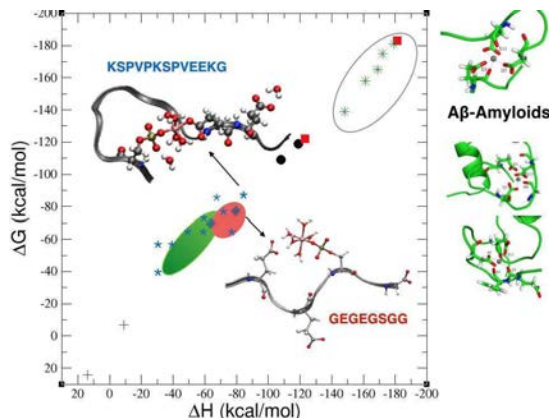


## Insights into the Structural Toxicity of Aluminum with Biomolecules, using a Computational Approach

Xabier Lopez<sup>1,2</sup>, Jon I Mujika<sup>1,2</sup>, Elena Formoso<sup>1,2</sup>, Gabriele dala Torre<sup>1,2a</sup> and Rafael Grande-Aztatzi<sup>1,2</sup>

<sup>1</sup>*Kimika Fakultatea, Euskal Herriko Unibertsitatea UPV/EHU, and Donostia International Physics Center (DIPC), P.K. 1072, 20080 Donostia, Euskadi, Spain*

The increased bioavailability of aluminum due to human intervention, raises concerns on the toxic effects that this so far "excluded from biology" metal might have on living organisms. Consequently, the bioinorganic chemistry of aluminum has emerged as a very active field of research. However, the experimental determination of structure and affinities of Aluminum-Bioligand complexes is not without difficulties and theoretical methods have emerged as a fundamental tool to unveil aluminum biochemistry. In the present talk I will review some of the recent advances made by our group on this field. We will show how computational methods (DFT, QM/MM and classical molecular dynamic simulations) can be combined to determine the relative affinity of aluminum towards potential biological chelators. This can shed light on the type of biological compounds responsible for the so-called structural toxicity mechanism of aluminium.



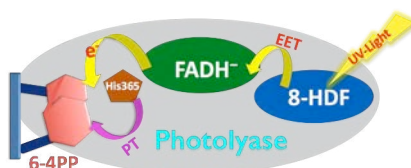
- [1] R. Grande-Aztatzi, E. Formoso, J. I. Mujika, J. M. Ugalde, X. Lopez, *Phys. Chem. Chem. Phys.* **18**, 7197 (2016)
- [2] E. Formoso, X. Lopez, *RSC Advances* **7**, 6064 (2016)
- [3] J. Beardmore, X. Lopez, J.I. Mujika, C. Exley, *Scientific Reports* **6**, 30913 (2016)
- [4] J.I. Mujika, J. Rodríguez-Guerra Pedregal, X. Lopez, J. M. Ugalde, L. Rodríguez-Santiago, M. Sodupe, J.D. Maréchal *Chem. Sci* (2017) DOI: 10.1039/c7sc01296a

## Utilizing light for repair of light-induced DNA damages: the clever mode of action of DNA photolyases

Shirin Faraji

*Theoretical Chemistry, Zernike Institute for Advanced Materials,  
University of Groningen, The Netherlands, [s.s.faraji@rug.nl](mailto:s.s.faraji@rug.nl)*

UV radiation triggers various chemical reactions in DNA such as intra-strand cross-linking between adjacent pyrimidines, causing genetic mutations. In fact, pyrimidine dimers are supposed to be the major players in the formation of skin cancer. DNA photolyases are enzymes initiating cleavage of mutagenic pyrimidine (6-4) pyrimidone photolesions by a photo-induced electron transfer from flavin adenine dinucleotide to the lesion.



Using hybrid quantum mechanical/molecular mechanical (QM/MM) dynamics, we have carried out series of simulations to completely map out the entire evolution of functional processes involved in the molecular mechanism of this important biological system. We have demonstrated that the electron catalyzing the repair is generated via an intermolecular Coulombic decay (ICD) process [1]. In fact, this is the first example for ICD as operating mechanism in a real biological system. We have presented the most energetically feasible electron-induced splitting mechanism in which the initial step is electron-coupled proton transfer from the protonated Histidine to the lesion, which proceeds simultaneously with intramolecular OH transfer along an oxetane-like transition state [2]. Our theoretical findings are in agreement with experimental time-resolved measurements [3]. The experimental spectroscopic signature of the detected 6-4PP intermediate is assigned theoretically to a specific molecular structure determining the operating molecular mechanism of the electron-induced restoration of (6-4) photolesions. Thereby, all pieces of the (6-4) photolesion repair puzzle are finally put together [4].

[1] P. Harbach, M. Schneider, S. Faraji, A. Dreuw, *J. Phys. Chem. Lett.* 4, 943 (2013).

[2] S. Faraji and A. Dreuw, *J. Phys. Chem. Lett.* 3, 227 (2012), S. Faraji, G. Groenhof and A. Dreuw, *J. Phys. Chem. B* 117, 10071 (2013)

[3] J. Li et al, *Nature* 466, 887 (2010). S. Faraji and A. Dreuw, *Ann. Rev. Phys. Chem.* 64, (2014).

[4] S. Faraji, D. Zhong, and A. Dreuw, *Angew. Chem. Int. Ed. Engl.* 55, 5175 (2016). S. Faraji, A. Dreuw, *Photochem. Photobiol.* 93, 37 (2017).

## Numerical exact MACGIC-QUAPI simulations of electron transfer dynamics in *Drosophila* cryptochrome (dCRY).

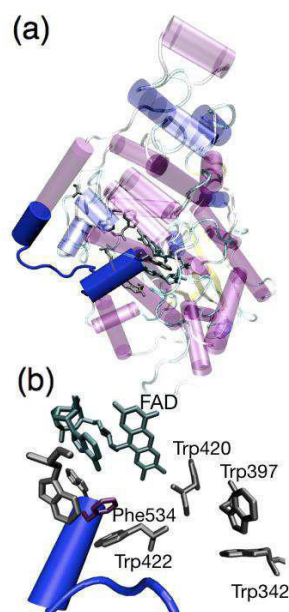
Martin Richter<sup>1</sup>, and Benjamin P. Fingerhut<sup>1</sup>

<sup>1</sup>Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, D-12489 Berlin, Germany.

The description of dissipative quantum dynamics subject to non-Markovian system-bath memory poses persistent challenges that arise in particular for systems of biological relevance, composed of multiple exciton states coupled to charge transfer states. Moreover the ‘sluggish’ protein environment imposes system-bath memory times of substantial length. The quasi-adiabatic propagator path integral (QUAPI) method [1] in principle allows for the numerical exact solution of such quantum dissipative dynamics but is limited by exponential scaling with growing memory time and system size.

We present a novel method, termed mask assisted coarse graining of influence coefficients (MACGIC)-QUAPI [2], that offers appealing computational savings due to an intermediate coarse grained representation of Feynman- Vernon influence coefficients, exploiting physical properties of system decoherence. The MACGIC-QUAPI method allows access to the regime of biological significant long-time system-bath memory (~100 propagation time steps) while retaining rapid convergence to exact QUAPI results.

Performance of the method is demonstrated for microscopically derived model Hamiltonians of multi-step electron transfer dynamics in dCRY, a flavoprotein that undergoes ultrafast charge separation upon electronic excitation (cf. Figure inlay). Site energies, inter-chromophore couplings and fluctuation dynamics were parametrized by first principles QM/MM (TD-DFT(BNL)/amber *ff14SB*) trajectory simulations. The simulated transfer dynamics is characterized by sub-picosecond initial charge separation that renders perturbative approaches inaccurate. Key protein residues responsible for an electrostatic control of active electron transfer pathways are identified and their influence on transfer dynamics will be discussed.



[1] E. Sim, N. Makri, *Comput. Phys. Commun.* **99**, 335 (1997).

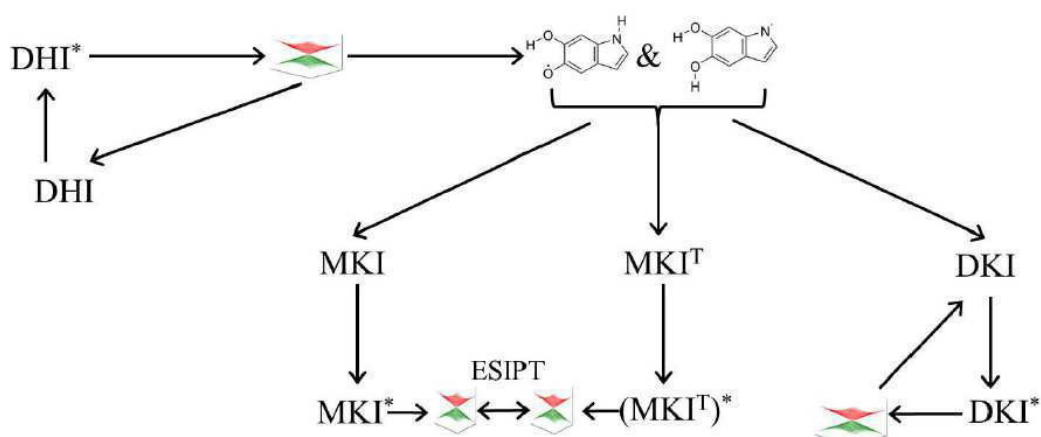
[2] M. Richter, B. P. Fingerhut, *J. Chem. Phys.* **146**, 214101 (2017).

## Photoprotection Mechanism in Eumelanin

Debashree Ghosh<sup>1</sup>

<sup>1</sup>Indian Association for the Cultivation of Science, Kolkata 700032, India

Eumelanin, the functional polymer in human skin, forms a heterogeneous layered structure intrinsic to its broadband monotonic spectra. The inherent structural heterogeneity of eumelanin makes the photoprocesses very complex and diverse in nature. In this study, we re-create the potential energy surfaces of the low-lying excited states of the multiple monomeric forms of eumelanin constituents that play a prominent role in either photoprotection or photo-damage pathways.[1] Our results indicate a diverse set of pathways for the photoexcited species to relax back to the ground state, which depends on the specific monomeric form. Furthermore, the excited state reaction channels show the scope of extensive interconversion between the different monomers and therefore, we propose that the heterogeneity of eumelanin is key to its photoprotection capability.[2] In this talk, I will describe the photoprotection channels and the novel role of heterogeneity in the channels.



[1] M. Mandal, T. Das, B. Grewal, D. Ghosh, *J. Phys. Chem. B*, **119**(42), 13288 (2015).

[2] P. Ghosh, D. Ghosh, *J. Phys. Chem. B* (just accepted) DOI : 10.1021/acs.jpcc.7b05123

## Chemically-induced excited-state chemistry

**Daniel Roca-Sanjuán**

*Institut de Ciència Molecular, Universitat de València, P.O.Box 22085, 46071 València,  
Spain*

Excited-state chemistry is often initiated by irradiating with light (photo-chemistry) a molecular system. By this means, chemical processes that are not typical of ground-state chemistry can then take place. In addition to photons, a chemical reaction can also induce excited-state processes [1,2,3]. Wonderful examples in Nature are worms, bugs, and deep-sea creatures, which produce bioluminescence for several purposes such as communication, mating, or to escape from predators [1]. Furthermore, “dark” photoproducts, such as E/Z isomers or cyclobutane dimers can be produced via chemical reactions without light [2]. All these phenomena are based on internal conversions and inter-system crossings, which require multiconfigurational methods for an accurate description [4]. In this contribution, we will discuss in detail the mechanisms of chemically-induced excited-state chemistry and their relevance in biology, medicine, and nanotechnology.

- [1] I. Navizet, Y.-J. Liu, N. Ferré, D. Roca-Sanjuán, R. Lindh, *ChemPhysChem* **12**, 3064 (2011).
- [2] P. Farahani, M. Lundberg, R. Lindh, D. Roca-Sanjuán, *Phys. Chem. Chem. Phys.* **17**, 18653 (2015).
- [3] W. J. Baader, C. V. Stevani, E. J. H. Bechara, *J. Braz. Chem. Soc.* **26**, 2430 (2015).
- [4] D. Roca-Sanjuán, F. Aquilante, R. Lindh, *WIREs Comput. Mol. Sci.* **2**, 585 (2012).

## Exploiting excited-state aromaticity for the design of efficient light-driven rotary molecular motors

Baswanth Oruganti<sup>1</sup>, Jun Wang<sup>1</sup>, Bo Durbeej<sup>1</sup>

<sup>1</sup>*Division of Theoretical Chemistry, IFM, Linköping University, Linköping, Sweden*

The most developed class of synthetic rotary molecular motors available today are the overcrowded alkenes introduced by Chemistry Nobel Laureate Ben Feringa in 1999. For example, owing to a concerted experimental effort in the subsequent years [1] and complementary insights from in silico modeling [2–4], a variety of ways have been found to drastically reduce the free-energy barriers of the critical thermal steps that, at first, severely restricted the performance of these motors. Unfortunately, however, there has not been a similar progress in improving the rather low (20–30%) quantum yields (QYs) of the photoisomerizations that actually power the rotary motion of overcrowded-alkene motors. In this light, we and other research groups have recently shown by means of non-adiabatic molecular dynamics (NAMD) simulations that motors containing a protonated or alkylated Schiff base constitute a viable alternative to overcrowded-alkene motors [5–7], at least as far as the efficiency of the photochemical steps goes.

In this presentation, a new motor design that – in contrast to Schiff-base motors – lacks a cationic nitrogen center but instead features a moiety that becomes aromatic in the photoactive excited state is proposed and evaluated based on NAMD simulations within the framework of multiconfigurational quantum chemistry. Remarkably, it is found that this design exhibits not only very high (~75%) quantum yields for the olefinic-bond *Z/E* photoisomerizations of one isomer into the other, but also a clear ~60% tendency for two consecutive photoisomerizations to produce a full 360° rotation. Such a tendency is a hallmark of a true rotary molecular motor. Furthermore, the two photoisomerizations are very fast, with associated excited-state lifetimes of about 200 fs only. Altogether, these results highlight the enormous but hitherto unexplored potential of exploiting excited-state aromaticity in the design of efficient light-driven rotary molecular motors.

- [1] J. Bauer, L. Hou, J. C. M. Kistemaker, B. L. Feringa, *J. Org. Chem.* **79**, 4446 (2014).
- [2] B. Oruganti, C. Fang, B. Durbeej, *Phys. Chem. Chem. Phys.* **17**, 21740 (2015).
- [3] B. Oruganti, J. Wang, B. Durbeej, *ChemPhysChem* **17**, 3399 (2016).
- [4] B. Oruganti, J. Wang, B. Durbeej, *Int. J. Quantum Chem.* DOI: 10.1002/qua.25405
- [5] G. Marchand et al, *J. Phys. Chem. Lett.* **6**, 599 (2015).
- [6] A. Nikiforov, J. A. Gamez, W. Thiel, M. Filatov, *J. Phys. Chem. Lett.* **7**, 105 (2016).
- [7] J. Wang, B. Oruganti, B. Durbeej, *Phys. Chem. Chem. Phys.* **19**, 6952 (2017).

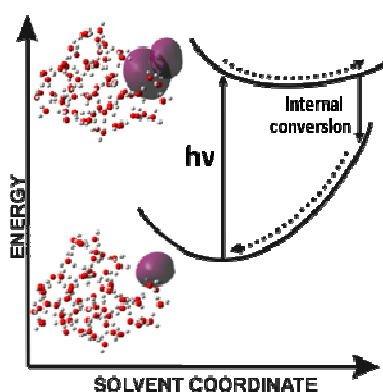
## Electronic Excited State Lifetimes of Anionic Water Clusters: A Quantized Time Correlation Function Approach.

László Turi<sup>1\*</sup>, Daniel Borgis<sup>2</sup>, Peter J. Rossky<sup>3</sup>

<sup>1</sup>*ELTE Eötvös Loránd University, Department of Physical Chemistry, Budapest 112, P. O. Box 32, H-1518, Hungary.*

<sup>2</sup>*Pôle de Chimie Théorique, UMR-CNRS PASTEUR, Ecole Normale Supérieure, 24, rue Lhomond, 75231 Paris Cedex 05, France.*

<sup>3</sup>*Department of Chemistry, Rice University, P. O. Box 1892, MS-60, Houston, Texas 77251-1892 USA.*



Despite numerous studies of negatively charged water clusters, a controversy remains regarding the electron-binding motif, whether the excess charge center is localized at the cluster surface or within the interior. Here, we address this via interpretation of recent experimental time-resolved photoelectron imaging data obtained for relatively warm clusters [1]. Mixed quantum-classical dynamics simulations and subsequent analysis of the solvent and electronic relaxation phenomena is reported for a wide range of cluster sizes

(up to  $n = 1000$ ) at  $T \sim 200\text{K}$  [2]. The calculated excited state lifetimes for surface state clusters are in nearly quantitative agreement with the reported experimental results ( $n \leq 200$ ). A minimum is predicted for  $n \sim 150\text{-}200$ , with an increase for larger clusters, approaching bulk state values from below. This implies that the electron resides in a surface-localized motif in all of these measured clusters, dominating at least up to a cluster size of 200.

Acknowledgment: PJR acknowledges the support of this research by the U. S. National Science Foundation (CHE-0910499, CHE-1362381). This work was supported by a research grant to LT from the National Research, Development and Innovation Office, Hungary (NKFIH, previously OTKA, K104237).

[1] R. M. Young, D. M. Neumark, *Chem. Rev.* **112**, 5553 (2012).

[2] D. Borgis, P. J. Rossky, L. Turi, *J. Phys. Chem. Lett.* **8**, 2304 (2017).



## How to Control the Absorption Wavelength of Light Harvesting Complexes

Luca De Vico<sup>1,2</sup>, André Anda<sup>1</sup>, Vladimir Al. Osipov<sup>3</sup>, Anders Ø. Madsen<sup>4</sup>,  
Thorsten Hansen<sup>1</sup>

<sup>1</sup>Dep. of Chemistry, Copenhagen Univ., Universitetsparken 5, 2100, Copenhagen Ø, Denmark

<sup>2</sup>Dep. of Biotechnology, Chemistry and Pharmacy, Siena Univ., via Moro 2, 53100 Siena, Italy

<sup>3</sup>Dep. of Chemical Physics, Lund Univ., Gatingevägen 60, 22240 Lund, Sweden

<sup>4</sup>Dep. of Pharmacy, Copenhagen Univ., Universitetsparken 2, 2100, Copenhagen Ø, Denmark

Light-harvesting systems 2 and 3 (LH2 and LH3) protein–chromophores complexes from the purple bacterium *Rhodoblastus acidophilus* have identical overall arrangements of bacteriochlorophyll *a* (BChl) chromophores (Figure 1), while the proteins differ in their primary structures. The 18 BChls ring (shown in red in Figure 1) absorbs at 850 and 820 nm in LH2 and LH3, respectively.[1] While previously suggested that such difference is due to a rotation of the BChl acetyl moiety,[2] we recently found that such changes cannot be responsible for a 30 nm blue shift.[3] In this work, we use our previously established methodology [3, 4] to analyze BChls from crystal structures of LH2 and LH3, and uncover which feature is the real cause of the blue shift. Thus, we employ state-of-the-art MS-RASPT2//RASSCF and TD-DFT/PBE0 technologies to follow changes in excitation energies, and subsequently translate them into changes in simulated absorption spectra of the whole complex. We find that the absorption wavelength is controlled, largely, by the curvature of the BChl macrocycle ring (Figure 2). Therefore, the protein scaffolding is responsible, primarily, for setting up such curvature, thus controlling the absorption wavelength, and only secondarily for fine tuning it, through the acetyl moiety torsion. Such idea can also be applied to future synthetic chromophores (Figure 3).

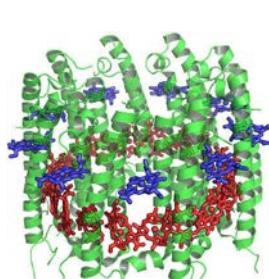


Figure 1

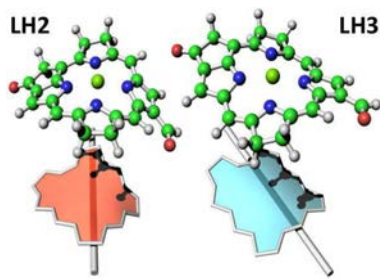


Figure 2

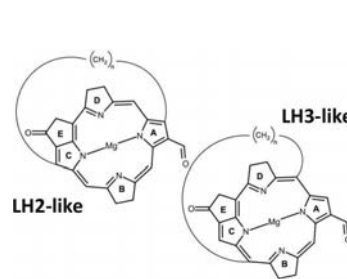


Figure 3

## References

- [1] A. T. Gardiner, R. J. Cogdell, S. Takaichi, *Photosynth. Res.* **1993**, 38, 159–167.
- [2] R. J. Cogdell et al., *Photosynth. Res.* **2002**, 74, 135–141.
- [3] A. Anda, L. De Vico, T. Hansen, *J. Phys. Chem. B*, DOI 10.1021/acs.jpcc.7b02071.
- [4] A. Anda, T. Hansen, L. De Vico, *J. Chem. Theory Comput.* **2016**, 12, 1305–1313.



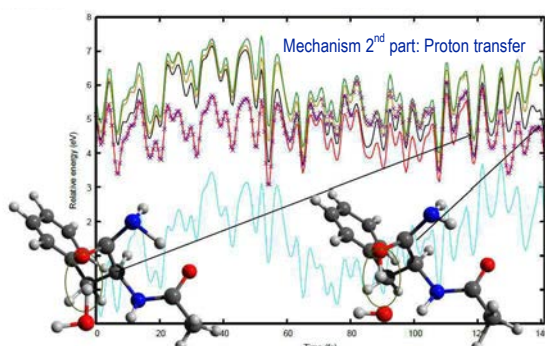
**Excited states deactivation in model proteins chains:  
Nonadiabatic dynamics simulations and *ab initio* methods.**

**V. Brenner<sup>1</sup>, T. Very<sup>1,2</sup>, S. Hoyau<sup>2</sup>, N. Ben Amor<sup>2</sup>, E. Gloaguen<sup>1</sup> and M. Mons<sup>1</sup>**

<sup>1</sup> LIDYL UMR 9222, DRF/IRAMIS, CEA Saclay, Bât 522, 91191 Gif sur Yvette - France

<sup>2</sup> LCPQ UMR 5626, IRSAMC, Université Paul Sabatier, 31000 Toulouse -France

**Abstract:** Following UV absorption, many **biomolecular systems** are endowed with mechanisms of **excited-states deactivation** that ensure their **photochemical stability**. One of the major goals of our research is to investigate conformer-selective dynamics of biologically relevant molecular systems by an original innovative computational strategy in order to document the **basic physical phenomena** controlling the **lifetime** of excited states, highlighting the **link between electronic dynamics and structure**. This **innovative**



**multi-step computational strategy** allows to both characterize the first excited states of bio-relevant systems and model efficiently their potential energy surfaces, using, first, **nonadiabatic dynamics simulations** based on TDDFT (NA-TDDFT) to provide hints about the critical motions that drive the deactivation, which will then be **investigated at a better level** with two families of methods: i) the **standard approximate coupled cluster** singles and doubles method (CC2) and ii) and **multireference** (MRCI) methods. **Developed** on small capped peptide models and always backed up by **key conformation-selective gas phase experiments** carried out in our team at several timescales,<sup>1,2</sup> this innovative strategy is now applied to monohydrated capped peptides as well as capped dipeptides. We will present here the last results obtained on these systems. In addition, **benchmark of the CC2 method** on a set of model peptide chains (structure, energetic and vibrational frequencies of the first  $\pi\pi^*$  excited state)<sup>3,4</sup> as well as **assessment of the CC2 method validity** from comparison with **MRCI methods**<sup>5</sup> will be also reported.

**Keywords:** Excited states computations, Photochemistry of biomolecules, Nonadiabatic dynamics, Size-extensive CC and MRCI linear scaling methods, TDDFT.

**References:**

- [1] M. Mališ, Y. Loquais, E. Gloaguen, E., H. S. Biswal, F. Piuze, B. Tardivel, B., V. Brenner, M. Broquier, C. Juvet, M. Mons, N. Došlić, I. Ljubić, , *J. Chem. Am. Soc.* **134**, 20340 (2012).
- [2] M. Mališ, Y. Loquais, E. Gloaguen, C. Juvet, V. Brenner, M. Mons, I. Ljubić, N. Došlić, *PCCP* **16**, 2285 (2014).
- [3] Y. Loquais, E. Gloaguen, M. Allaudin, V. Brenner, B. Tardivel, M. Mons, *PCCP*, **16**, 22192 (2014).
- [4] W. Y. Sohn, V. Brenner, E. Gloaguen, M. Mons, *PCCP*, **18**, 29959 (2016).
- [5] N. Ben Amor, S. Hoyau, D. Maynaud, V. Brenner, *to be submitted*.

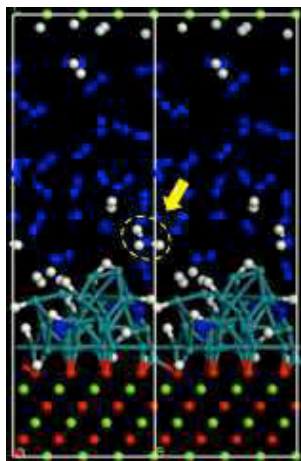
## First-Principles Molecular Dynamics Simulations on Ammonia Synthesis and Decomposition

Manabu Sugimoto

*Faculty of Advanced Science and Technology, Kumamoto University,  
2-39-1, Kurokami, Chuo-ku, Kumamoto 860-8555, Japan*

*<sup>2</sup>My Address in Times New Roman 11pt italics*

We report the first-principles molecular dynamics calculations on catalytic reactions of (i) ammonia formation from nitrogen and hydrogen gas mixtures and (ii) ammonia decomposition to hydrogen and nitrogen molecules. As a catalyst, we focus on Ru/MgO catalysts. We aim at revealing important reaction sites on Ru nano particles in the supported catalyst, the reaction mechanism, and a role of the catalyst support. The calculations were carried out using the density functional theory with the periodic boundary condition at finite temperature. The two types of chemical reactions were successfully carried out in several simulations. Figure 1 indicates a snap shot of one of simulations of ammonia formation. In the lecture, we will mainly discuss on surface topology playing an important role in each elementary reaction.



**Figure:** A snap shot of the ammonia formation simulation  
using the first-principles molecular dynamics method

## Reaction-Path Bifurcation Analyses based on Valley-Ridge Transition and Global Reaction Route Mapping

Tetsuya Taketsugu<sup>1</sup>, Yu Harabuchi<sup>1,2</sup>, Yuriko Ono<sup>1</sup>, Takuro Tsutsumi<sup>3</sup>,  
Satoshi Maeda<sup>1</sup>

<sup>1</sup>*Faculty of Science, Hokkaido University, N10-W8, Kita-ku, Sapporo, Japan.*

<sup>2</sup>*PRESTO, Japan Science and Technology Agency, Honcho 4-1-8, Kawaguchi, Japan.*

<sup>3</sup>*Graduate School of Chemical Sciences and Engineering, Hokkaido University, N10-W8, Kita-ku, Sapporo, Japan.*

In theoretical chemistry, the "reaction path" concept has been utilized as a basic tool to provide an intuitive picture of the structural change as the reaction proceeds. The intrinsic reaction coordinate (IRC), defined as the minimum energy path connecting two minima and one transition state on the potential energy surface (PES) in mass-weighted coordinates, has been accepted as the reference reaction pathway for elementary reaction processes, and is used to discuss the reaction mechanism. It is known that the IRC sometimes becomes unstable with respect to a vibrational coordinate orthogonal to the IRC through valley-ridge inflection (VRI) or valley-ridge transition (VRT). The VRI or VRT causes a branching of the reaction pathways, and its dynamical aspect has been discussed in applications to some organic reactions. The reaction-path bifurcation has been studied from various viewpoints, i.e., a second-order Jahn-Teller effect [1], an attempt to define a bifurcating pathway [2,3], isotope effects [4,5], totally-symmetric VRT [6], trifurcation [7,8], and bifurcation analyses on a global reaction route map [9,10]. In this presentation, I will discuss the significant roles of the totally-symmetric VRT [6], and introduce new analyses of the reaction-path bifurcation based on a global reaction route mapping [9,10].

- [1] T. Taketsugu, T. Hirano, *J. Chem. Phys.* **99**, 9806 (1993)
- [2] T. Taketsugu, N. Tajima, K. Hirao, *J. Chem. Phys.* **105**, 1933 (1996).
- [3] T. Yanai, T. Taketsugu, K. Hirao, *J. Chem. Phys.* **107**, 1137 (1997).
- [4] Y. Kumeda, T. Taketsugu, *J. Chem. Phys.* **113**, 477 (2000).
- [5] T. Taketsugu, Y. Kumeda, *J. Chem. Phys.* **114**, 6973 (2001).
- [6] Y. Harabuchi, T. Taketsugu, *Theo. Chem. Acc.* **130**, 305 (2011).
- [7] Y. Harabuchi, A. Nakayama, T. Taketsugu, *Comp. Theo. Chem.* **1000**, 70 (2012).
- [8] Y. Harabuchi, Y. Ono, S. Maeda, T. Taketsugu, K. Keipert, M. S. Gordon, *J. Comp. Chem.* **37**, 487 (2016).
- [9] Y. Harabuchi, Y. Ono, S. Maeda, T. Taketsugu, *J. Chem. Phys.* **143**, 014301 (2015).
- [10] Y. Harabuchi, Y. Ono, S. Maeda, T. Taketsugu, *J. Chem. Phys.* **143**, 177102 (2015).

## Retrosynthesis and Reaction Prediction with Deep Neural Networks

**Marwin H. S. Segler<sup>1</sup>, Mark P. Waller<sup>2</sup>**

<sup>1</sup>*Organisch-Chemisches Institut and Center for Multiscale Theory and Computation,  
Westfälische Wilhelms-Universität Münster Corrensstr.40, 48149 Münster, Germany*

<sup>2</sup>*Department of Physics and International Center for Quantum and Molecular Structures,  
Shanghai University, Shangda Road 99, 200444 Shanghai, China*

In the recent years, Deep Learning with neural networks has transformed computer vision, speech processing (built in in all modern smartphones), and many other pattern recognition tasks. Earlier last year, a system based on neural networks has even beaten the world champion in Go, a strategic game far more complex than chess. Remarkably however, smart assistants are basically absent from the chemical lab.

In our work, we combine Deep Learning with the core concept of named reactions, or more generally, reaction types. Our model can learn overnight which are the most likely reactions to make a molecule for retrosynthesis, or under which reaction type the starting materials will likely react (Forward Reaction Prediction). The key point is that we train the machine with essentially the complete published knowledge of organic chemistry (>3.5 million reactions acquired from the Reaxys database). This allows our model to learn reactivity conflicts and the selectivity of transformations from data with an unprecedented precision. Before, this information had to be laboriously encoded by hand.

In the largest scale comparison of reaction prediction systems ever conducted, we show that our approach has a higher than 95% accuracy when allowed to suggest up to 10 different routes for a target molecule on a test set of around 1 million reactions. Furthermore, preliminary studies indicate that coupling the neural networks with modern tree search techniques, it outperforms traditional computational synthesis planning with handcoded heuristics.

[1] Marwin H.S. Segler, Mark P. Waller, Neural-Symbolic Machine Learning for Retrosynthesis and Reaction Prediction, *Chem. Eur. J.* (2017) 23, 5966–5971.

[2] Marwin H. S. Segler and Mark P. Waller, Modelling Chemical Reasoning to Predict and Invent Reactions, *Chem. Eur. J.* (2017), 23, 6118–6128.

[3] Marwin H. S. Segler, Mike Preuß, Mark P. Waller, Towards ‘AlphaChem’: Chemical Synthesis Planning with Tree Search and Deep Neural Network Policies, *International Conference on Learning Representations 2017, Workshop Track*.

## Graph Theory Approach in Exploration of Reaction Path Networks: Rh(I)BINAP-Catalyzed Isomerization of Allylic Amines

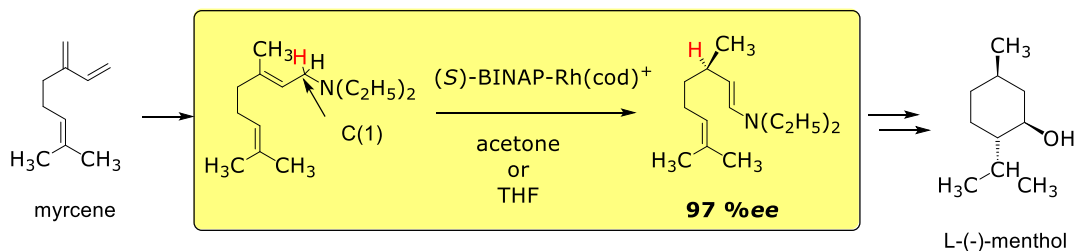
Seiji Mori<sup>1</sup>, Takayoshi Yoshimura<sup>1</sup>, Satoshi Maeda<sup>2</sup>, Tetsuya Taketsugu<sup>2</sup>,  
Masaya Sawamura<sup>2</sup>, Keiji Morokuma<sup>3</sup>

<sup>1</sup>*Institute of Quantum Beam Science, Ibaraki University, Mito, Japan*

<sup>2</sup>*Department of Chemistry, Faculty of Science, Hokkaido University, Kita-10, Nishi-8, Kita-ku, Sapporo 060-0810, Japan*

<sup>3</sup>*Fukui Institute for Fundamental Chemistry, Kyoto University, 34-4 Takano Nishihiraki-cho, Sakyo, Kyoto 606-8103, Japan*

Quantum chemical methods are very useful to analyze the reaction mechanisms for design and develop a new catalysis. Cationic Rh(I)-BINAP complex is used for asymmetric isomerization of allylic amines to enamines, which reaction is very important not only in organic synthesis but also in industry.<sup>1</sup> This catalyst is also used in hydrogenation of enamides. Our group previously reported the origin of excellent enantioselectivity by using QM/MM calculations for Rh(I)-BINAP catalyzed hydrogenation of enamides.<sup>2</sup> Whereas there are numerous reports to explain the enantioselectivity of the Rh(I)-catalyzed asymmetric hydrogenation reactions of enamides, only a few reports exist for the asymmetric isomerization of allylic amine. In this study, we explored the associative (with additional amine coordinate Rh-complex) and dissociative pathways by using Artificial Force Induced Reaction (AFIR) and ONIOM methods<sup>3</sup> followed by Prim's method based on graph theory. Prim's algorithm is deterministic to select and visualize the most economical reaction pathways from the complicated reaction path network. The procedure and the results presented in this manuscript will provide a good example of a comprehensive reaction path search using the AFIR method combined with graph theory.<sup>4</sup>



[1] K. Tani, T. Yamagata, S. Akutagawa, H. Kumobayashi, T. Taketomi, H. Takaya, A. Miyashita, R. Noyori, S. Otsuka, *J. Am. Chem. Soc.* **106**, 5208-5217(1984).

[2] S. Mori, T. Vreven, K. Morokuma, *Chem. Asian J.* **1**, 391 (2006).

[3] S. Maeda, K. Morokuma, *J. Chem. Theory Comput.* **7**, 2335-2345 (2011).

[4] T. Yoshimura, S. Maeda, T. Taketsugu, M. Sawamura, K. Morokuma, S. Mori, *Chem. Sci.* in press.

## Automated searching method for reaction paths using molecular graphs and chemical reaction network

Yeonjoon Kim<sup>1</sup>, Jin Woo Kim<sup>1</sup>, Zeehyo Kim<sup>1</sup>, Woo Youn Kim<sup>1</sup>

<sup>1</sup>*Department of chemistry, KAIST, 291 Daehak-ro, Yuseong-gu, Daejeon, Korea*

Reaction intermediates including reactants and products are local minima composed of a reaction path, but their brute-force sampling is too demanding because of their large degrees of freedom. A stochastic sampling method inherently requires many trials no matter how effective it is, because it cannot guarantee 100% probability of finding a designated target structure within a finite number of samplings [1]. Therefore, a deterministic sampling method would be desirable. We are developing such a deterministic method based on molecular graphs [2]. Combinatorial sampling of molecular graphs gives a number of possible reaction intermediates. A chemical reaction network can be made by connecting the resultant molecules, followed by the kinetic analysis. Our method quickly estimates the activation energy of each elementary reaction with a reasonable accuracy based on molecular graph analysis. Therefore, very efficient searching for reaction paths is feasible as compared to other approaches resorting to transition state calculations. Our method predicts favorable reaction paths just from reactants and products in a fully automated fashion within a few hours on a single workstation. In this talk, we show the recent progress in this project with several examples that include famous organic reactions, complicated unimolecular reactions, and organometallic reactions.

[1] Yeonjoon Kim, Sunghwan Choi, Woo Youn Kim, *J. Chem. Theo. Comput.* **10**, 2419 (2014).

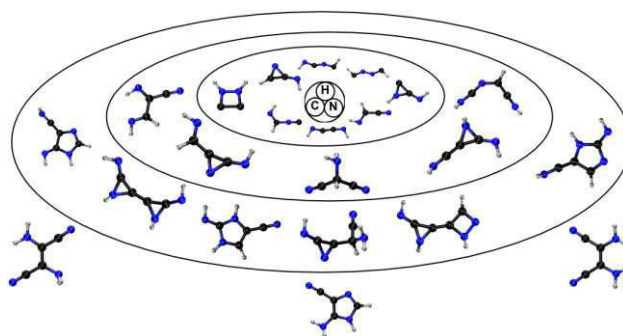
[2] Yeonjoon Kim, Jin Woo Kim, Zeehyo Kim, Woo Youn Kim, *manuscript under preparation*.

## Exploring Chemical Evolution using Tabu-Search Based Automated Reaction Finding Algorithm

Surajit Nandi<sup>1</sup>, Debankur Bhattacharyya<sup>1</sup>, Anoop Ayyappan<sup>1</sup>

<sup>1</sup>Department/of Chemistry, Indian Institute of Technology Kharagpur, 721302, West Bengal, India

Understanding the chemical origin of life is an evergreen scientific interest. Oligomerization of hydrogen cyanide is proposed as one of the important pathways towards the prebiotic synthesis of elementary biomolecules. Theoretical and experimental studies suggests that HCN is a precursor to the formation of purines[1][2][3][4][5]. We used our Tabu-Search based automated reaction finding algorithm, implemented in PyAR software, [6] to explore the reaction pathways for the sequential addition of HCN or HNC to form the tetramer ( $\text{H}_4\text{C}_4\text{N}_4$ ). We calculated the minimum energy path (MEP) connecting the minima using nudged elastic band (NEB) method for a selected set of products and optimized the TS. Our study led to several possible oligomers of HCN, some of the previously reported ones and many new gemoetries. We were able to explore the vast and complicated reaction network in the chemical space of HCN oligomerization process.



- [1] J. Oró, A.P. Kimball, *Arch. Biochem. Biophys.* **94**, 223-232 (1979).
- [2] Sun Hwa Jung, Joong Chul Choe, *Astrobiology*. **13**, 465-475 (2013)
- [3] Richard A. Evans, Primož Lorencak, Tae Kyu Ha, Curt Wentrup, *J. Am. Chem. Soc.* **113**, 7261–7276 (1991)
- [4] Karl J. Jobst, M. Ruzni Hanifa, Johan K. Terlouw, *Chem. Phys. Lett.* **462**, 152-157 (2008)
- [5] James P. Ferris, William J. Hagan Jr, *Tetrahedron*, **40**, 1093-1120 (1984)
- [6] S. Nandi and A. Anoop, *Comp. Theo. Chem.*, **1111**, 60-81 (2017)



## Patterns of Moving Saddle Points in Catalysis and Mechanochemistry

Wolfgang Quapp<sup>1</sup>, Josep Maria Bofill<sup>2</sup>, Jordi Ribas-Ariño<sup>3</sup>

<sup>1</sup>*Mathematisches Institut, Universität Leipzig, Augustus-Platz PF 100920, D-04009 Leipzig, Germany; email: quapp@uni-leipzig.de*

<sup>2</sup>*Departament de Química Orgànica, Universitat de Barcelona, and Institut de Química Teòrica i Computacional, Universitat de Barcelona, (IQTCUB), Martí i Franquès, 1, 08028 Barcelona Spain; email: jmbofill@ub.edu*

<sup>3</sup>*Departament de Ciència de Materials i Química Física, Secció de Química Física and IQTCUB, Universitat de Barcelona, Martí i Franquès, 1, 08028 Barcelona Spain; email: j.ribas@ub.edu*

The description of a chemical process under mechanical stress or catalytic enhancement is performed by the generation of an effective potential energy surface (PES). Changes for minima and saddle points by the stress are described by Newton trajectories (NTs) on the original PES [1, 2]. Families of NTs define pulling corridors. If there are different exit saddles then there can exist saddles of index two, at least, in between. Then the case that a full pulling corridor crosses a saddle of index two, is the normal case. It leads to an intrinsic hysteresis of such pullings for the forward or the backward reaction, see Figure 1. Assuming such relations we can explain strange results in the literature, as well as the existence of roundabout corridors which can switch between different saddle points by a reversion of the direction. The findings concern the mechanochemistry of molecular systems under a mechanical load as well as the electrostatic force and can be extended to catalytic and enzymatic accelerated reactions. The ansatz includes both kinds of forces in a natural way without an extra modification.

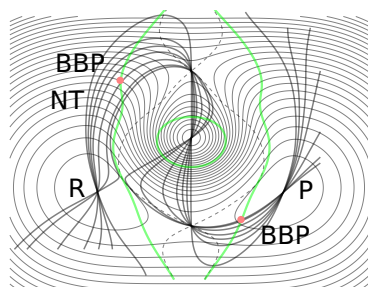


Figure 1: Bold NTs are good directions for a pulling force for successful pulling scenarios. An asymmetric chemical corridor by Newton trajectories (NT) from left to right minimum (R→P). The red points are the optimal barrier breakdown points (BBP).

[1] W.Quapp, J.M.Bofill, *Theor. Chem. Acc.*, **135**, 113 (2016).

[2] W.Quapp, J.M.Bofill and J.Ribas-Ariño *J. Phys. Chem. A*, **121**, 2820 (2017)



## On the Theoretical Optimization of Properties.

**Michael Springborg**

*Physical and Theoretical Chemistry, University of Saarland, 66123 Saarbrücken,  
Germany*

*Tianjin University, Tianjin, 300072, China*

During the last few decades, theoretical calculations have become of increasing importance in providing supporting and complementary information to what is provided by experiment. On the one side, such studies can help in the interpretation of experimental results and, on the other side, through such calculations a first screening of systems can be carried through, ultimately allowing for reducing the synthetic work in the lab. In all those cases, the conventional approach is to start with a realistic structure for the system of interest whose stoichiometry is known, subsequently let the system relax to a close structure of a local total-energy minimum, and finally for this calculate the properties of interest.

The situation is different when essentially nothing is known about the structure of the system of interest. This is, e.g., the case for clusters and nanoparticles. For such systems, specialized theoretical methods that aim at identifying the global total-energy minima have to be applied. Another challenge is to identify molecular systems with optimal properties without specifying the stoichiometry.

In the present contribution we shall at first demonstrate how methods based on genetic algorithms can be used in optimizing the structure of nanoparticles. Subsequently, related methods will be used in identifying molecular systems with optimal properties, whereby, as a playground system, mixed Ge-Si clusters with optimal properties in solar-energy harvesting shall be identified. The purpose of this method, PooMa, is to provide useful information for experiments about interesting systems with predefined properties. It is based on many approximations and is not aimed at providing exact information on any detail. PooMa is developed as a simple, efficient method that does not rely on heavy computations or results from, e.g., high-throughput studies.



PooMa: M. Springborg, S. Kohaut, Y. Dong, and K. Huwig: *Mixed Si-Ge clusters, solar-energy harvesting, and inverse-design methods*, Comp. Theo. Chem. 1107 (2017) 14-22.

## Carbon nanotubes immersed in superfluid helium: An incomplete flooding due to quantum effects

Andreas W. Hauser<sup>1</sup>, María Pilar de Lara-Castells<sup>2</sup>

<sup>1</sup>*Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, A-8010  
Graz, Austria*

<sup>2</sup>*Instituto de Física Fundamental (C.S.I.C.), Serrano 123, E-28006, Madrid, Spain*

Carbon-based nanoporous materials have attracted much attention due to their outstanding adsorption capabilities with potential applications for gas storage and separation. Among them, single-walled nanotubes stand out because of their one-dimensional flow channels, which can be adjusted in terms of helicity, channel length and diameter. A recent experiment of Ohba [1] of gas adsorption on single-walled carbon nanotubes at temperatures between 2 and 5 K reported a quenched propagation of helium through carbon nanotubes with diameters below 7 Å despite the small kinetic diameter of helium atoms. This unexpected outcome caught our interest and triggered a series of computational studies on the interaction of helium with carbon-based structures at ultracold temperatures. [2, 3]

After assessing the performance of a potential model for the He-nanotube interaction via *ab initio* calculations with DFT-based symmetry adapted perturbation theory, we apply orbital-free helium density functional theory to show that the counterintuitive experimental result is a consequence of the exceptional high zero-point energy of helium in comparison to the dwell-depth of the He-He interaction potential, and the tendency to form spatially separated layers of helium upon adsorption at lowest temperatures. We attribute this unusual finding to an even increased zero-point energy for helium atoms inside the nanotube due to the confinement, paired with the tendency to keep the overall helium distribution minimally distorted. This is particularly evident for nanotubes with helicity (8,8), which show an axial cavity even after full submersion into the He droplet. Helium filling factors are derived for a series of carbon nanotubes and compared to the available experimental data. Moreover, we propose a new additive pairwise potential model for the interaction of atoms and molecules to carbon materials. The performance of our model is demonstrated for the interaction of a single He atom or molecule of N<sub>2</sub> with carbon nanotubes [3].

[1] T. Ohba, *Sci. Rep.* **6**, 28992 (2016).

[2] A. W. Hauser, M. P. de Lara-Castells, *J. Phys. Chem. Lett.* **7** (23) 4929-4935 (2016).

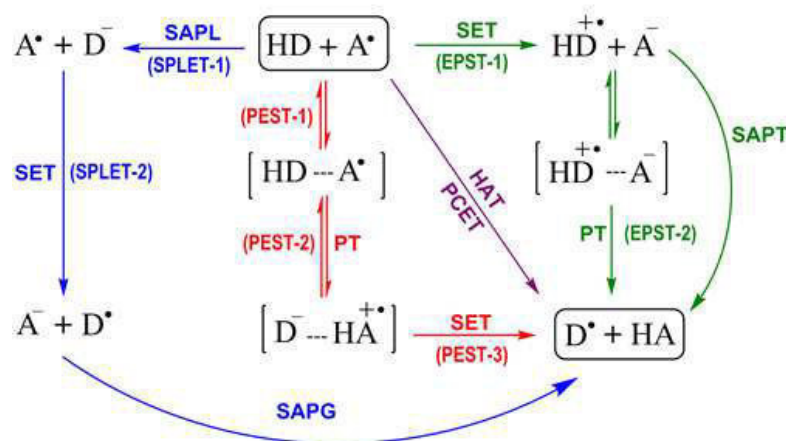
[3] A.W. Hauser, A. O. Mitrushchenkov, M. P. de Lara-Castells, *J. Phys. Chem. C* **121** (7), 3807-3821 (2017).

## The Role of Acid-Base Equilibria in Formal Hydrogen Transfer Reactions: Uric Acid with tryptophanyl radical

Leonardo Muñoz-Rugeles<sup>1</sup>, Annia Galano, J. Raul Alvarez-Idaboy

<sup>1</sup> Facultad de Química, Departamento de Física y Química Teórica, Universidad Nacional Autónoma de México, México DF 04510, México.

<sup>2</sup> Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, San Rafael Atlixco 186, Col. Vicentina. Iztapalapa. C. P. 09340, México D. F., México.



The results presented in this work demonstrate the high complexity of chemical reactions involving species with multiple acid-base equilibria. For the study case investigated here, it was necessary to consider two radical species for tryptophan and the three fractions of uric acid<sup>1</sup> (all of them formed via acid-base equilibria) in order to properly reproduce the experimental results. At pH = 7.4, two main reaction mechanisms were identified: Proton-Electron Sequential Transfer (PEST)<sup>2</sup> and Sequential Proton Gain-Electron Transfer (SPGET). They –combined– account for more than 99 % of the overall reaction despite they involve minor species, i.e.,  $H_3Ur$  and  $Trp^{+\bullet}$ , respectively. The excellent agreement between the calculated overall rate constant and the experimental value seems to support this proposal. In addition, if only the dominant species at pH = 7.4 ( $H_2Ur^-$  and  $Trp_{(H)}^\bullet$ ) were considered, there would be a large discrepancy with the experimental value (about 4 orders of magnitude). This result also supports the finding that the key species in this case are not the most abundant ones. The influence of the pH on the kinetics of the investigated reaction was explored.

[1] L. Muñoz-Rugeles, A. Galano, J. R. Alvarez-Idaboy, *Phys.Chem.Chem.Phys*, DOI: 10.1039/c7cp01557g

[2] L. Muñoz-Rugeles, A. Galano, J. R. Alvarez-Idaboy, *Phys.Chem.Chem.Phys*, 2015, 17, 28525

## Thermodynamics of the partition of Ibuprofen in a lipid bilayer

Natalia Rojas-Valencia<sup>1</sup>, Isaias Lans<sup>2</sup>, Marcela Manrique-Moreno<sup>1</sup>,

Cacier Hadad<sup>1</sup>, Martha Daza<sup>2</sup>, and Albeiro Restrepo<sup>1</sup>

<sup>1</sup>*Instituto de Química, Universidad de Antioquia Udea, Calle 67 # 53-108, Medellín, Colombia.*

<sup>2</sup>*Grupo de Bioquímica Teórica, Universidad Industrial de Santander, Bucaramanga, Colombia.*

Sodium ibuprofen, a Nonsteroidal Anti-Inflammatory Drug (NSAID) has been extensively used for decades as pain-killer, and reduction of fever and swelling. However, despite its therapeutic effects, there are several indications that ibuprofen has serious gastrolesive properties [1]. Diverse experimental and computational studies suggest that side effects produced by ibuprofen could be related to the interaction between the drug and the phospholipids that make up the cell membrane [1-3]. Nonetheless, the mechanism involved in the changes occurring at the membrane is not well understood.

In this work, we carry out a classical molecular dynamics simulation coupled to umbrella sampling to investigate, from the molecular perspective, how the cell membrane environment is affected when the NSAID is present. A model system was built. This includes one anionic ibuprofen molecule and a hydrated phospholipid bilayer, constituted by dimyristoylphosphatidylcholine (DMPC) and water molecules. The system was simulated using the CHARMM36 force field that considers all atoms. Our results suggest that ibuprofen prefers to reside at the interface between the lipid's polar head group and the hydrocarbon region and that entropy is the driving factor behind structural preferences.

### References.

- [1] Lichtenberger, L. Zhou, Y. Jayaraman, V. Doyen, J. O'Neil, R. Dial, E. Gorenstein, D. Boggara, M. Krishnamoorti, R. *Biochimica et Biophysica Acta*. **1821**, 994 (2012)
- [2] Manrique, M. Villena, F. Sotomayor, C. Edwards, A. Garidel, P. Suwalsky, M. *Biochimica et Biophysica Acta*. **1808**, 2656 (2011).
- [3] Lichtenberger, L. Zhou, Y. Dial, E. Raphael, R. *Journal of Pharmacology*. **58**, 1421 (2006).

## Automatization of the Nwat-MMGBSA method to rescore docking results in medium-throughput virtual screening applications

Irene Maffucci, Xiao Hu, Valentina Fumagalli and Alessandro Contini

*Dipartimento di Scienze Farmaceutiche, Università degli Studi di Milano*

*Via Venezian, 21 20133 Milano, Italy*

*alessandro.contini@unimi.it*

Nwat-MMGBSA is a variant of MM-PB/GBSA based on the inclusion of a number of explicit water molecules that are the closest to the ligand in each frame of a molecular dynamics trajectory.[1] This method can increase the correlation between predicted and experimental binding energies in both ligand-receptor and protein-protein complexes,[2] compared to standard MM-GBSA. The protocol for molecular dynamic (MD) simulations, preparatory to subsequent Nwat-MMGBSA calculations, has now been optimized to maximize efficacy and efficiency, thus making the calculations practical in low-to-medium throughput virtual screenings. Three systems, penicillopepsin, HIV1-protease and BCL-XL, have been used as test cases. Calculations have been performed in triplicates on both classic HPC environments as well as on workstations equipped by GPU cards, evidencing no statistical differences in the results, but a dramatic decrease of the “cost per nanosecond” for the latter systems. With the optimized protocol, the whole calculation, from equilibration to production MD and subsequent Nwat-MMGBSA rescoring, averagely took about one hour per ligand using a single GPU.

A set of scripts for automatic structure based virtual screening, from library setup to docking and rescoring, has also been designed and tested within a retrospective virtual screening for inhibitors of the Rac1-Tiam1 protein-protein interaction. The screening library has been built using compounds experimentally tested, with a ratio between actives

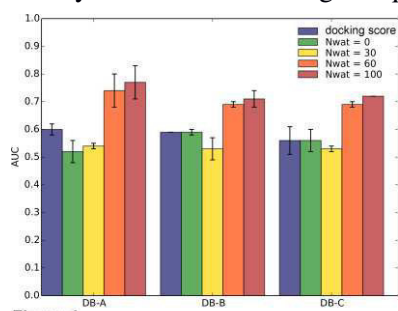


Figure 1

and real inactives of 1 to 10, and different protocols were used to process the library prior to docking (DB-A, DB-B and DB-C, Figure 1).

The results, summarized in Figure 1, confirmed the benefit of including explicit water molecules MM-GBSA calculation and the validity of Nwat-MMGBSA to rescore virtual screening results.

[1] I. Maffucci and A. Contini, *J. Chem. Theor. Comput.* **9**, 2706 (2013)

[2] I. Maffucci and A. Contini, *J. Chem. Inf. Model.* **56**, 1692 (2016)

Xiao Hu is supported the H2020 MSCA joint doctoral project MoGglyNet, grant # 675527

## Stressed Disulfide Bonds in Alkaline solution.

Przemysław Dopieralski<sup>1,2</sup>, Jordi Ribas-Arino<sup>3</sup>, Padmesh Anjukandi<sup>4</sup>,

Martin Krupicka<sup>1,5</sup>, Dominik Marx<sup>1</sup>

<sup>1</sup>*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany*

<sup>2</sup>*Faculty of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland*

<sup>3</sup>*Departament de Química Física and IQTCUB, Universitat de Barcelona,  
Av. Diagonal 645, 08028, Barcelona, Spain*

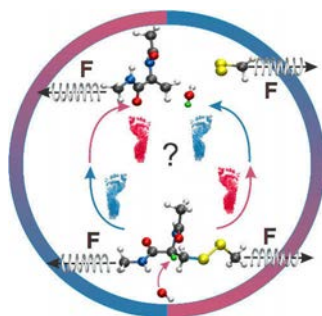
<sup>4</sup>*Department of Chemistry, Indian Institute of Technology Palakkad,  
Ahalia Integrated Campus, Kozhippara PO. 678557, Kerala, India*

<sup>5</sup>*Department of Organic Chemistry, University of Chemistry and Technology, Technická 5,  
16628 Prague, Czech Republic*

<sup>1</sup> [przemyslaw.dopieralski@chem.uni.wroc.pl](mailto:przemyslaw.dopieralski@chem.uni.wroc.pl)

Research on the impact of tensile forces on the disulfide bond reductions is crucial in order to understand the mechanisms by which disulfide switches regulate the activity of certain proteins.

By using *ab initio* molecular dynamics and metadynamics simulations in the condensed phase, we investigate the response of the  $\beta$ -elimination channel [1] of a disulfide bond reduction [2] in alkaline solution to mechanical stress. Our simulations reveal that the rate-determining first step of the reaction, which is the abstraction of a proton of the disulfide by an hydroxide ion, is not accelerated by external tensile forces. Even more interestingly, forces larger than ca. 1 nN are able to revert the order in which the steps of the  $\beta$ -elimination mechanism take place.



[1] P. Dopieralski, J. Ribas-Arino, P. Anjukandi, M. Krupicka, D. Marx, *Angewandte Chemie International Edition* 55, 1304 (2016).

[2] P. Dopieralski, J. Ribas-Arino, P. Anjukandi, M. Krupicka, J. Kiss, D. Marx, *Nat. Chem.* 5, 685 (2013).

## Wetting Behavior of a Surface Decorated with Periodic Pillars

Zhengqing Zhang<sup>1</sup>, Liyi Bai<sup>1</sup>, Hyojeong Kim,<sup>2</sup> Joonkyung Jang<sup>1,3</sup>

<sup>1</sup>*Department of Nanofusion Technology, Pusan National University, Busan, South Korea*

<sup>2</sup>*Max Planck Institute for Intelligent Systems, Heisenbergstr. 3, Stuttgart, Germany*

<sup>3</sup>*Department of Nanoenergy Engineering, Pusan National University, Busan, South Korea*

Using Monte Carlo (MC) and molecular dynamics (MD) simulations, we examined the phase behavior of water confined between hydrophobic pillars by varying the size and shape of pillar and the inter-pillar spacing. The drying transition of water with decreasing the inter-pillar spacing is related to the Wenzel (WZ) to Cassie-Baxter (CB) transition of droplet. A continuum theory is developed for the inter-pillar spacing and pressure at which the CB to WZ transition occurs for a droplet deposited on a periodic array of pillars. With increasing interpillar spacing or pressure, the liquid on top of the domed pillars penetrated smoothly down into the gap between the pillars [1]. This wetting transition contrasts with that observed for the gap between rectangular or cylindrical pillars, where a liquid abruptly fills in the interpillar gap at a critical interpillar spacing or pressure. The gap between the domed pillars was more susceptible to the intrusion of the bulk liquid on top of the pillars, due to the open geometry of the gap between the domed pillars. Also, the liquid penetrating into the gap between the domed pillars was locally more fluctuating in density and compressible than that penetrating into the gap between square or cylindrical pillars. Simple analytic expressions of the critical spacing and pressure at which the wetting transition occurs for the domed pillars were derived using continuum theory. These continuum results agreed reasonably well with the present molecular simulations, even for pillars as small as a few nanometers in width. We also replot a large scale MD simulation study of the wettability of a gold surface engraved with (hemi)spherical cavities [2]. By increasing the depth of cavities, the contact angle (CA) of a water droplet on the surface was varied from a hydrophilic ( $69^\circ$ ) to a hydrophobic value ( $>109^\circ$ ). The nonmonotonic behavior of the CA vs the depth of the cavities was consistent with the Cassie–Baxter theory, as found in the experiment by Abdelsalam et al. [3]. Depending on the depth of cavities, however, the droplet existed not only in the CB state, but also in the WZ or an intermediate state, where the cavities were penetrated partially by the droplet.

[1] H. Kim, S. I. Lee, M. A. Matin, Z. Zhang, J. Jang, M. Y. Ha, and J. Jang, *J. Phys. Chem. C*, **118**, 26070 (2014).

[2] Z. Zhang, M. A. Matin, M. Y. Ha, and J. Jang, *Langmuir* **32**, 9658 (2016)

[3] M. E. Abdelsalam, P. N. Bartlett, T. Kelf, J. Baumberg, *Langmuir* **21**, 1753 (2005)

## Communication in proteins and protein-substrate complexes.

**Tahereh Ghane<sup>1</sup>, Mahdi Bagherpoor Helabad<sup>1</sup>, Moritz Krügener<sup>1</sup>, Rene Gorritz<sup>1</sup>, Senta Volkenandt<sup>1</sup>, Petra Imhof<sup>1</sup>**

<sup>1</sup>*Institute of Theoretical Physics, Free University Berlin, Arnimallee 14, Berlin, Germany*

Cellular function often need to be controlled at the molecular level, between molecules as well as within the same molecule or molecular complex. In allosteric processes information, i.e. a ligand binding, a reaction step, or a conformational change, taking place in one part of a molecule is propagated to another, distant part of the molecule, causing a response effect at that ('allo-steric') 'other-space'. Often, allosteric proteins are homo-oligomers where e.g. co-operative effects are due to substrate binding manifested in major conformational transitions between apo form, intermediate, and bound states. Communication within a protein is also observed to signal more local changes such as the protonation of a residue via e.g. re-wiring hydrogen-bonded networks, to sites distant from the protonation site. We use molecular dynamics simulations of proteins in different states of substrate binding or a reaction and analyse the communication between different parts of the protein-substrate complexes so as to reveal optimal communication paths. By employing different metrics for communication, we show that not only the strength and pathways of communication can be altered upon substrate binding but also the optimal means of communication.

include figures the usual way:



Figure 1: Optimal communication path between two residues in protein Cytochrome c Oxidase



## Camphore's and Huperzine's adventures in Proteinland

Jakub Rydzewski<sup>1</sup>, Wiesław NOWAK<sup>1</sup>

<sup>1</sup>*Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Toruń, Poland*

Biologically relevant ligands often migrate between solvent environments and enzymatic active sites to complete their physiological missions. Theoretical prediction of such transport paths is a challenging task [1,2]. Recently, we have developed an advanced computational scheme, based on memetic sampling (MS) during molecular dynamics simulations [3]. MS effectively predicts pathways of medium-size (27 – 36 atoms) ligands within crowded protein matrices. After dimensionality reduction of ligand-protein conformational space and calculating reaction coordinates [4], we selected ligand exit paths in two enzymatic systems: cytochrome P450cam-camphor and acetylcholine esterase-huperzine A. For these paths comprehensive metadynamics simulations [5,6] revealed free-energy barriers encountered by both ligands during the unbinding from their enzymatic active sites. Chemical nature of these rate-limiting regions was determined. Based on our thermodynamical data for wild type proteins, possible biological roles of selected point mutations are discussed.

JR acknowledges funding (grants no. 2015/19/N/ST3/02171 and 2016/20/T/ST3/00488) from National Science Centre, Poland and UMK grants 2406-F, 2539-F. The results were obtained using Interdisciplinary Centre for Modern Technologies computational facilities, NCU Toruń, Poland.

- [1] J. Rydzewski, W. Nowak, [doi.org/10.1016/j.plrev.2017.03.003](https://doi.org/10.1016/j.plrev.2017.03.003) (2017).
- [2] W. Nowak, in “*Handbook of Computational Chemistry*”, 2<sup>nd</sup> ed. J. Leszczyński, Springer (2017).
- [3] J. Rydzewski, W. Nowak, *J. Chem. Phys.* **143**, 09B617\_1 (2015).
- [4] J. Rydzewski, W. Nowak, *J. Chem. Theory Comp.* **12**, 2110 (2016).
- [5] J. Rydzewski, W. Nowak, *Sci. Rep.*, *submitted* (2017).
- [6] J. Rydzewski, R. Jakubowski, W. Nowak, H. Grubmueller, *in prep.* (2017).

## Conductance Switching in Expanded Porphyrins through Aromaticity and Topology Changes

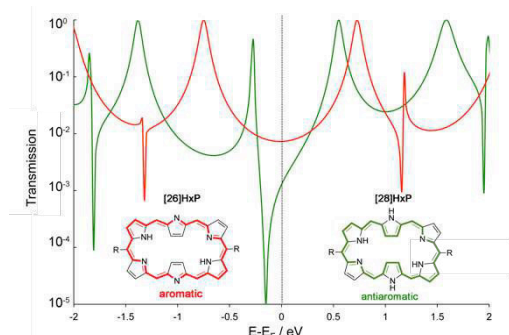
Mercedes Alonso, Thijs Stuyver, Frank De Proft

General Chemistry Department (ALGC), Vrije Universiteit Brussel (VUB), Pleinlaan 2,  
1050 Brussels, Belgium, mercedes.alonso.giner@vub.be

Expanded porphyrins are flexible enough to switch between different  $\pi$ -conjugation topologies (Möbius, Hückel and twisted-Hückel) encoding distinct electronic properties and aromaticity.[1] Since the topological/aromaticity switch can be induced by different external stimuli, expanded porphyrins represent a promising platform to develop a novel type of molecular switches for molecular electronic devices.[2] In recent years, aromaticity emerged as the key concept determining the electronic, magnetic and photophysical properties of expanded porphyrins and accordingly, we proposed different methods to quantify the Hückel and Möbius aromaticity.[2,3]

In this work, we assess computationally the feasibility of conductance switches based on expanded porphyrins for the first time. Thus, the electron transport properties of single thiol-terminated expanded porphyrins bound to gold electrodes with different  $\pi$ -conjugation topologies and aromaticity were investigated using DFT methods and Green's function formalism. This study is particularly relevant since the link between transmission and key concepts in chemistry, such as aromaticity and polarizability, is

established allowing a chemical understanding of conductance.[4] Our results highlight the importance of the macrocyclic aromaticity on determining the transmission functions of the different states. Finally, we provide a set of qualitative rules to predict the presence of a quantum interference close to the Fermi level based on a simple model for Hückel and Möbius systems.



[1] T. Tanaka, A. Osuka, *Chem. Rev.* **117**, 2584 (2017).

[2] M. Alonso, P. Geerlings, F. De Proft, *Chem. Eur. J.* **18**, 10916 (2012); *J. Org. Chem.* **78**, 4419 (2013); *Chem. Eur. J.* **19**, 1617 (2013), *Phys. Chem. Chem. Phys.* **16**, (2014), 14396; *Chem. Eur. J.* **21**, 17631 (2015).

[3] T. Woller, J. Contreras-García, P. Geerlings, F. De Proft, M. Alonso, *Phys. Chem. Chem. Phys.* **18**, 11885 (2016); *Phys. Chem. Chem. Phys.* **18**, 11829 (2016).

[4] T. Stuyver, F. De Proft, P. Geerlings, M. Perrin, M. Alonso, manuscript in preparation.

## Spin-dependent transport and magnetoresistance in metalloporphyrin-based supramolecular wires at room temperature

Albert Aragonès<sup>1,2,3</sup>, Alejandro Martín-Rodríguez<sup>1,2</sup>, Arantzazu Gonzalez Campos<sup>5</sup>, Nuria Aliaga-Alcalde<sup>5,6</sup>, Daniel Aravena<sup>7</sup>, Fausto Sanz<sup>1,3</sup>, Eliseo Ruiz,<sup>2,4</sup> Ismael Díez-Pérez<sup>1,2,3</sup>

<sup>1</sup>*Dep. de Ciència de Materials i Química Física, Universitat de Barcelona, and Institut de Bioenginyeria de Catalunya (IBEC), Barcelona, Spain*

<sup>2</sup>*Institut de Química Teòrica i Computacional, Universitat de Barcelona, Barcelona, Spain*

<sup>3</sup>*Centro Investigación Biomédica en Red (CIBER-BBN), Zaragoza, Spain.*

<sup>4</sup>*Dep. de Química Inorgànica i Orgànica, Universitat de Barcelona, Barcelona, Spain*

<sup>5</sup>*CSIC-ICMAB (Institut de Ciència dels Materials de Barcelona), Bellaterra, Spain.*

<sup>6</sup>*ICREA (Institució Catalana de Recerca i Estudis Avançats)*

<sup>7</sup>*Dep. de Química de los Materiales, Universidad de Santiago de Chile, Santiago, Chile*

Paramagnetic coordination compounds are appealing candidates for the design of single molecule devices if their spin degrees of freedom can be controlled by external stimuli (such as magnetic or electric fields). Complexes with two or more accessible and readable states can be envisioned as switches, which could be integrated to form more complex devices, as molecular transistors. Electronic conductance is a technologically convenient way to distinguish between binary states (“read”). Thus, magnetoresistance phenomena in molecular systems is a desired property to design molecular devices.

Recently, we observed huge magnetoresistance effects at room temperature in STM molecular junctions incorporating octahedral M<sup>II</sup> complexes (M = Mn, Fe, Co, Ni).[1,2] Electronic structure calculations clarified the role of electronic configuration of the transition metal in the observed behavior. These studies were extended for a family of metalloporphyrin molecular wires with M<sup>II</sup> (M : Co, Ni, Cu and Zn) cations and the 5,15-diphenylporphyrin ligand (DPP). Co and Cu complexes exhibit magnetoresistance effects, independent of the current direction. Non-equilibrium Green Functions (NEGF) + DFT calculations [3] reproduce the experimental trend and help to assign the alpha channel as the responsible for electron transport.

[1] A. C. Aragonès, D. Aravena, F. J. Valverde-Muñoz, J. A. Real, F. Sanz, I. Díez-Pérez, E. Ruiz, *J. Am. Chem. Soc.* DOI:10.1021/jacs.6b11166 (2017).

[2] A. Aragonès, D. Aravena, J. Cerda, Z. Acis-Castillo, H. Li, J. A. Real, F. Sanz, J. Hihath, E. Ruiz, I. Díez-Pérez; *Nano Lett.* **16**, 218 (2016).

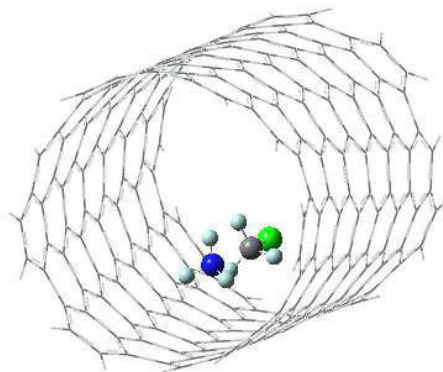
[3] A. Martín-Rodríguez, D. Aravena, E. Ruiz, *Theor. Chem. Acc* **135**, 192. (2016)

## Catalyzing chemical reactions inside carbon nanotubes

Magalhães A.L.<sup>1</sup>, Tavares I.S.<sup>1</sup>, Figueiredo C.F.B.R.<sup>1</sup>

<sup>1</sup>UCIBIO/Requimte, Department of Chemistry and Biochemistry, Faculty of Sciences,  
University of Porto, Porto, Portugal

Kinetic and thermodynamic properties of chemical reactions might be highly dependent on the surrounding medium. Recently, computational studies have shown that some  $S_N2$  reactions suffer a significant increase in their rates when they occur inside single-walled carbon nanotubes (SWNTs) as compared to gas-phase.[1,2]



The present work is a systematic quantum mechanical DFT study of the effect of SWNT structure on the kinetics and thermodynamics of reacting systems. In particular, this work analyzes the impact of different types of SWNTs, namely *armchair*(n,n), *zigzag*(n,0) and *chiral*(n,m), on the Menshutkin  $S_N2$  reaction between ammonia and chloromethane. Calculations have been performed with flexible and finite SWNT models at the M06-2X/6-31++G(d,p)/3-21G level.

All SWNTs considered in this work reduce significantly the activation energy,  $E_a$ , and the endothermicity,  $\Delta H$ , of the reaction when compared to the gas-phase [3]. As nanotubes become wider, they all converge to the values 28 kcal.mol<sup>-1</sup> and 21 kcal.mol<sup>-1</sup>, respectively for  $E_a$  and  $\Delta H$ , which correspond to the reaction occurring near a graphene surface. On the other hand, as diameters decrease, a differentiation of the nanotubes is observed and each type of SWNT shows a different potential well, with chiral (6,4) SWNT (diameter 6.8 Å) exhibiting the lowest energy barrier,  $E_a = 17.9$  kcal.mol<sup>-1</sup>.

[1] M.D. Halls, H.B. Schlegel, *J. Phys. Chem. B* **106**, 1921 (2002)

[2] P. Giacinto, A. Bottoni, M. Calvaresi, F. Zerbetto, *J. Phys. Chem. C* **118**, 5032 (2014)

[3] A.L. Magalhães, I.S. Tavares, C.F.B.R. Figueiredo, *J. Phys. Chem. C* **121**, 2165 (2017)

## Theoretical Calculations of Endohedral Fullerenes: From Chemical Bonding to Single-Molecule Switches

J. Kaminský,<sup>1</sup> C. Foroutan-Nejad,<sup>2</sup> J. Vicha,<sup>1</sup> V. Andrushchenko,<sup>1</sup> M. Straka<sup>1</sup>

<sup>1</sup>*Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences,  
Flemingovo nám. 2, 16610, Prague, Czech Republic*

<sup>2</sup>*CEITEC - Central European Institute of Technology, Masaryk University  
Kamenice 5/A4, CZ-62500 Brno, Czech Republic*

Endohedral fullerenes have attracted wide interest due to their potential applications in science and technology, e.g. as MRI contrast agents, sensors, or molecular switches. We will present some of our recent findings in the area of **endohedral actinide fullerenes**, particularly the phenomenon of *unwilling* actinide-actinide bonding along  $An_2@C_{80}$  ( $An=Th-Cm$ ) series<sup>[1]</sup> and theoretical investigations of the only Th fullerene,  $Th@C_{84}$  (Figure 1).<sup>[2]</sup>

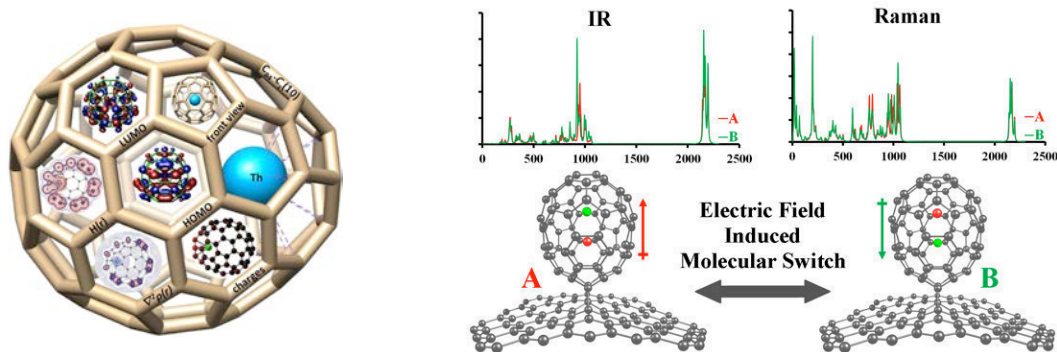


Figure 1:  $Th@C_{84}$  (left) and model of endohedral single-molecule switch(right)

The proposal of a **two-state electric field-driven room-temperature single-molecule switch**<sup>[3]</sup> based on a dipolar molecule enclosed inside ellipsoidal fullerene  $C_{70}$  (Figure 1) will be presented. We have shown that the two low-energy minima of the molecular dipole inside the  $C_{70}$  cage provide distinguishable molecular states of the system that can be switched by application of an external electric field. Such systems may provide base for high-density memory materials.

**Acknowledgments:** Czech Science Foundation (No. 17-07091S)

- [1] C. Foroutan-Nejad, J. Vicha, R. Marek, M. Patzschke, M. Straka, *Phys. Chem. Chem. Phys.* **2015**, *17*, 24182-24192.
- [2] J. Kaminský, J. Vicha, P. Bouř, M. Straka, *J. Phys. Chem. A* **2017**, *121*, 3128-3135.
- [3] C. Foroutan-Nejad, V. Andrushchenko, M. Straka, *Phys. Chem. Chem. Phys.* **2016**, *18*, 32673-32677.

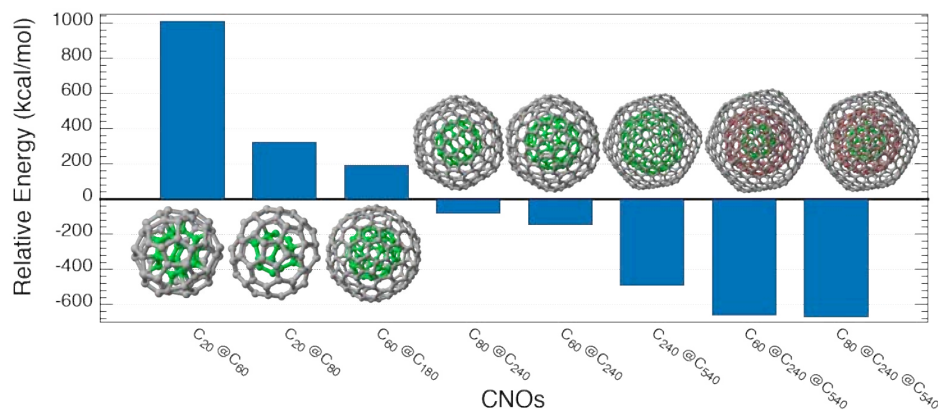
## Structural and Electronic Properties of Carbon Nano-Onions

Muhammad Ali Hashmi<sup>1</sup> and Matthias Lein<sup>1,2\*</sup>

<sup>1</sup> School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington, 6012 (New Zealand)

<sup>2</sup> Centre for Theoretical Chemistry and Physics, New Zealand Institute for Advanced Study, Massey University Auckland, Private Bag 102904, North Shore MSC 0632 Auckland (New Zealand)

We have investigated the double-layered carbon nano-onions (CNOs)  $C_{20}@C_{60}$ ,  $C_{20}@C_{80}$ ,  $C_{60}@C_{180}$ ,  $C_{60}@C_{240}$ ,  $C_{80}@C_{240}$ , and  $C_{240}@C_{540}$  as well as their triple-layered analogues  $C_{60}@C_{240}@C_{540}$ , and  $C_{80}@C_{240}@C_{540}$  with high-level electronic structure calculations. We were able to confirm earlier work that showed the free rotation of the inner Fullerene inside a CNO against the outer shell. However, we also show that this behaviour is an exception that only applies to the innermost Fullerene, and only in the case of good size-matching with the second shell of a CNO. We predict that strong dispersion interactions between individual layers of CNOs prevent this behaviour for all other shells. We show that the likely reason for this is the superadditivity of the interaction energies between individual shells; *i.e.* the total interaction energy of all shells is larger than the sum of all individual interaction energies between pairs of shells. We conjecture that this is also the reason for the experimentally observed growth of CNOs with many layers. We also show how the electronic states of individual Fullerenes are polarised, but essentially preserved in CNOs and how charge-transfer excitations between layers arise.



### References:

- [1]. R. Kleingeld, J. Wang, M. Lein *Polyhedron*, 114, 110-117, 2016
- [2]. I. Welsh, M. Lein *J. Comp. Chem*, 35, 181-191, 2013

## Nickel effect on the spacing of 002 plane in a graphite-like structure

**Juan F. Espinal<sup>1</sup>, Jaime Gallego<sup>1</sup>, and Julian D. Correa<sup>2</sup>**

<sup>1</sup>*Química de Recursos Energéticos y Medio Ambiente, Instituto de Química, Facultad de Ciencias Exactas y Naturales, Universidad de Antioquia UdeA, Calle 70 No. 52-21, Medellín, Colombia*

<sup>2</sup>*Departamento de Ciencias Básicas, Universidad de Medellín, Medellín, Colombia*

Metal catalysts are commonly used for the growth of multi-walled carbon nanotubes (MWCNT). Some metal nanoparticles of the catalyst remain encapsulated in the MWCNT while other metal nanoparticles may be attached to the external wall of the MWCNT as an inorganic functionalization. Additionally, for some specific applications the presence metal nanoparticles with the MWCNT is desired. Either case, the interaction with metal nanoparticles affects the physicochemical properties of the nanotubes. For instance, it has been reported by using high-resolution transmission electron microscopy (HR-TEM) that the intershell spacing in MWCNT changes by the interaction with the metal [1]. The study of this interaction is important for improving our understanding of the system. The use of computational methods gives information at atomic and electronic level that is useful for explaining the phenomena that is involved. Therefore, as a first approximation to study the effect of nickel nanoparticles on the geometry of MWCNT, we evaluated the effect of a nickel surface on the spacing of graphene multilayers since similar interactions are expected for metal-MWCNT and it will give us a qualitative description of the interactions in this system. For this study we carried out DFT calculations using the SIESTA *ab initio* package [2]. A Ni(111) surface was used to simulate the interaction with graphene layers (from 1 to 5) in order to obtain information about the changes in the graphene spacing compared to the graphite spacing.

[1] J. Gallego, J. Barrault, C. Batiot-Dupeyrat, F. Mondragon, *Micron*. **44**, 463 (2013).

[2] J.M. Soler, et al, *J. Phys. Condens. Matter*. **14**, 2745 (2002).

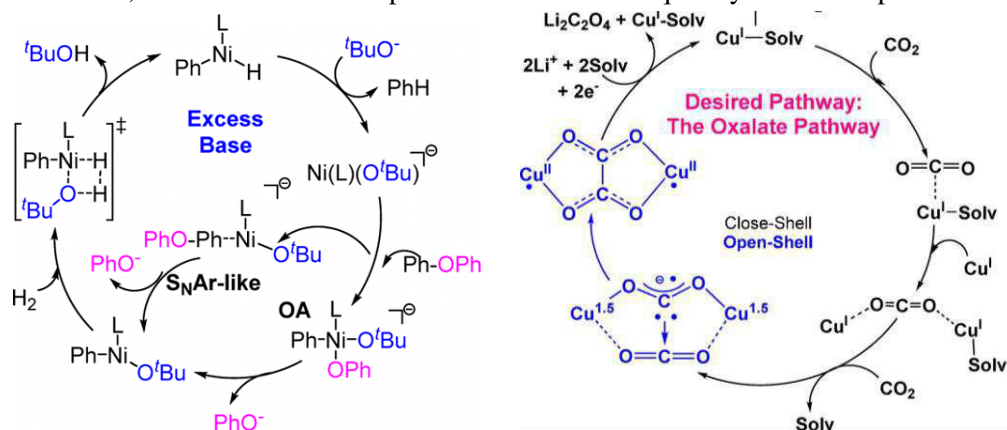


## Mechanistic Insights on Ni-catalyzed Selective C-O Activation & Cu-catalyzed Reductive CO<sub>2</sub> Coupling to Form Oxalate

Jialing Lan<sup>1</sup>, Liping Xu<sup>2</sup>, Xiaoyong Zhang<sup>1</sup>, Yun-Donng Wu<sup>2</sup>, (Oscar) Lung Wa CHUNG<sup>1,\*</sup>

<sup>1</sup>Department of Chemistry, South University of Science and Technology of China Shenzhen 518055, China; <sup>2</sup>Key Laboratory of Chemical Genomics, Peking University Shenzhen Graduate School, Shenzhen 518055, China

Computational chemistry has played an important role in elucidating mechanisms of metal-mediated organic and enzymatic reactions (including the origins of chemo-, regio-, and stereo-selectivities).<sup>[1]</sup> Some of our recent studies revealed new mechanistic insights on unusual Ru-catalyzed *trans*-hydrofunctionalization (Wu-Trost mechanism),<sup>[2a-b]</sup> Ni-catalyzed selective C-O activation,<sup>[2c-d]</sup> Cu(I)-catalyzed reductive CO<sub>2</sub> coupling via a mixed-valence state<sup>[2e-f]</sup>, dispersion-driven Pd-catalyzed asymmetric diboration<sup>[2g]</sup> and Ni-dependent lactate racemase (LarA).<sup>[2h]</sup> These examples not only explain the experimental observations, but also some of our predictions were subsequently verified experimentally.



[1] (a) L.W. Chung, et al. *Chem. Rev.* **115**, 5678 (2015). (b) X. Zhang, L. W. Chung, Y.-D. Wu, *Acc. Chem. Res.* **49**, 1302 (2016). (c) G.-J. Cheng, X. Zhang, L. W. Chung, L. Xu, Y.-D. Wu, *J. Am. Chem. Soc.* **137**, 1706 (2015).

[2] (a) L.-J. Song, T. Wang, X. Zhang, L. W. Chung, Y.-D. Wu, *ACS Catal.* **7**, 1361 (2017). (b) L. W. Chung, Y.-D. Wu, B. M. Trost; Z. T. Ball, *J. Am. Chem. Soc.* **125**, 11578 (2003). (c) A. G. Sergeev, J. F. Hartwig, *Science* **332**, 439 (2011). (d) L. Xu, L. W. Chung, Y.-D. Wu, *ACS Catal.* **6**, 483 (2016). (e) J. Lan, T. Liao, T. Zhang,; L. W. Chung, *Inorg. Chem.* DOI: 10.1021/acs.inorgchem.6b03080 (2017). (f) R. Angamuthu, P. Byers, M. Lutz; A. L. Spek, E. Bouwman, *Science* **327**, 313 (2010). (g) J.; Liu, M. Nie, Q. Zhou, L. W. Chung, W. Tang, K. Ding, *Chem. Sci.* DOI: 10.1039/C7SC01254C (2017). [h] X. Zhang, L. W. Chung, *Chem. Eur. J.* **23**, 3623 (2017).



## Mechanistic investigation on the Pd-Catalyzed Hydrogenation of 1,6-Enynes: A DFT Approach.

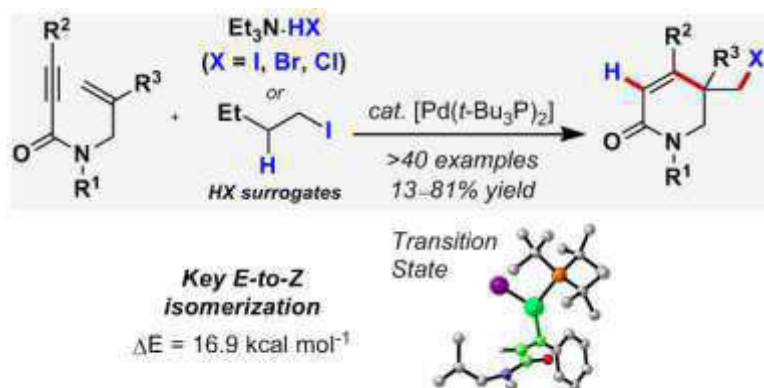
D. A. Petrone<sup>1</sup>, I. Franzoni<sup>1</sup>, J. Ye<sup>1</sup>, J. F. Rodríguez<sup>1</sup>, A. I. Poblador-Bahamonde<sup>2\*</sup>, and M. Lautens<sup>1\*</sup>

<sup>1</sup>*Davenport Research Laboratories, Department of Chemistry, University of Toronto, Toronto, Canada*

<sup>2</sup>*Department of Organic Chemistry, University of Geneva, Geneva, Switzerland*

Handling small molecules as H<sub>2</sub> or CO in metal catalyzed process is not trivial. The use of convenient hydrogen halide sources facilitates its use in the laboratory minimizing safety issues. Despite of these developments, their application on transition metal catalysis remains challenging [1]. Recent results on the group of Professor Mark Lautens accomplish Pd-catalyzed hydrogenation of enynes thanks to the use of ammonium halides salts as HX surrogates [2].

Herein, we present a comprehensive mechanistic investigation of this reaction by the use of Density Functional Theory (DFT). The initial alkyne insertion into the [Pd-H] species describes the observed selectivity while an unusual *E* to *Z* isomerization and the final halogen bond-forming reductive elimination steps reveal to be key processes and, therefore they will be discussed in detail.



[1] D. A. Petrone, J. Ye, M. Lautens, *Chem. Rev.* **116**, 8003 (2016)

[2] D. A. Petrone, I. Franzoni, J. Ye, J. F. Rodríguez, A. I. Poblador-Bahamonde and M. Lautens, *J. Am. Chem. Soc.* **139**, 3546 (2017)

## NOF-MP2: A global method for the electron correlation

Mario Piris<sup>1,2,3</sup>

<sup>1</sup>*Donostia International Physics Center (DIPC), 20018 Donostia, Spain*

<sup>2</sup>*Euskal Herriko Unibertsitatea (UPV/EHU), P.K. 1072, 20080 Donostia, Spain*

<sup>3</sup>*IKERBASQUE, Basque Foundation for Science, 48013 Bilbao, Spain*

In electronic structure theory, accurate solutions require a balanced treatment of both static (non-dynamic) and dynamic correlation. Nowadays, it is necessary to resort to multi-reference methods for correctly handling both types of correlation, however, these techniques are often expensive and demand prior knowledge of the system. On the other hand, single-reference correlation methods are well-established for dynamic correlation, but are unsatisfactory for systems with static correlation. In this presentation, a single-reference method is proposed capable of achieving both dynamic and static correlation even for those difficult cases in which both types of correlation are equally present.

The starting-point is a determinant wavefunction formed with natural orbitals obtained from a new interacting-pair model. The latter leads to a natural orbital functional (NOF) [1, 2] named PNOF7 capable of recovering the complete intra-pair, but only the static inter-pair correlation. Using the solution of the NOF, two new energy functionals are defined for both dynamic ( $E^{dyn}$ ) and static ( $E^{sta}$ ) correlation.  $E^{dyn}$  is derived from a modified second-order Møller-Plesset perturbation theory (MP2) [3], while  $E^{sta}$  is obtained from the static component of the PNOF7. Double counting is avoided by introducing the amount of static and dynamic correlation in each orbital as a function of its occupation. The total energy is represented by the sum  $\tilde{E}_{hf} + E^{dyn} + E^{sta}$ , where  $\tilde{E}_{hf}$  is the Hartree-Fock energy obtained with natural orbitals. The resulting working formulas allow for static and dynamic correlation to be achieved in one shot, as is the case in the standard single-reference perturbation theory.

The new procedure called NOF-MP2 is extraordinarily simple, has fifth order formal scaling of computational cost, and the property of size-consistency, essential for applying the method to extended systems. It is applied successfully to the homolytic dissociation of a selected set of diatomic molecules that encompass very dissimilar interactions ranging from weak to strong bonds, thus sweeping a wide range of interelectronic interactions and correlation regimes. The values obtained are in outstanding agreement with the experimental data.

[1] M. Piris, *Adv. Chem. Phys.* **134**, 387 (2007).

[2] M. Piris, J. M. Ugalde, *Int. J. Quantum Chem.* **114**, 1169 (2014).

[3] C. Møller, M. S. Plesset, *Phys. Rev.* **46**, 618 (1934).

## Recovering the flat plane condition in electronic structure theory at semi-local density functional theory cost

Heather J. Kulik<sup>1</sup>, Akash Bajaj<sup>1,2</sup>, J. P. Janet<sup>1</sup>, Terry Z. H. Gani<sup>1</sup>, Qing Zhao<sup>1,3</sup>

<sup>1</sup>*Department of Chemical Engineering, MIT, 77 Massachusetts Ave, Cambridge, MA, USA*

<sup>2</sup>*Department of Materials Science and Engineering, MIT, 77 Massachusetts Ave,  
Cambridge, MA, USA*

<sup>3</sup>*Department of Mechanical Engineering, MIT, 77 Massachusetts Ave, Cambridge, MA,  
USA*

**Abstract:** Piecewise linearity of the energy with respect to fractional electron removal or addition is a requirement of an electronic structure method that necessitates the presence of a derivative discontinuity at integer electron occupation. Semi-local density functional theory (DFT) exhibits instead convex behavior with electron removal or addition that has in recent years been corrected through incorporation of Hartree-Fock exchange either globally, in range-separated hybrids, or with Hubbard model corrections[1,2]. The additional requirement that the energy is invariant with respect to the spin of an electron in isoenergetic orbitals produces a tighter constraint known as the flat plane condition, wherein two linear planes meet at a fractional spin line seam. All approaches that have aimed to correct deviations from piecewise linearity in semi-local DFT are known to worsen already concave behavior on the fractional spin line, increasing static correlation error. We return to the original functional form of semi-local DFT errors along the flat plane and quantify the convexity along the fractional charge line and concavity along the fractional spin line. Analysis of the functional form of this error enables identification of the first no-computational-overhead corrections that can recover the flat plane condition within semi-local DFT. We compare these functional forms to more established approaches, including range-separated hybrid functionals and our earlier observations on how Hubbard model functionals[2] recover the derivative discontinuity. Finally, we conclude with some observations[3] on how recovery of the flat plane also impacts density properties and magnetic moments with respect to accurate correlated wavefunction theory references.

[1] H. J. Kulik, *J. Chem. Phys.* **142**, 240901 (2015).

[2] Q. Zhao, E. I. Ioannidis, and H. J. Kulik, *J. Chem. Phys.* **145**, 054109 (2016).

[3] T. Z. H. Gani and H. J. Kulik, *J. Chem. Theory Comput.* **12**, 5931-5945 (2016).

## Dressing the CI matrix with explicit correlation

Pierre-François Loos<sup>1,2</sup>, Anthony Scemama<sup>1</sup>, Yann Garniron<sup>1</sup>, Michel Caffarel<sup>1</sup>

<sup>1</sup>*Laboratoire de Chimie et Physique Quantiques, Université de Toulouse, CNRS, UPS, France*

<sup>2</sup>*Research School of Chemistry, Australian National University, ACT 2601, Australia*

One of the most fundamental problem of conventional electronic structure methods is their slow energy convergence with respect to the size of the one-electron basis set. As pioneered by Kutzelnigg [1], one way to speed up the convergence of such methods is to introduce explicitly the correlation between electrons via a correlation factor  $f_{12}$ , leading to a prominent improvement of the energy convergence from  $O(L^{-3})$  to  $O(L^{-7})$  (where  $L$  is the maximum angular momentum of the one-electron basis). This gave birth to the so-called explicitly-correlated F12 methods which can achieve chemical accuracy for small organic molecules with relatively small Gaussian basis sets [2, 3].

In this talk, following Kutzelnigg's seminal idea, we propose to show that one can introduce the explicit correlation between electrons within the configuration interaction (CI) method via a dressing of the CI matrix [4]. This method, involving effective Hamiltonian theory, has been shown to be also successful in other scenario [5]. Compared to other explicitly-correlated methods, this dressing strategy has the advantage of introducing the explicit correlation at a low computational cost. The present idea is completely general and can be applied to any type of truncated, full, or even selected CI method [6]. Illustrative examples will be given on atomic and molecular systems.

- [1] W. Kutzelnigg, *Theor. Chim. Acta* **68**, 445 (1985).
- [2] C. Hattig, W. Klopper, A. Kohn, and D. P. Tew, *Chem. Rev.* **112**, 4 (2012).
- [3] L. Kong, F. A. Bischo, and E. F. Valeev, *Chem. Rev.* **112**, 75 (2012).
- [4] J.-L. Heully and J.-P. Malrieu, *Chem. Phys. Lett.* **199**, 545 (1992).
- [5] J.-P. Daudey, J.-L. Heully and J.-P. Malrieu, *J. Chem. Phys.* **99**, 1240 (1993).
- [6] M. Caffarel, T. Applencourt, E. Giner, and A. Scemama, *J. Chem. Phys.* **144**, 151103 (2016).

## Performance of the Random Phase Approximation for first-row transition metal catalysis

**Henk Eshuis<sup>1</sup>, Julianna Chedid<sup>1</sup>, Nashali Ferrara<sup>1</sup>, Craig Waitt<sup>1</sup>**

<sup>1</sup>*Department of Chemistry and Biochemistry, Montclair State University, 1 Normal Ave, Montclair, NJ, USA*

This presentation will give an overview of the performance of the (direct) random phase approximation method (RPA) for first-row transition metal catalysis. The random phase approximation gained considerable interest in recent years as an efficient method to obtain ground state correlation energies, particularly because of its seamless inclusion of non-covalent interactions. For main-group chemistry, its performance is similar to commonly used hybrid functionals with a Grimme-type dispersion correction [1]. RPA presents itself as a cost-efficient alternative to Møller-Plesset second order perturbation theory (MP2) for transition metal chemistry, an area where MP2 often fails and density functionals can produce mixed results. In this work, direct RPA based on a Kohn-Sham reference is benchmarked for a variety of properties of (mainly) first-row transition metal complexes, such as binding energies, reaction energies, and structural parameters [2]. High-level theory and experimental data are used as reference for the benchmark. Comparison is made to MP2 and several density functionals. Preliminary results are presented on C-CN bond activation through Nickel catalysis and Copper catalyzed trifluoromethylation of boronic acids. Overall, RPA outperforms MP2 and give results of the same quality as the best-performing commonly used density functionals. RPA is thus a strong alternative method for the study of transition metal chemistry.

[1] H. Eshuis and F. Furche, *J. Phys. Chem. Lett.* **2**, 983 (2011).

[2] C. Waitt, N. M. Ferrara and H. Eshuis, *J. Chem. Theo. Comp.* **12**, 5350 (2015).

## Highly accurate binding energies from the random phase approximation with singles corrections

Jiri Klimes<sup>1</sup>, David P. Tew<sup>2</sup>

<sup>1</sup>*Department of Chemical Physics and Optics, Faculty of Mathematics, and Physics, Charles University, Prague, Czech Republic*

<sup>2</sup>*School of Chemistry, University of Bristol, Bristol, United Kingdom*

To make reliable predictions of physical and chemical properties of materials using theoretical methods, accurate schemes need to be used. The random phase approximation (RPA) to the correlation energy has emerged as a promising tool for this task. However, a general tendency to underbind has been observed for systems such as molecular solids or for adsorption. One of the ways that have been proposed to improve the accuracy of RPA are the so-called singles corrections, originally developed by Ren and coworkers [1] and later modified to improve their accuracy for systems with delocalised electrons [2]. Here we give a brief overview of this scheme and show the results of two applications to systems of wide interest. First, we present the results obtained for lattice energies of molecular solids [3]. The differences from the reference data are only about 4%. This makes RPA with singles currently the best scheme for the calculation of lattice energies within periodic boundary conditions. Moreover, the differences are similar or even lower than the errors of the reference data themselves. Second, we show the results for adsorption of small molecules in zeolites, which is another difficult test case for current density functional theory functionals. Here RPA with singles yields adsorption energies in a very good agreement with adsorption energies obtained with MP2 for most of the systems. However, for molecules with unsaturated bonds, the results of MP2 and RPA with singles differ. Reference quality CCSD(T) calculations on finite clusters show that in such cases it is RPA with singles that produces more accurate results. Together with the only cubic scaling of the RPA with singles, this makes it an extremely promising tool for the studies of extended systems, from molecular and atomic solids, over liquids, to interfaces.

[1] X. Ren, A. Tkatchenko, P. Rinke, M. Scheffler, *Phys. Rev. Lett.* **106**, 153003 (2010)

[2] J. Klimes, M. Kaltak, E. Maggio, G. Kresse, *J. Chem. Phys.* **143**, 102816 (2015)

[3] J. Klimes, *J. Chem. Phys.* **145**, 094506 (2016)

## Separation of dynamic and nondynamic correlation

**Eduard Matito<sup>1, 2, 3</sup>, Eloy Ramos-Cordoba<sup>1, 2, 4</sup>, Mauricio Rodríguez-Mayorga<sup>1, 2, 5</sup>, Mireia Via-Nadal<sup>1, 2</sup>, Pedro Salvador<sup>5</sup>**

<sup>1</sup>*Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU), Euskadi, Spain*

<sup>2</sup>*Donostia International Physics Center (DIPC), Euskadi, Spain.*

<sup>3</sup>*IKERBASQUE, Basque Foundation for Science, Bilbao, Euskadi, Spain*

<sup>4</sup>*Department of Chemistry, University of California, Berkeley, California 94720, United States*

<sup>5</sup>*Institut de Química Comp. i Catàlisi, Depart. de Química, Univ. Girona, Catalonia, Spain*

The account of electron correlation and its efficient separation into dynamic and nondynamic parts plays a key role in the development of computational methods such as hybrid, range-separated[1] or local methods[2]. In this work we split the correlated part of the pair density into two correlation functions that account for nondynamic and dynamic correlation effects[3]. These functions are used in a two-electron model, giving rise to dynamic and nondynamic correlation functions that (i) depend only on natural orbitals and their occupancies, (ii) can be straightforwardly decomposed into orbital contributions, and (iii) admit a local form[4] (see Fig. 1). Finally, using the same strategy we present a separation of the Coulomb Hole into dynamic and nondynamic correlation. The long-range part of the dynamic-correlation hole can be used to identify dispersion interactions[5]. These expressions can aid in the development of density matrix functional theory (DMFT), density functional theory (DFT) and the development of local hybrid methods.

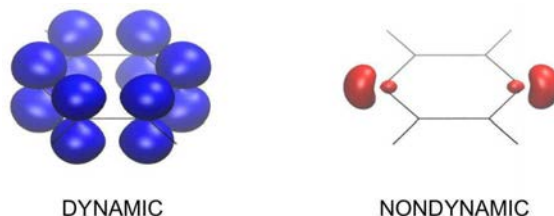


Figure 1: A real-space picture of electron correlation in *para*-benzyne.

- [1] A. Savin, *Int. J. Quant. Chem.* **34**, 59 (1988).
- [2] R. Zalesny, M. G. Papadopoulos, P. G. Mezey and J. Leszczynski, *Linear Scaling Techniques in Comp. Chemistry and Physics*. (Springer, 2011)
- [3] E. Ramos-Cordoba, P. Salvador, E. Matito, *Phys. Chem. Chem. Phys.* **18**, 24105 (2016).
- [4] E. Ramos-Cordoba, E. Matito, *J. Chem. Theory Comput.* **10**, 1021/acs.jctc.7b00293.
- [5] M. Via-Nadal, M. Rodríguez-Mayorga, E. Ramos-Cordoba, E. Matito, *in preparation*.

## Describing non-covalent interactions in semiempirical QM methods: state of the art and future.

Jan Řezáč<sup>1</sup>

<sup>1</sup>*Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences,  
Flemingovo nám. 2, Prague, Czech republic*

Recent improvements in the description of noncovalent interactions in semiempirical quantum-mechanical methods (SQM, also comprising the density-functional tight-binding method, DFTB) enabled their application to large, complex systems including biomolecules. While this field is still dominated by molecular mechanics, SQM methods provide several advantages. Not only can they describe a wide range of effects of quantum-mechanical origin that are difficult to capture in classical forcefields, but they are also more practical because they do not require any system-specific parameterization. One of the successful applications of modern SQM methods is computer-aided drug design, where they may be used for large-scale calculations of protein--ligand interactions.[1]

The approximations involved in all the SQM methods lead to a rather poor description of non-covalent interactions. This can be addressed by specific corrections. The missing London dispersion can be added rather easily as a pairwise correction. The next most important issue is hydrogen bonding; here, we developed a series of corrections among which the latest version, D3H4 corrections for both PM6 and DFTB, became very successful.[2,3]

Nevertheless, these *a posteriori* corrections independent of the electronic structure have reached their limits and can hardly be improved. Careful analysis of the nature and origins of the errors in the description of hydrogen bonds[3] led us to a development of next generation of corrections for DFTB, named D3H5,[4] where the correction is integrated into the method and acts at the appropriate place, it is in the treatment of electrostatics. The D3H5 corrections improve over the previous versions not only in overall accuracy, but they also properly describe many-body effects that become extremely important in larger systems. With the latest corrections, the accuracy of the SQM methods becomes limited by other issues – I will also outline the steps needed to improve the methodology further.

- [1] A. Pecina, J. Řezáč et al., *J. Chem. Inf. Model.* **57**, 127 (2017).
- [2] J. Řezáč, P. Hobza, P., *J. Chem. Theory Comput.* **8**, 141 (2012).
- [3] V. M. Miriyala, J. Řezáč, *J. Comput. Chem.* **38**, 688 (2017).
- [4] J. Řezáč, *manuscript in preparation*.



## A new Spin Ratio Scaled MP2 (SRS-MP2) method for the prediction of intermolecular interactions

Samuel Y. S. Tan<sup>1</sup>, Luke Wylie<sup>1</sup>, Ivan Begic<sup>1</sup>, Dennis Tran<sup>1</sup> and Ekaterina I Izgorodina<sup>1</sup>

<sup>1</sup>*School of Chemistry, Monash University, 17 Rainforest Walk, Clayton, Victoria, 3800 AUSTRALIA*

Accurate prediction of intermolecular interactions is essential in understanding physicochemical properties of condensed systems such as molecular crystals as well as biological systems such as DNA and polymers. Intermolecular interactions vary in nature and strength from weak van der Waals interactions to strong hydrogen bonding. For a wavefunction-based method or a density function theory (DFT) functional method to be reliable, its accuracy needs to be within chemical accuracy for all types of interactions. Recent developments in DFT and Møller-Plesset (MP) perturbation theory have identified the importance of treating dispersion interactions accurately in order to achieve chemical accuracy.<sup>1,2</sup> Recently we have shown that the original modification of the second order Møller-Plesset (MP) perturbation theory by scaling the opposite-spin (OS) and same-spin (SS) components of correlation energy can be successfully extended to studying intermolecular complexes.<sup>3</sup> We have identified that the ratio of the opposite spin component to same-spin component when applied to correlation interaction energy,  $\epsilon_{\Delta s}$ , falls into a narrow range of 0.1 to 1.6, thus requiring the separation of intermolecular complexes into two groups: 1)  $\epsilon_{\Delta s} < 1$  and 2)  $\epsilon_{\Delta s} \geq 1$ . A separate set of scaling coefficients,  $c_{OS}$  and  $c_{SS}$ , were obtained for both groups and accounted for basis set superposition error.<sup>4</sup> The coefficients were initially fitted to intermolecular complexes of the well-known S22,<sup>5</sup> S66<sup>6</sup> and IL174<sup>7</sup> databases consisting of both ionic and neutral complexes. The newly developed method, termed spin ratio scaled MP2 (SRS-MP2), shows remarkable accuracy with a relatively small basis set, cc-pVTZ, with maximum errors falling well within chemical accuracy. Recently we have applied the SRS-MP2 method for the prediction of interaction energies for a variety of intermolecular complexes ranging from radicals interacting with ionic liquids to strong hydrogen-bonded complexes and weak halogen-halogen interactions. Again, the method has achieved outstanding accuracy for all types of intermolecular interactions, with an average error falling within 2 kJ mol<sup>-1</sup>.

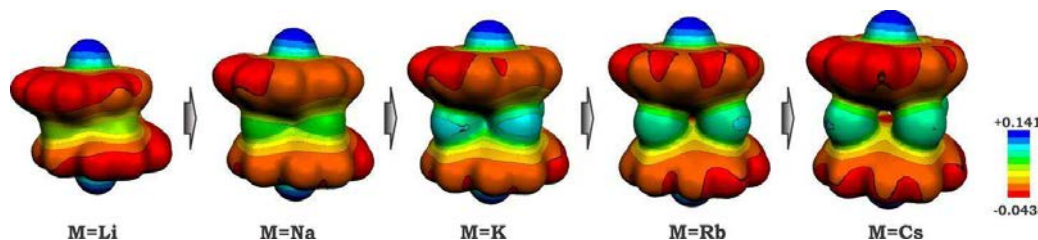
- [1] S. Grimme, A. Hansen, J. G. Brandenburg and C. Bannwarth, *Chem. Rev.*, **116**, 5105 (2016)
- [2] G. J. O. Beran, *Chem. Rev.*, **116**, 5567 (2016)
- [3] S. Y.S. Tan, S. Barrera Acevedo and E. I. Izgorodina, *J. Chem. Phys.*, **146**, 064108 (2017)
- [4] J. Rigby and E.I. Izgorodina, *J. Chem. Theory Comput.*, **10**, 3111 (2014)
- [5] P. Jurečka, J. Šponer, J. Černý & P. Hobza, *Phys. Chem. Chem. Phys.*, **8**, 1985 (2006)
- [6] J. Řezáč, K. E. Riley and P. Hobza, *J. Chem. Theory Comput.*, **7**, 2427–2438 (2011)
- [7] E. I. Izgorodina *et al.* *Phys. Chem. Chem. Phys.*, **16**, 7209–7221 (2014)

## Trianionic Corannulene: Tuning Stability of Supramolecular Aggregates with Alkali Metal Size

Andrey Rogachev

*Department of Chemistry, Illinois Institute of Technology, Chicago, IL, 60616, USA*

Experimental achievements in chemistry of reduced corannulene ( $C_{20}H_{10}$ , the smallest bucky bowl) revealed a tendency of highly reduced curved polyaromatic molecules to form sandwich-like aggregates.<sup>1</sup> Recently, it was found that these supramolecular aggregates can be efficiently used for stabilization and isolation of highly unstable transient species such as polyaromatic trianions.<sup>2</sup> In this study, the strategy of manipulating of stability of these supramolecular traps by changing size of alkali metals in positively charged belt between two negatively charged bowl fragments was investigated in detail.<sup>3</sup> The whole series of alkali metals, from Li to Cs, was considered. The electronic structure of suggested new sandwich-like systems was studied with help of tools of modern theoretical chemistry, including highly-accurate multi-reference perturbation theory of the second order (in XMCQDPT2 variant). Importantly, the magnetic coupling between curved polyaromatic radicals was also found to be the function of alkali metal size. Theoretical results are in perfect agreement with subsequent experimental observations.



[1] A.V. Zabula, A.S. Filatov, S.N. Spisak, A.Yu. Rogachev, M.A. Petrukhina, *Science*. **333**, 1008 (2011).

[1] A.V. Zabula, S.N. Spisak, A.S. Filatov, A.Yu. Rogachev, R. Clerac, M.A. Petrukhina, *Chem. Sci.* **7**, 1954 (2016).

[3] S.N. Spisak, A.Yu. Rogachev, A.V. Zabula, A.S. Filatov, R. Clerac, M.A. Petrukhina, *Chem. Sci.* **8**, 3137 (2017).

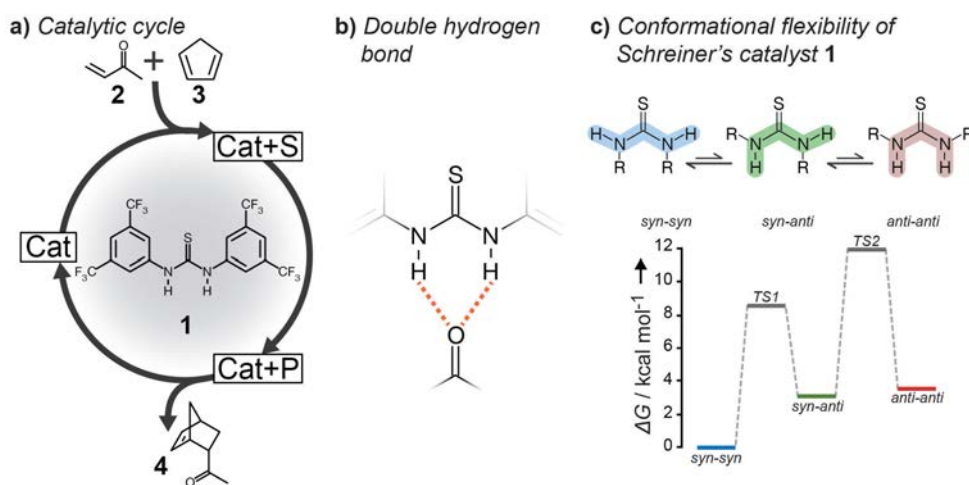
## About underappreciated, yet active conformations of thiourea organocatalysts

Adriana Supady<sup>1</sup>, Stefan Hecht<sup>2</sup>, Carsten Baldauf<sup>1</sup>

<sup>1</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

<sup>2</sup>Department of Chemistry, Humboldt-Universität zu Berlin, Germany

Catalysts speed-up reactions by binding substrates and transition states, thereby lowering reaction barriers. Noncovalent organocatalysts represent a highly selective and sustainable design alternative to conventional metal based catalysts, e.g. by utilizing a combination of hydrogen bonding with entropic and enthalpic effects to accelerate reactions. An example is illustrated below in panel **a**: Schreiner's catalyst **1** catalyzes the Diels-Alder reaction of the dienophile methyl vinyl ketone (**2**) with cyclopentadiene (**3**) to the *endo* product **4**. The established mechanism exploits the capability of NH protons in the *anti-anti* conformation of the central thiourea moiety to form a double hydrogen bond to the keto-group of **2** (see panel **b**). Organocatalysts such as **1** are flexible compounds with rich structural dynamics and their activity may be regulated via their conformational dynamics. Consequently, we performed first-principles structure searches and finally estimated Gibbs energies in dichloromethane. The global minimum structure is associated with the *syn-syn* conformation of the thiourea moiety, followed by the 3.1 kcal mol<sup>-1</sup> less stable *syn-anti* conformer (panel **c**). The *anti-anti* conformation, capable of forming the double hydrogen bond depicted in panel **b**, is energetically disfavored and 3.5 kcal mol<sup>-1</sup> less stable than the *syn-syn* conformer. Conformational changes between the minima involve barriers that are low enough to be overcome at room temperature. Starting from this, we investigate populations of the different conformers of **1** in presence of substrates. Our *ab initio* study reveals that substrate binding prefers *syn-anti* conformations of **1**. Furthermore, we find a new catalytic mechanism for Schreiner's catalyst featuring  $\pi$  stacking interactions. Our work highlights the need for extensive structure searches for flexible molecules, especially when aiming for structure-based design of catalytic activity.



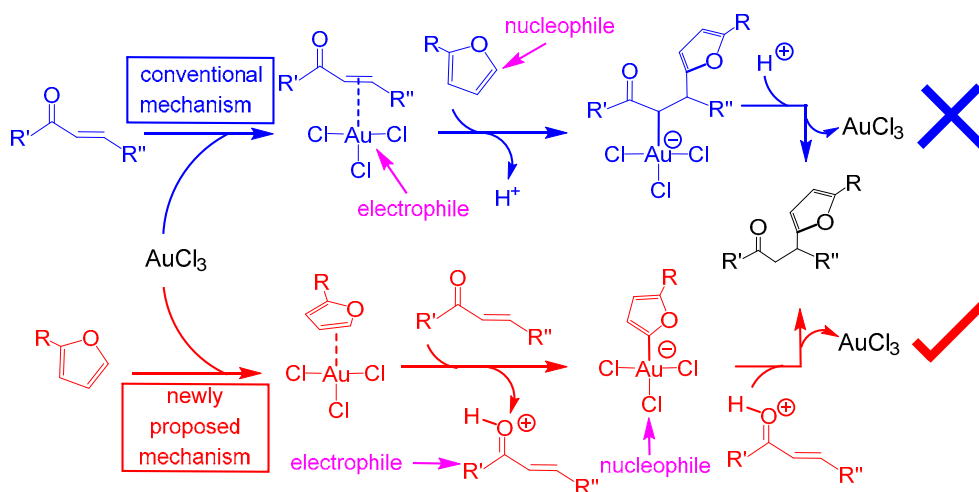
## A New Mechanism for Gold Catalysis

Yates, B. F.<sup>1</sup>, Ariafield, A.<sup>1</sup>, Hashmi, A. S. K.<sup>2</sup>

<sup>1</sup>University of Tasmania, Hobart, Australia

<sup>2</sup>Universität Heidelberg, Heidelberg, Germany

Gold complexes have attracted broad attention from the research community as efficient catalysts for the synthesis of many pharmaceutical drugs and natural products. A well-accepted role for the gold centre in catalysis is to activate unsaturated bonds as electrophiles, facilitating the attack of nucleophiles (Nu-H) on the gold-activated unsaturated bonds. We have used density functional theory to show that this picture is not always true and the gold centre sometimes plays a different role and serves as a proton producer via coordination to Nu-H to give Nu-Au and H<sup>+</sup>. The in-situ generated proton then serves as a strong electrophile and accelerates nucleophilic attack of Nu-Au on the unsaturated bonds through proton-activation. In this unprecedented mechanism, the nucleophile consists of the gold centre while in the traditional one the gold centre plays a reverse role. We investigated hydrofurylation of allenyl ketone, vinyl ketone, ketone and alcohol substrates catalysed by AuCl<sub>3</sub> and found that the corresponding functionalisations are best rationalised in terms of this novel mechanism [1]. This new reaction pathway is expected to receive greater consideration in other reactions catalysed by gold in future work.



[1] A. H. Bagi, Y. Khaledi, H. Ghari, S. Arndt, A. S. K. Hashmi, B. F. Yates, A. Ariafield, *J. Am. Chem. Soc.*, **138**, 14599 (2016).

## Magnetic coupling between f magnetic centers.

Hélène Bolvin<sup>1</sup>

<sup>1</sup>*Laboratoire de Chimie et de Physique Quantiques  
Université Toulouse 3, France*

The field of molecular magnetism explores more and more molecules containing lanthanide or actinide atoms. The large spin-orbit coupling and the semi-core character of the 4f and 5f orbitals confer to these molecules novel magnetic properties. Since a decade, there has been a large investigation of complexes with one magnetic center and first principles calculations have become an essential tool to interpret the experimental data, providing the nature of the ground state, the energy of exciting states and the corresponding directions of the magnetic moments.

The next experimental challenge is to gather several magnetic centers in a rational way in order to get a synergetic building of the local bricks. To achieve that, a fine knowledge of the magnetic interaction between centers is necessary. Due the semi-core character of the magnetic orbitals, the magnetic coupling between two f centers is very small, and the mechanism is still in question. The aim of this presentation is to show that quantum chemistry brings physical insights for the analysis of this magnetic coupling.

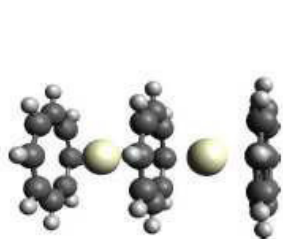


Fig. 1:  $[\text{Ce}(\text{COT})_3]^{2-}$

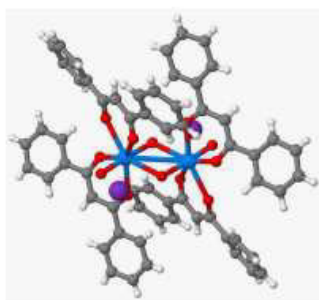


Fig. 2:  $[(\text{UO}_2)\text{dbm}_2 \cdot \text{K}]_2$

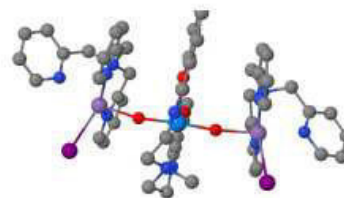


Fig. 3:  $[(\text{Mn}(\text{TPA})\text{I})_2 \text{UO}_2 (\text{Mesalden})]^+$

I will present our results on a 4f-4f dimer of Cerium(III) (Fig. 1), a 5f-5f dimer of Uranium(V) (Fig. 2) and a 3d-5f-3d trimer of Mn(V)-U(V)-Mn(V) (Fig. 3). These molecules are described using correlated wave functions based theory. The analysis of these calculations permits to determine i) the nature and magnetic properties of the local magnetic centers ii) the coupling between these centers which in each case is strongly anisotropic. In order to recover the experimental coupling, highly correlated CI methods have to be used. All calculations are simulated using Spin Hamiltonians.

## Study on Metal Nanocluster Catalysts Based on Quantum Chemical Calculation and Informatics

**Masato Kobayashi<sup>1,2,3</sup>, Takeshi Iwasa<sup>1,3</sup>, Maki Nakahara<sup>4</sup>, Min Gao<sup>1,3</sup>,  
Andrey Lyalin<sup>5</sup>, Makito Takagi<sup>4</sup>, Satoshi Maeda<sup>1,3,6</sup>, Tetsuya Taketsugu<sup>1,3,5</sup>**

<sup>1</sup>*Faculty of Science, Hokkaido University, Kita 10 Nishi 8, Kita-ku, Sapporo, Japan.*

<sup>2</sup>*PRESTO, Japan Science and Technology Agency, Honcho 4-1-8, Kawaguchi, Japan.*

<sup>3</sup>*ESICB, Kyoto University, Goryo-Ohara 1-30, Nishikyo-ku, Kyoto, Japan*

<sup>4</sup>*Graduate School of Chemical Sciences and Engineering, Hokkaido University,  
Kita 10 Nishi 8, Kita-ku, Sapporo, Japan.*

<sup>5</sup>*GREEN, National Institute for Materials Science, Namiki 1-1, Tsukuba, Japan.*

<sup>6</sup>*CREST, Japan Science and Technology Agency, Honcho 4-1-8, Kawaguchi, Japan.*

The combination of the quantum chemical calculations with the informatics technologies has recently been attracted considerable attention as a candidate for predictive computational chemistry. In this study, we analyzed the results of the quantum chemical calculations of metal nanoclusters using the informatics technologies. The metal nanoclusters consisting of tens or less atoms show catalytic activity depending on many factors such as the size, composition, and shape [1]. As the first example, we focused on the catalytic activity of Cu<sub>13</sub> cluster for the NO dissociation reaction in this study. To extract the key factors for the catalytic activity, we utilized the regularized regression as typified by LASSO [2] and MC+ [3], where the regression coefficients for most of descriptors can be zero. Namely, the transition-state energy for the NO dissociation on Cu cluster is predicted from a few numbers of important descriptors obtained from the quantum chemical calculations of the adsorption states.

We next focused on the Au nanocluster (Au<sub>n</sub>) catalysts supported by hexagonal boron nitride (h-BN)/Au surface. Although the h-BN and Au surfaces themselves are inactive, the combined h-BN/Au surface shows catalytic activity. Furthermore, Au<sub>n</sub>/h-BN/Au shows higher activity for the oxygen reduction reaction [4]. The number of adsorption structures of Au<sub>n</sub>/h-BN/Au grows drastically as *n* increases. To prescreen the adsorption structures before the quantum chemical calculation, we utilized the non-linear regression method for predicting the adsorption energy from the graph structure of the Au nanocluster.

[1] M. Gao, A. Lyalin, S. Maeda, and T. Taketsugu, *J. Chem. Theory Comput.* **10**, 1623 (2014).

[2] R. Tibshirani, *J. Roy. Stat. Soc. B* **58**, 267 (1996).

[3] C.-H. Zhang, *Ann. Stat.* **38**, 894 (2010).

[4] G. Elumalai, H. Noguchi, A. Lyalin, T. Taketsugu, and K. Uosaki, *Electrochem. Commun.* **66**, 53 (2016).

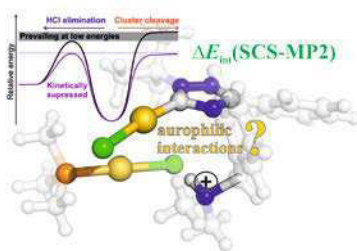
## Calibrating Auophilic Interactions in Weakly Bound [L Au X]...[L' Au X] Dimers by Experiment and Theory

Erik Andris,<sup>1</sup> Prokopis C. Andrikopoulos,<sup>3</sup> Jiří Schulz,<sup>1</sup> Jana Roithová,<sup>1</sup> Jan Turek,<sup>2</sup> Aleš Růžička,<sup>2</sup> Lubomír Rulíšek<sup>3</sup>

<sup>1</sup> Department of Organic Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030, 128 40 Prague 2; <sup>2</sup> Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ-532 10, Pardubice; <sup>3</sup> Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, Flemingovo náměstí 2, 166 10 Prague 6, Czech Republic

Attractive metallophilic (auophilic, argentophilic, cuprophilic, ...) interactions play an important role in arrangement and stabilization of oligonuclear metal ion complexes.[1] We report a combined experimental and theoretical assessment of auophilic interactions in closed-shell gold(I) dimers. The experimental binding energies in [(LH)AuX]<sup>+</sup>...[(L')AuX] dimers (where X = Cl and L is a ligand derived from phosphine or N-heterocyclic carbene) charged by protonation of a remote amine group at the ligand L were determined by collision induced dissociation of mass-selected dimers in the gas phase. The results were used for benchmarking correlated quantum chemical calculations (obtained by employing the CCSD(T)-calibrated SCS-MP2 method), which were then also applied for neutral [(L)AuX]...[(L')AuX] dimers (X = Cl, Br, I). Experiments and theory have shown that the overall attractive interactions between monomeric units of the gold(I) dimers are in the order of 100–165 kJ mol<sup>-1</sup> in the charged dimers and 70–105 kJ mol<sup>-1</sup> in the corresponding neutral dimers. By comparison with smaller model systems, we demonstrate that pure auophilic interactions account for 35–40 kJ mol<sup>-1</sup> of the overall interaction energy (40–50 %). The dipole dipole interaction term contributes by approximately the same amount of energy (20–40 kJ mol<sup>-1</sup>) whereas the L...L' “inter-ligand” dispersion interactions are smaller (< 10 kJ.mol<sup>-1</sup>). Our experimental and theoretical findings confirm the overall importance of auophilic interactions – comparable or even stronger than very strong hydrogen bonds – but at the same time suggest that they may not always be the primary determinants of the complex molecular structures of polynuclear gold(I) complexes. [2]

**Acknowledgments:** Czech Science Foundation (No. 17-24155S)



[1] H. Schmidbaur, W. Graf, G. Müller, *Angew. Chem., Int. Ed.* **1988**, 27, 417-419.

[2] E. Andris, P. C. Andrikopoulos; J. Schulz, J. Roithová, J. Turek, A. Růžička, L. Rulíšek, *submitted for publication*.

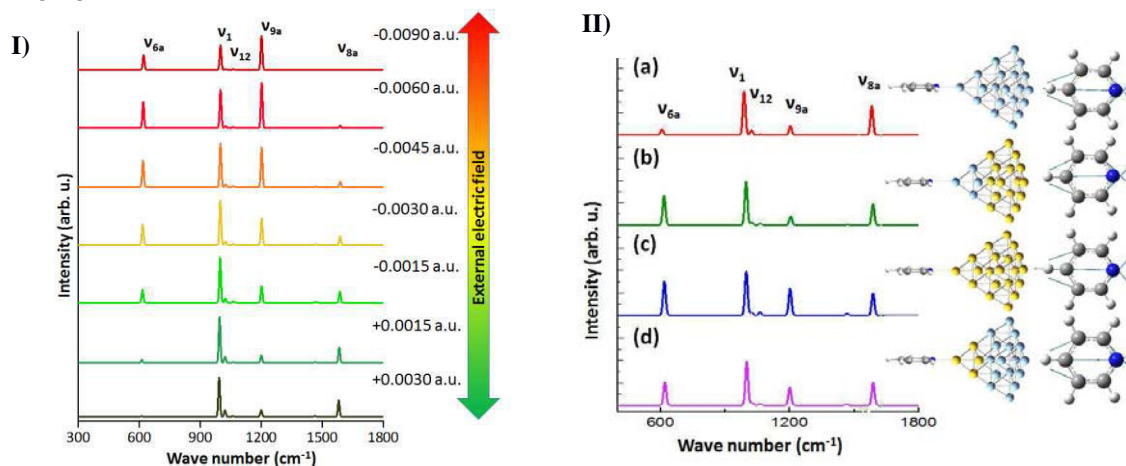


## Surface-Enhanced Raman Spectroscopy Due to Charge-Transfer Chemical Mechanism: Effect of Surface and Electric Field

Zahra Jamshidi

Chemistry & Chemical Engineering Research Center of Iran (CCERCI), Tehran, Iran

Surface-enhanced Raman scattering (SERS) is one of the most sensitive spectroscopic techniques for a wide range of applications. The charge-transfer SERS as the resonance chemical mechanism is an important phenomenon and a topic of great studies. The electronic transition from filled metal orbitals (near the Fermi level) to unfilled orbitals in the molecule is usually the source of the resonance Raman CT enhancement, and it is important as represents the properties of combined system. The recognition of CT resonance selection rules is a difficult task due to the various factors that affect this process. It is known that the energies and electronic structure properties of CT-states can be influenced by the chemical nature of the surface and also the electronic potential of the interface. The quantum mechanical calculations can help to get an insight into the mechanism of CT and the source of each factor that controls this process. In our studies the calculations have been done by means of an excited-state gradient approximation for a pyridine molecule interacting with a silver cluster,<sup>1</sup> and the effect of electrode potential on the SERS-CT spectra has been modelled theoretically by applying an external electric field and provided a satisfactory agreement with the experimental studies.<sup>2</sup> Moreover, the effect of chemical nature of the surface on the pattern of SERS-CT spectra has been investigated for pyridine interacted with pure and bimetallic silver and gold clusters.<sup>3</sup> The relative intensities of simulated spectra match well with the available experimental results and suggest that changing the surface, which reveals the trend by applying negative potential on a given surface, could be explained by variation of the effective charge of the cluster. These calculations also show the importance of variation of the excited-state vector gradient and dimensionless displacement by changing the surfaces and electric field and also their effects on the selection rules.



**Figure 1.** Calculated SERS-CT spectra of (I) pyridine with silver cluster under an applied external electric field (II) different clusters.

[1] M. Mohammadpour and Z. Jamshidi *J. Chem. Phys.* **144**, 194302 (2016).

[2] M. Mohammadpour, M.H. Khodabandeh, L. Visscher, Z. Jamshidi *Phys. Chem. Chem. Phys.* **19**, 7833 (2017).

[3] M. Mohammadpour and Z. Jamshidi *J. Phys. Chem. C* **121**, 2858 (2017).



## Irreversible Tautomerization in Porphycene on Cu(111) Induced by Scanning Tunnelling Microscopy

Jean Christophe Tremblay<sup>1</sup>, Dino Novko<sup>1, 2</sup>, María Blanco-Rey<sup>2</sup>

<sup>1</sup>*Institute für Chemie und Biochemie, Freie Universität Berlin, Takustraße 3, 14195 Berlin, Germany*

<sup>2</sup>*Departamento de Física de Materiales UPV/EHU and Donostia International Physics Center Paseo Manuel de Lardizabal, 4, 20018 Donostia-San Sebastian, Spain*

Scanning tunnelling microscopy (STM) is a widely appreciated characterization technique in surface science. The applications range from imagery to catalysis and nanoelectronics, to name but a few. In recent experiments, STM was further used to selectively induce reactions in the vicinity of metallic surfaces. It is well-known that non-adiabatic coupling to hot electrons impinging from the STM tip can play an important role in such phenomena (see Refs. [1,2] and references therein). To demonstrate their dynamical effect, we will investigate the irreversible tautomerization in porphycene on a Cu(111) surface induced by hot electrons injected by a neighbouring STM tip [3]. We demonstrate that the reaction can be understood as a quasi-thermal hydrogen migration mechanism and rationalized in terms of non-adiabatic coupling and intramolecular vibrational energy redistribution: hot electrons from the STM-tip excite a large number of skeletal vibrations of the molecule, which distorts the potential energy landscape along the hydrogen transfer coordinate [4].

- [1] M. Blanco-Rey, M. Alducin, J. I. Juaristi, and P. de Andres “Diffusion of Hydrogen in Pd Assisted by Inelastic Ballistic Hot Electrons” *Phys. Rev. Lett.* **108** 115902 (2012).
- [2] J.C. Tremblay “A unifying model for non-adiabatic coupling at metallic surfaces beyond the local harmonic approximation: from vibrational relaxation to STM-driven transitions” *J. Chem. Phys.* **138** 244106 (2013).
- [3] J. N. Ladhentin, L. Grill, S. Gawinkowski, S. Liu, J. Waluk, T. Kumagai “Hot Carrier-Induced Tautomerization within a Single Porphycene Molecule on Cu(111)” *ACS Nano* **9** 7287 (2015).
- [4] D. Novko, M. Blanco-Rey, and J.C. Tremblay “Intermode Coupling Drives the Irreversible Tautomerization in Porphycene on Copper(111) Induced by Scanning Tunnelling Microscopy” *J. Phys. Chem. Lett.* **8** 1053 (2017).

## Quantum Master Equation Approach to Singlet Fission Dynamics in Molecular Aggregates

**Masayoshi Nakano<sup>\*,1,2</sup>, Takanori Nagami<sup>1</sup>, Soich Ito<sup>3</sup>, Kenichiro Watanabe<sup>1</sup>,  
Masaki Yamane<sup>1</sup>, Ryohei Kishi<sup>1</sup>, Yasutaka Kitagawa<sup>1,2</sup>, Takashi Kubo<sup>4</sup>**

<sup>1</sup>*Department of Materials Engineering Science, Graduate School of Engineering Science,  
Osaka University, Toyonaka, Osaka 560-8531, Japan*

<sup>2</sup>*Center for Spintronics Research Network (CSRN), Graduate School of Engineering  
Science, Osaka University, Toyonaka, Osaka 560-8531, Japan*

<sup>3</sup>*Institute for Molecular Science, 38 Nishigo-Naka, Myodaiji, Okazaki 444-8585, Japan*

<sup>4</sup>*Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka,  
Osaka 560-0043, Japan*

Singlet fission (SF), which is a photophysical process with splitting a singlet exciton generated by light irradiation into two triplet excitons, has attracted much attention both experimentally and theoretically due to its potential of improving photoelectric conversion efficiency through multi-exciton generation in organic solar cells [1]. The study of SF is composed of three steps: (i) energy level matching at single molecular level, (ii) electronic coupling at molecular aggregate level, and (iii) exciton dynamics including exciton-phonon (vibronic) couplings [2]. In this study, first, the SF dynamics of realistic/artificial pentacene dimer models is investigated using the quantum master equation method. In order to obtain new insight into the SF dynamics, we clarify the effects of the energy offsets of diabatic Frenkel exciton (FE) and charge transfer (CT) exciton states to the double-triplet (TT) exciton state, excitonic couplings, and state-dependent vibronic couplings on the exciton population dynamics using relative relaxation factors (RRFs) between the adiabatic exciton states [3]. Second, for multimers beyond dimer, we derive the quantum master equation and investigate the aggregate-size dependence of the SF rate and TT yield. On the basis of these results, we discuss the structure-property relationships for SF dynamics in various molecular aggregate models.

### References

- [1] (a) M. B. Smith, J. Michl, *Chem. Rev.* **110**, 6891 (2010). (b) M. B. Smith, J. Michl, *Annu. Rev. Phys. Chem.* **64**, 361 (2013).
- [2] (a) T. Minami, M. Nakano, *J. Phys. Chem. Lett.* **3**, 145 (2012). (b) T. Zeng, N. Ananth, R. Hoffmann, *J. Am. Chem. Soc.* **136**, 12638 (2014), (c) L. Wang, Y. Olivier, O. V. Prezhdo, D. Beljonne, *J. Phys. Chem. Lett.* **5**, 3345 (2014). (d) S. Ito, T. Nagami, M. Nakano, *Phys. Chem. Chem. Phys.* **19**, 5737 (2017).
- [3] M. Nakano, S. Ito, T. Nagami et al. *J. Phys. Chem. C* **120**, 22803 (2016).

## Pathways in molecular conductance and spin coupling

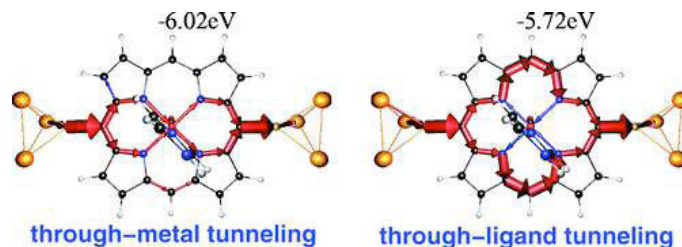
Carmen Herrmann<sup>1</sup>

<sup>1</sup>*Institute of Inorganic and Applied Chemistry, University of Hamburg, Martin-Luther-King-Platz 6, 20146 Erlangen, Germany*

For understanding spin-polarized electron transport through molecular bridges and (exchange) spin coupling between local spin centers within in a molecule, it is interesting to know which parts of the molecule are responsible for mediating transport or spin interactions.

In the case of spin coupling, ferro- and antiferromagnetic pathways may add up or partially cancel, which is hidden if only the total spin coupling is considered. A new approach to decomposing spin coupling based on Green's functions [1] allows not only identifying which molecular parts are responsible for spin coupling in isolated molecules, but may also allow for distinguishing, e.g., between intramolecular and through-surface contributions [2].

In electron transport through molecular junctions, local decomposition of electron transmission will be used to highlight the importance of spin-polarized parts of the molecule for transport [3-7], and compared with the effect of introducing spin polarization in bridging ligands on spin coupling [8].



- [1] T. Steenbock, J. Tasche, A. Lichtenstein, C. Herrmann, *J. Chem. Theory Comput.* **11**, 5651 (2015).
- [2] T. Steenbock, C. Herrmann, submitted.
- [3] G. C. Solomon, C. Herrmann, T. Hansen, V. Mujica, M. A. Ratner, *Nature Chem.* **2**, 223 (2010).
- [4] R. Hayakawa, M. A. Karimi, J. Wolf, T. Huhn, M. S. Zöllner, C. Herrmann, E. Scheer, *Nano Lett.* **16**, 4960 (2016).
- [5] C. Herrmann, G. C. Solomon, *J. Phys. Chem. C*, **114**, 20813 (2010).
- [6] C. Herrmann, G. C. Solomon, M. A. Ratner, *J. Am. Chem. Soc.* **132**, 3682 (2010).
- [7] C. Herrmann, G. C. Solomon, M. A. Ratner, *J. Chem. Phys.* **134**, 224306 (2011).
- [8] T. Steenbock, D. Shultz, M. Kirk, C. Herrmann, *J. Phys. Chem. A* **121**, 216 (2017).

## Exciton Dynamics in Organic Optoelectronic Materials

Takatoshi Fujita<sup>1</sup>,

<sup>1</sup>*Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan*

There has been a growing interest in electronic and optical properties in organic semiconductors due to their potential applications for optoelectronic devices. However, it is difficult to theoretically study the excited states and photophysical processes. First, computation of large number of excited states in large molecular systems is still a challenging issue in quantum chemistry. Second, to investigate the photophysical processes such as electronic energy transfer or charge separation, one has to simulate real-time dynamics with exciton-phonon coupling being incorporated. We have been developing the simulation method based on the fragment-based electronic structure method and quantum dynamics theory. The model exciton Hamiltonian is constructed by the ab initio electronic structure calculations utilizing the fragment molecular orbital method. Exciton dynamics coupled to the nuclear vibrations is modeled by the stochastic Schrödinger equation, which allows to describe ultrafast coherent dynamics and subsequent thermal relaxation.

In the first part, we present optical properties and exciton dynamics in the dinaphtho[2,3-b:2',3']-thieno[3,2-b]-thiophene (DNTT), a p-type organic semiconductor. The calculated absorption spectrum based on the first principle is in qualitative agreement in the experiment; it is composed of main excitations of Frenkel-dominant states with partial admixture of CT states and CT-dominant states with slight admixture of Frenkel states. Next we show real time dynamics in a DNTT thin film. The localized Frenkel and CT excitons is relaxed to the lowest exciton state in about 1.5 and 2.5 ps, respectively. We observe the mixing of CT excitons with Frenkel state in 50 fs after the excitation. Accordingly, electron-hole separation increases and shows an oscillation pattern as a result of delocalization of electron and hole and electron-hole Coulomb interactions. We discuss the roles of charge delocalization and localization in the Frenkel-CT mixings.

In the second part, we discuss the excited states of pentacene/C<sub>60</sub> interface. It is known that the interfacial charge transfer states across the interface play essential roles in the charge separation and recombination. The ab initio FMO calculations for an extended pentacene/C<sub>60</sub> interface allows us to discuss the effects of structural disorder, electronic polarization, and charge delocalization. The implication to the charge separation and recombination will be discussed.

[1] T. F. S. Atahan-Evrenk, N.P.D. Sawaya, A. Aspuru-Guzik, J. Phys. Chem. Lett. **7** (2016) 1374.

## **Photophysical properties of macrocycles: a computational and experimental study.**

**Felipe C. T. Antonio, Mateus Zanotto, Thalita F. M. de Souza, Anderson O. Ribeiro, Paula Homem-de-Mello<sup>1</sup>**

<sup>1</sup>*Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Av. dos Estados, 5001, Santo André, São Paulo, Brazil – [Paula.mello@ufabc.edu.br](mailto:Paula.mello@ufabc.edu.br)*

Macrocyclic compounds are widely applied as industrial dyes, since they present a large  $\pi$ -conjugated system. Particularly, phthalocyanines can be employed also in different devices, such as solar cells and electrochromic devices, as well photodynamic therapy (PDT). On the other hand, new molecules can be developed aiming to increase the efficiency as photosensitizers. For instance, naphthalocyanines (Nc) are phthalocyanines derivatives with a more extended  $\pi$ -conjugated system, that is responsible for bathochromic shift in absorption bands in comparison to phthalocyanine. However, due to this conjugated system, these compounds tend to aggregate, what affect their photophysical and photochemical properties. In order to avoid such effect, a common strategy is to propose derivatives with large groups as substituents. In this work, we have conducted experimental and computational studies in order to verify the influence of different substituents on the photophysical properties of phthalocyanine and naphthalocyanine, as well on the aggregation energetics. Computational methodology was based on density functional theory (DFT), the inclusion of dispersion was made by means of Grimme's correction (D3-BJ) and solvent effects by IEFPCM continuum model. [1] TD-DFT calculations pointed out the molecular orbitals involved in Q-band transition, corresponding to HOMO to LUMO transition with a concentration of charge along x-axis, while the transition to LUMO+1 is in y-axis direction. Substitutions with tert-butyl groups was found not disturb this behavior, but it is important for molecular orbitals energies. DFT studies indicated that stacked-dimers are preferred to rotated-stacked conformation due the interaction between Zn(II) and nitrogen atom from different monomers.

[1] F. Bettanin, TA Fontinelles, CD Maciel, LG Dias, MD Coutinho Neto, P Homem-de-Mello, P. Theor. Chem. Acc. **152**, 1-11, 2015.

## Modeling the Photochromism of Sulphur-Doped Sodalites using DFT, TD-DFT and SAC-CI methods.

Antton Curutchet<sup>1</sup>, Tangui Le Bahers<sup>1\*</sup>

<sup>1</sup>Univ Lyon, ENS de Lyon, CNRS, Université Lyon 1, Laboratoire de Chimie UMR 5182, F-69342, Lyon, France

\*tangui.le\_bahers@ens-lyon.fr

Photochromic materials are deeply investigated experimentally and theoretically because of their numerous possible high-tech applications going from adaptive glasses to optical memories. Geologists have known for almost one century the existence of natural photochromic minerals, calling this phenomenon tenebrescence, of the sodalite family. Although the community is mainly trying to develop new type of photochromic materials, almost no efforts were devoted to understand and developed these tenebrescent minerals known by the geologists for a long time.

In this presentation, we will focus on natural sulphur-doped sodalite minerals of  $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{Cl},\text{S})_2$  formula, also known as hackmanites, that are computationally investigated for the first time, in order to understand their photochromic properties. By combining periodic boundary conditions and embedded cluster-type approaches, we bring a theoretical overview of the photochromism mechanism. Our TD-DFT calculations of sodalite systems containing electrons trapped into chlorine vacancies (called F-center) showed absorption spectrum and a simulated color in agreement with experiment. This modelling highlights the huge effects of F-center's environment such as the direct contribution of the  $\beta$ -cage on the trapped electron and a strong vibronic coupling of the absorption spectrum. TD-DFT and post-Hartree-Fock (SAC-CI) calculations were also operated on  $\text{S}_2^{2-}$ -containing systems in order to determine the exact mechanism of coloration and discoloration, supporting that the key step is a direct through space charge-transfer between  $\text{S}_2^{2-}$  ion and a chlorine vacancy. The geometry modification induced by this charge-transfer leads to a large electronic reorganization stabilizing the F-center thus explaining the high stability of the colored state of the mineral. The results and methodology presented during this talk are published in ref [1].

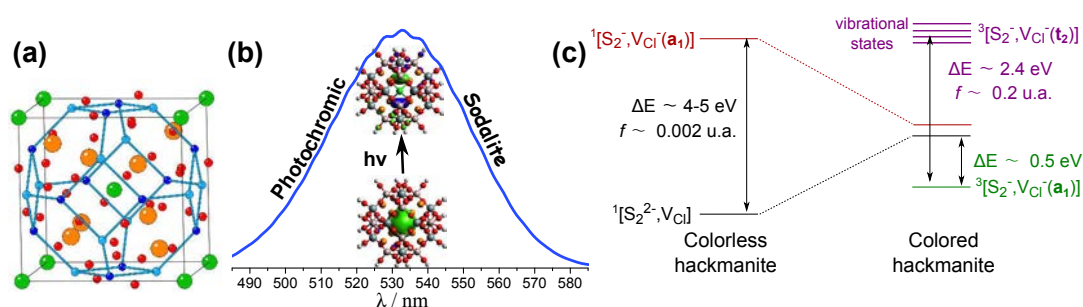


Figure 1: (a) Sodalite unit cell, the blue lines depict the  $\beta$ -cage cage. (b) Simulated absorption spectrum of the F-center including vibronic coupling. (c) Jablonski diagram of the photochromic phenomenon obtained by the combined TD-DFT/SAC-CI approaches.

[1] A. Curutchet, T. Le Bahers, *Inorg. Chem.* **56**, 414 (2017).

# Shedding Light on the Approximations Underlying Ab Initio Multiple Spawning

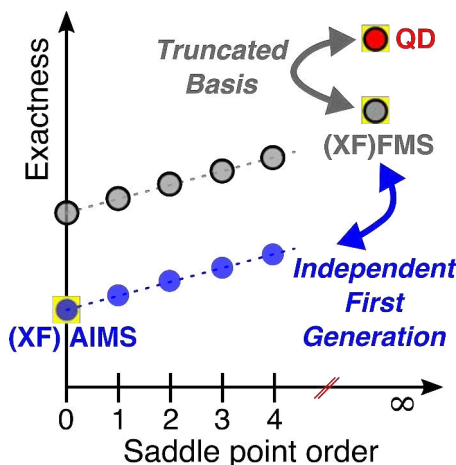
Basile F. E. Curchod<sup>1</sup>

<sup>1</sup>*Centre for Computational Chemistry, School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom*

Ab initio multiple spawning (AIMS) aims at an accurate yet efficient *in silico* description of photochemical and photophysical processes in molecules. AIMS describes the nonadiabatic dynamics of nuclear wavepackets by means of linear combinations of coupled frozen Gaussians, which follow classical trajectories and whose number can be adapted when required.

An important feature of the AIMS formalism is the flexibility of its coupling elements between Gaussians, which permits the incorporation of critical effects for a realistic simulation of photochemical processes. We recently extended AIMS to the description of intersystem crossing processes by including spin-orbit couplings (Generalized AIMS – GAIMS) and to simulate photoexcitation processes (eXternal Field AIMS – XFAIMS).[1, 2]

XFAIMS further offers the possibility to generate complex superpositions of nuclear wavepackets in different electronic states by using pump-probe schemes. Such intricate nuclear dynamics constitute a *unique* opportunity to test the influence on computed observables, like state populations or the time-dependent dipole moment, of (i) approximating the couplings between traveling Gaussians and (ii) the definition of initial conditions. Hence, I will show in this Contribution that XFAIMS allows us to shed light on the two central approximations of the AIMS method, and that – even within these two approximations – AIMS offers a qualitatively correct description of nonadiabatic phenomena involving complex interference effects between nuclear wavepackets.[3]



- [1] B. F. E. Curchod, C. Rauer, P. Marquetand, L. González, and T. J. Martínez, *J. Chem. Phys.* **144**, 101102 (2016).
- [2] B. Mignolet, B. F. E. Curchod, and T. J. Martínez, *J. Chem. Phys.* **145**, 191104 (2016).
- [3] B. Mignolet and B. F. E. Curchod, to be submitted (2017).

## **Polarizable QM/MM for excited-state dynamics**

**William J. Glover<sup>1,2</sup>**

<sup>1</sup>*NYU-ECNU Center for Computational Chemistry at NYU Shanghai, 3663 Zhongshan Road North, Shanghai, China*

<sup>2</sup>*Department of Chemistry, New York University, 100 Washington Square East, New York, United States*

Many electronically excited processes involve non-adiabatic transitions between neutral and charge transfer (CT) states, e.g. in photosynthesis and organic photovoltaic cell operation. An understanding of the dynamics in these systems requires an accurate description of both neutral excited-states, CT states, and their intersections. Quantum Mechanics/Molecular Mechanics (QM/MM) holds a lot of promise since it limits the electronic structure calculations to a small chemically-active region, allowing a high-level treatment. It is important, however, to use a polarizable model that captures the electronic polarization of the MM system in response to a CT state. Here a problem arises: the MM system must polarize differently to neutral states compared to CT states, implying a state-specific approach. Unfortunately, this would mean each electronic state is of a different Hamiltonian, and therefore intersections between the states will not be described correctly.

Borrowing from our recently developed DWS-CASSCF method,[1] we have developed a new polarizable QM/MM approach that solves the above issue. The basic idea is to self-consistently optimize MM dipoles in a polarizable QM/MM calculation in response to a weighted average of the fields from each electronic state. When the electronic states are energetically separated, the weight becomes unity for the state of interest, and zero for all others, giving the state-specific approach in this limit. When electronic states cross, the field weights for the intersecting states becomes equal, meaning these states share the same Hamiltonian, and therefore the topology of the intersection is correctly described.

We have tested our new QM/MM-DWpol method on the electronic states of LiF, a simple and widely-studied system exhibiting a neutral and CT crossing. When a polarizable atom is placed near LiF, the energy of the CT state is lowered relative to the neutral states, thereby shifting the position of the state crossing. We show that our QM/MM-DWpol method reproduces the entire potential energy surface with near quantitative accuracy compared to high-level multireference configuration interaction calculations on the full system. Furthermore, our method has a computational cost that is comparable to traditional QM/MM approaches. We expect this development will open the way to studying excited-state charge-transfer reactions in complex systems with a high-level of accuracy.

[1] W. J. Glover, *J. Chem. Phys.* **141**, 171102 (2014)



## Hydrogen conversion in [NiFe]-enzymes and bio-inspired complexes

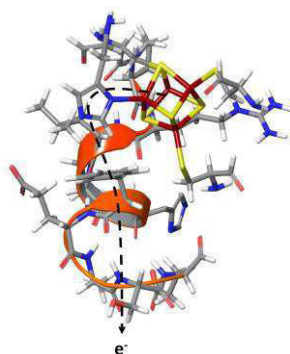
Matthias Stein<sup>1</sup>

<sup>1</sup>*Molecular Simulations and Design Group, Max Planck Institute for Dynamics of Complex Technical Systems, Sandtorstrasse 1, Magdeburg, Germany.*

Molecular hydrogen (H<sub>2</sub>) is one of the future energy carriers in particular for individual transportation. Hydrogen converting enzymes can either oxidize hydrogen or reduce protons to release H<sub>2</sub>. They utilize highly evolved active sites consisting of non-noble metals such as iron and nickel. The oxygen-sensitivity of standard [NiFe]-hydrogenase enzymes is overcome in a subfamily of membrane-bound enzymes which possess a novel type of [4Fe4S](Cys)<sub>6</sub>-cluster to prevent oxidative damage to the active site [1,2,3].

The active site of the enzymes has led to the design of a large number of bio-inspired mono- and di-nuclear complexes (for a review see e.g. [4]). Quantum chemical calculations are indispensable to elucidate structural and electronic properties of those complexes and to identify critical parameters for catalytic activity in solution.

The enzyme can also be used in an enzymatic fuel cell. Brownian Dynamics (BD) simulations were used to investigate the diffusion of the enzyme to the graphite electrode surface, identify preferred orientations and amino acid residues establishing contacts between enzyme and surface. The QM calculated rates of electron transfer from the Marcus equation are in excellent agreement with experiments and identify different electron transfer routes via the histidine of the distal FeS-cluster to the electrode [5,6].



- [1] T. Goris, A.F. Wait, M. Saggi, et al., *Nat. Chem. Biol.* **7**, 310-318 (2011).
- [2] J. Fritsch, S. Löscher, O. Sanganas, et al., *Biochemistry* **50**, 5858-5869 (2011).
- [3] M. Stein, S. Kaur-Ghumaan, *Biochem. Soc. Trans.* **41**, 1317-1324 (2013).
- [4] S. Kaur-Ghumaan, M. Stein, *Dalton Trans.* **43**, 9392-9405 (2014).
- [5] A. Petrenko, M. Stein, *J. Phys. Chem. B* **119**, 13870-13882 (2015).
- [6] A. Petrenko, M. Stein, *Int. J. Mol. Sci.* **18**, 100 (2017).

## Unraveling the magnetic transition temperature from changes in spin correlation

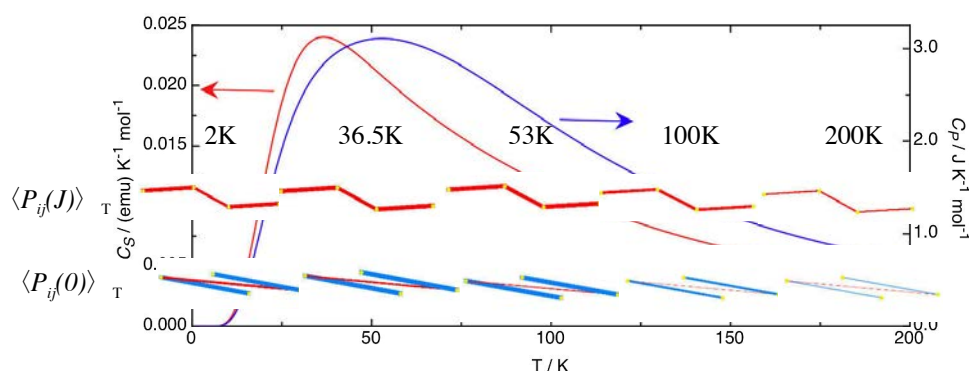
**J. Jornet-Somoza<sup>1,2</sup>, M. Deumal<sup>1</sup>, J. Borge<sup>2</sup>, J. J. Novoa<sup>1</sup>, M. A. Robb<sup>3</sup>**

<sup>1</sup> *Dept Ciència de Materials i Química Física and IQTCUB, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1, 08028-Barcelona*

<sup>2</sup> *Nano-Bio Spectroscopy Group and ETSF, Universidad del País Vasco, CFM CSIC-UPV/EHU, 20018-San Sebastián*

<sup>3</sup> *Dept Chemistry, Imperial College London, South Kensington Campus, SW7 2AZ London UK*

The current definition of the critical temperature  $T_c$  for magnetic systems is ambiguous. Indeed, a maximum in  $\partial [\chi T(T)] / \partial T$ , the magnetic spin capacity ( $C_S$ ) associated with a change in spin order/disorder, is the 'physically correct' definition of the magnetic transition temperature. The definition of the magnetic capacity is shown to be useful because it can be interpreted in terms of the molecular structure of the crystal using the magnetic wavefunction for each magnetic microstate. Analysis of the magnetic wavefunction using the concept of a Boltzmann magnetic bond order and the exchange density matrix  $P_{ij}$  (+0.5, -0.5 and -0.25 for antiparallel, parallel and non-ordered spin alignment, respectively) provides information about the spin correlation between magnetic units. Thus in the analysis of magnetic effects there are two second-order transitions, involving energy (the usual  $T_c$  from  $C_p$ ), and spin ordering ( $C_S$ ), respectively. We observe a systematic shift between the two phase-transition temperatures that we believe can be attributed to the loss of long-range spin correlation. The application of this new concept [1] on real magnets suggests it is a very promising tool in order to analyze and rationalize the main factors that govern the magnetism of molecular crystals, and to predict whether the magnet has potential. In addition, this type of analysis will enable further research to better understand what happens in the region close to the magnetic transition regime depending on the magnetic topology.



[1] J. Jornet-Somoza, M. Deumal, J. Borge, J.J. Novoa, M.A. Robb, *submitted*

## The magnetic couplings sensitivity to Fock exchange in DFT is not due to spin over-delocalization

**Nathalie Guihéry<sup>1</sup>, Grégoire David<sup>2</sup>, Nicolas Ferré<sup>2</sup>**

<sup>1</sup> *Laboratoire de Chimie et Physique Quantiques, Université de Toulouse 3, Paul Sabatier, 118 route de Narbonne, 31062 Toulouse, France*

<sup>2</sup> *Institut de Chimie Radicalaire UMR7273, CNRS Université d'Aix Marseille, Case 521-Faculté de Saint-Jérôme Avenue Esc. Normandie Niemen, 13397 Marseille, France*

Abstract: Following a recently proposed method[1,2] of decomposition of the magnetic exchange contributions (direct exchange, kinetic exchange and spin polarization) and using a new method[3] of spin decontamination, the interactions of both Hubbard and Heisenberg Hamiltonians have been extracted from Broken Symmetry DFT calculations[4]. Analytical expression of these interactions have been derived as functions of both the energy of various broken symmetry solutions and their expectation value of  $S^2$ . These interactions strongly depend on the functionals and more particularly on the percentage of Hartree Fock exchange (HFX). The overestimation of the magnetic couplings calculated in DFT has always been attributed to the overestimation of the spin delocalization resulting from the use non-hybrid functionals or hybrid functionals with small amounts of HFX. Using non self-consistent calculations, it has been possible to separate the impact of the HFX amount from that of the spin delocalization. It will be shown that, contrarily to what it usually believed, spin delocalization has a little impact on the values of the interactions and that the HFX amount plays a crucial role. A deeper analysis rationalizes the obtaining of strong dependences of both the kinetic hopping integral and the on-site repulsion on the HFX amount while keeping the same density, which is physically aberrant as both interactions should be fixed for a given density.

[1] E. Coulaud, N. Guihéry, J.-P. Malrieu, D. Hagebaum-Reignier, D. Siri and N. Ferré, *J. Chem. Phys.*, **137**, 114106 (2012).

[2] Esther Coulaud, Jean-Paul Malrieu, Nathalie Guihéry and Nicolas Ferré, *J. Chem. Theory Comput.*, **9**, 3429–3436 (2013).

[3] Nicolas Ferré, Nathalie Guihéry and Jean-Paul Malrieu, *Phys. Chem. Chem. Phys.*, **17**, 14375-14382 (2015).

[4] This work, submitted for publication in *J. of Chem. Theor. Comp.*

## Quantum dot inter-Coulombic decay governed by the quantum size effect

**Fabian Weber<sup>1</sup>, Praphasiri Dolbundalchok<sup>2</sup>, Daniel Peláez<sup>3</sup>, Emad F. Aziz<sup>1,4,5</sup>, Annika Bande<sup>1</sup>**

<sup>1</sup>*Institute of Methods for Material Development, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Albert-Einstein-Str. 15, 12489, Berlin, Germany*

<sup>2</sup>*Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 229, Heidelberg, 69120, Germany*

<sup>3</sup>*Laboratoire PhLAM - UFR Physique Bâtiment P5, Université Lille 1, 59655 Villeneuve d'Ascq Cedex, France*

<sup>4</sup>*Department of Physics, Freie Universität Berlin, Arnimallee 14, 14195, Berlin, Germany*

<sup>5</sup>*School of Chemistry, Monash University, Clayton 3800, VIC, Australia*

Quantum dots (QDs), i.e. three-dimensional semiconductor nanomaterials have a discrete electronic structure which sensibly depends on the size of the QDs. This quantum size effect makes QDs attractive device materials for instance for a potential next-generation infrared photodetector based on the elementary inter-Coulombic decay (ICD [1]) energy transfer process.

In the given example of QD ICD an acceptor QD (AQD) absorbs infrared light by which one electron is promoted from the ground to the excited state. On an isolated QD a radiative decay and a phonon-mediated decay channel exist of which the latter is faster by about one order of magnitude. With a second QD in the vicinity energy transfer becomes an additional decay channel, which leads to the emission of one electron from the second emitter QD (EQD) [2].

We recently showed by MCTDHF electron dynamics calculations how the size of each individual QD, including its time-dependent phononic fluctuations, governs the ICD rate[3, 4]. Moreover, we found a complex interdependence of the parameters depending on the competing effects of polarization and Coulomb repulsion.

We acknowledge financial support from Volkswagen foundation (Freigeist Fellowship), the Deutsche Forschungsgemeinschaft, and the Thai government.

[1] L. S. Cederbaum, J. Zobeley, F. Tarantelli, *Phys. Rev. Lett.*, **79**, 4778 (1997).

[2] A. Bande, K. Gokhberg, L. S. Cederbaum, *J. Chem. Phys.*, **135**, 144112 (2011).

[3] P. Dolbundalchok, D. Peláez, E. F. Aziz, A. Bande, *J. Comput. Chem.*, **37**, 2249 (2016).

[4] F. Weber, E. F. Aziz, A. Bande, *J. Comput. Chem.*, DOI:10.1002/jcc.24843 (2017).

## Ternary Gold Hydrides: A New Class of Stable and Potentially Superconducting Compounds

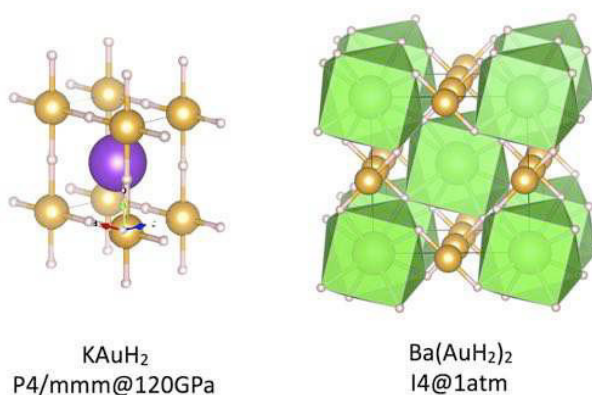
Martin Rahm<sup>1</sup>, Roald Hoffmann<sup>2</sup>, N. W. Ashcroft<sup>3</sup>

<sup>1</sup> Department of Chemistry and Chemical Engineering, Physical Chemistry, Chalmers University of Technology, Gothenburg, SE-412 96, Sweden

<sup>2</sup> Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York, 14853, USA

<sup>3</sup> Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York, 14853, USA

Our focus in this work is theoretical predictions of stability, properties, and realistic routes to the synthesis of an as of yet unknown class of compounds, those based on hydrogen and gold. Binary alloys of gold and hydrogen cannot be made by the application of high pressure,[1] but we calculate that the introduction of certain alkali and alkaline earth metal counterions should enable the synthesis of stable  $\text{AuH}_2^-$ -based ionic solids. Related  $[\text{A}]_2\text{PdH}_2$  (A=Alkali metal) compounds are stable,[2] some Au-H bonds can be stabilized in large organic scaffolds,[3] and fleeting  $\text{AuH}_x$  species are known from matrix isolation experiments.[4] The materials studied here would, once made, represent the first ternary gold hydrides likely stable under ambient conditions. Our work broaches use of chemical arguments to guide the design of chemically accessible metallic gold hydride ternaries predicted to be superconducting.



**Figure 1.**  $\text{KAuH}_2$  and  $\text{Ba}(\text{AuH}_2)_2$ , two examples of gold hydride ternaries predicted to be stable and superconducting under different conditions.

- [1] C. Donnerer, T. Scheler and E. Gregoryanz, *J. Chem. Phys.*, **138**, 134507/1 (2013).
- [2] M. Olofsson-Mårtensson, U. Häussermann, J. Tomkinson and D. Noréus, *J. Am. Chem. Soc.*, **122**, 6960 (2000).
- [3] A. Pintus, L. Rocchigiani, J. Fernandez-Cestau, M. Bochmann and P. H. M. Budzelaar, *Angew Chem Int Ed*, **55**, 12321 (2016).
- [4] U. Ringström, *Nature*, **198**, 981 (1963).

## Density Functional Theory as a Predictive Tool for Superconductivity

Ian D R Mackinnon, Peter C Talbot and Jose A Alarco

*Institute for Future Environments and Science and Engineering Faculty, Queensland  
University of Technology, 2 George Street, Brisbane, Australia 4001.*

Density Functional Theory (DFT) of electronic structure is widely used to simulate many structures and systems in chemistry and physics [1]. In many cases, these simulations have been highly successful at explaining IR spectra, binding sites and activation energies [1, 2] while there are also some critical failures due to delocalization and correlation errors of commonly used functionals [2]. In some cases, such as the prediction of superconducting properties using band structures, experimental data more commonly inform *post-facto* estimates of physical properties [3]. In this work, we demonstrate the efficacy of DFT in modern computational programs for prediction of the superconducting transition temperature ( $T_c$ ) for diboride structures. The key difference in approach compared with past estimates is the use of phonon dispersion (PD) plots to recognize the presence (or absence) of an anomaly and then to measure the extent and energy of the anomaly. PD plots are directly related to band structure models and, in the case of diborides, are a critical indicator of the electron-phonon interaction in a superconducting structure. DFT calculations are undertaken using the CASTEP module of Materials Studio 8.0 to calculate vibrational properties [4]. Both LDA and GGA methods with norm-conserving pseudo-potentials, a plane-wave basis set and a dense  $k$ -grid (at  $k < 0.03 \text{ \AA}^{-1}$ ) provide the most consistent model outcomes for a wide range of  $\text{AlB}_2$ -type compositions [5]. We find that for a range of chemical and physical variations to  $\text{MgB}_2$  – such as pressure dependence [6], metal substitution [5, 7] and isotopic variations [8] – evaluation of the  $E_{2g}$  phonon anomaly provides a direct, *ab initio*, estimate of  $T_c$  for this class of materials. In addition, this approach leads to prediction of  $T_c$  values for new, as yet unknown, compounds of the same structure type [5, 7].

- [1] W. Kohn, *Rev. Modern Phys.*, **71**, 1253-1266, 1999.
- [2] A. J. Cohen, P. Mori-Sánchez, and W. Yang, *Science*, **321**, 792-794, 2008.
- [3] J. Kortus, *Physica C*, **456**, 54-62, 2007.
- [4] K. Refson, P. R. Tulip, and S. J. Clark, *Phys. Rev. B*, **73**, 155114, 2006.
- [5] I. D. R. Mackinnon, P. C. Talbot, and J. A. Alarco, *Comp. Mater. Sci.*, **130**, 191-203, 2017.
- [6] J. A. Alarco, P. C. Talbot, and I. D. R. Mackinnon, *Physica C: Superconductivity and its applications*, **536**, 11-17, 2017.
- [7] J. A. Alarco, P. C. Talbot, and I. D. R. Mackinnon, *Phys. Chem. Chem. Phys.*, **17**, 25090-25099, 2015.
- [8] J. A. Alarco, P. C. Talbot, and I. D. R. Mackinnon, *Phys. Chem. Chem. Phys.*, **16**, 25386-25392, 2014.

## Design of New Disulfide-Based Organic Compounds for the Improvement of Self-Healing Materials.

**Jon M. Matxain<sup>1</sup>, José M. Asua<sup>2</sup>, Fernando Ruipérez<sup>2</sup>**

<sup>1</sup>*Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU) and Donostia International Physics Center (DIPC), P.K. 1072, 20080 Donostia, Euskadi, Spain*

<sup>2</sup>*POLYMAT, University of the Basque Country UPV/EHU, Donostia – San Sebastián, Spain*

Self-healing materials are a very promising kind of materials due to their capacity to repair themselves. Among others, diphenyl disulfide-based compounds ( $\text{Ph}_2\text{S}_2$ ) appear to be among the best candidates to develop materials with optimum self-healing properties. However, few is known regarding both the reaction mechanism and the electronic structure that makes possible such properties. In this vein, theoretical approaches are of great interest. In this work, we have carried out theoretical calculations on a wide set of different disulfide compounds, both aromatic and aliphatic, in order to elucidate the prevalent reactions mechanism and the necessary electronic conditions needed for improved self-healing properties [1]. Two reaction mechanisms were compared, namely, the [2+2] metathesis and the [2+1] radical-mediated mechanism. No computational evidence for the existence of any transition state for the metathesis mechanism was found, which indicates that the radical-mediated mechanism is the one responsible in the self-healing process. Besides, this has been recently confirmed experimentally [2]. The formation of sulfenyl radicals strongly depends on the S-S bond strength, which can be modulated chemically by the use of proper derivatives. At this point, amino derivatives appear to be the most promising ones. In addition to the S-S bond strength, hydrogen bonding between disulfide chains seems to be relevant to favour the contact among disulfide units. This is crucial for the reaction to take place. The calculated hydrogen bonding energies are of the same order of magnitude as the S-S bond energies. Finally, reaction barriers have been analyzed for some promising candidates. Interestingly, these barriers are around 10 kcal/mol regardless the substituent employed. All these results suggest that the radical formation and the structural role of the hydrogen bonding prevale over kinetics. Having this in mind, some new compounds are proposed for the design of future self-healing materials with improved features.

[1] J. M. Matxain, J. M. Asua and F. Ruipérez, *Phys. Chem. Chem. Phys.* **18**, 1758 (2016).

[2] S. Nevejans, N. Ballard, J. I. Miranda, B. Reck and J. M. Asua, *Phys. Chem. Chem. Phys.* **18**, 27577 (2016).



## Computational Modeling of Thermal Energy Storage Materials

Toyokazu Ishida<sup>1,2</sup>

<sup>1</sup>*Research Center for Computational Design of Advanced Functional Materials (CD-FMat), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 2, 1-1-1 Umezono, Tsukuba, 305-8568, Japan.*

<sup>2</sup>*Thermal Management Materials and Technology Research Association (TherMAT)*

Effective handling of reusable waste heat is one of the important future technologies for reducing energy consumption as well as promoting energy conservation. Among possible ways of handling waste heat, thermal energy storage is the key technology in thermal energy management. Basically, there are two major classes of materials for achieving thermal energy storage, phase change materials (PCMs) and thermo chemical materials (TCMs). Although some of them are familiar in our daily life and widely used in various social systems, the detailed molecular mechanism of thermal energy storage remains elusive at present. Especially, how to improve chemical properties of these materials, and also control chemical reactivity are important issues for developing new PCMs/TCMs. In the TherMAT project [1], we are now investigating the basic mechanism of thermal energy storage for both material systems based on a computational approach. In the WATOC 2017 meeting, I would like to present recent progress in our computational work.

As for PCM, sugar alcohols are known as one of the promising candidates for achieving large amounts of thermal energy storage. Based on the molecular and crystal structures of known sugar alcohols, we have computationally designed and predicted a new organic molecular material which can achieve larger amounts of thermal energy storage than ever before. In the first step, we carefully analyzed molecular properties of known C4, C5 and C6 sugar alcohols based on classical MD simulations [2]. Then we clarified the molecular factors that control physical properties, such as melting point and latent heat. On the basis of these detailed analyses, we proposed molecular design guidelines to achieve effective thermal energy storage; linear elongation of carbon backbone, separated distribution of OH groups, and even numbers of carbon atoms inside the carbon skeleton. Our computational results clearly demonstrated that if we carefully design molecular structures, non-natural sugar alcohols have potential ability to achieve thermal storage density up to 450-500 kJ/kg, which is larger than the best value of the present known organic PCMs (~350 kJ/kg) [3].

We also conducted first principle calculations for typical TCMs, and clarified the correlation between the electronic character and thermo-physical / chemical properties of alkali earth metal oxides.

[1] Thermal Management Materials and Technology Research Association:  
<http://www.thermat.jp>

[2] Taichi Inagaki, Toyokazu Ishida, *J. Phys. Chem. C*. **120**, 7903 (2016). Cover Art

[3] Taichi Inagaki, Toyokazu Ishida, *J. Am. Chem. Soc.* **138**, 11810 (2016).

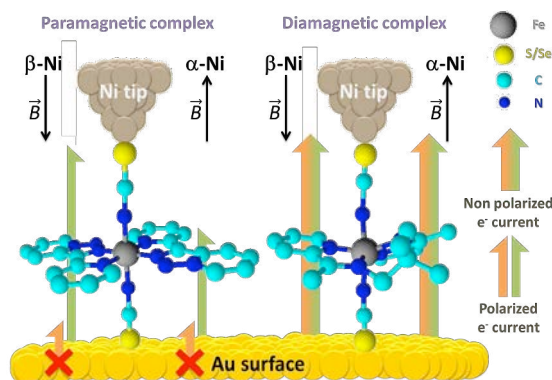


## Spin Crossover Complexes: A Challenge from Theory to Single-Molecule Devices

Eliseo Ruiz,<sup>1</sup> Alejandro Martín,<sup>1</sup> Jordi Cirera<sup>1</sup>

<sup>1</sup>*Departament de Química Inorgànica i Orgànica and Institut de Química Teòrica i Computacional, Universitat de Barcelona, Diagonal 645, 08028 Barcelona*

Spin crossover complexes (SCO), most of them Fe<sup>II</sup> complexes, have remarkable magnetic properties based on ground-state spin switching (for Fe<sup>II</sup> systems, between the diamagnetic  $S = 0$  low-spin  $t_{2g}^6 e_g^0$  and paramagnetic  $S = 2$  high-spin  $t_{2g}^4 e_g^2$  electron configurations) controlled by means of an external stimulus, *i.e.* temperature, light, pressure, solvent interactions or electric field.[1] From the theoretical point of view, such systems are big challenge because many exchange-correlation functionals completely fail in the prediction of the energy difference between the high- and low-spin states. Also, the calculation of the entropic vibrational contributions is fundamental to estimate the transition temperature between the two states. In this communication, our goal is to provide an extensive test of DFT methods to analyze SCO complexes with many different metals not only with the Fe<sup>II</sup> cations. Furthermore, in our group we have employed such systems to perform experimental and theoretical studies of single-molecule junctions being particularly interesting because they present magnetoresistance effect at room temperature (see Figure).[2] DFT+NEGF methods have been employed to rationalize such property, to clarify which are the main requirements of the magnetic molecules to show such behavior. Theoretical results have been confronted with scanning tunneling microscopy data.[3]



[1] E. Ruiz *Phys. Chem. Chem. Phys.* (Perspective) **16**, 14, (2014).

[2] A. C. Aragonès, D. Aravena, J. I. Cerdá, Z. Acís-Castillo, H. Li, J. A. Real, F. Sanz, J. Hihath, E. Ruiz, I. Díez-Pérez *Nano Letters* **16**, 218, (2016).

[3] A. C. Aragonès, D. Aravena, F. J. Valverde-Muñoz, J. A. Real, F. Sanz, F., I. Díez-Pérez, E. Ruiz *J. Am. Chem. Soc.* **139**, 5768, (2017).

## Accelerating metal-directed protein folding and molecular recognition with enhanced sampling techniques

**Ferran Feixas<sup>1</sup>, Martí Gimferrer<sup>1</sup>, Pedro Salvador<sup>1</sup>, Marc Garcia-Borràs<sup>2</sup>**

<sup>1</sup>*Institut de Química Computacional i Catàlisi, University of Girona, Campus Montilivi s/n  
17071, Girona, Spain*

<sup>2</sup>*Department of Chemistry and Biochemistry, University of California Los Angeles, Los Angeles, USA*

Metal ions are found in the core of several phenomena such as biomolecular recognition and protein (un)folding. Some of these important processes usually take place on the  $\mu$ s to ms time scales. Low-energy states relevant for these processes may be separated by high-energy barriers, which are rarely crossed over the course of molecular dynamics simulations. Methods that enhance conformational sampling are needed to elucidate the role of metal ions in these biological phenomena at a reasonable computational cost. Accelerated molecular dynamics (aMD) enhances sampling in a relatively simple way (a priori knowledge of the underlying free energy landscape is not needed).[1,2] Recently, we explored the performance of aMD to predict the detailed mechanisms of protein folding. The folding and the free energy landscape of a set of fast-folding proteins was simulated with aMD. This allowed us to identify distinct conformational states (e.g. unfolded and intermediate) other than the native structure and the protein folding energy barriers.[3]

Here, we combine aMD simulations with electronic structure calculations for the metal parametrization[4] to study the the redox conformational protection of nitrogenase. A protein called Shethna Protein II (FeSII, homodimer), which contains two [Fe<sub>2</sub>S<sub>2</sub>] clusters, forms a stable ternary complex with nitrogenase that is able to protect this enzyme from oxygen. Interestingly, FeSII can alter from an open to a closed conformation depending on the levels of O<sub>2</sub>. The hypothesis is that this conformational change, that connects the open and closed states, is linked to a change in the oxidation state of the [Fe<sub>2</sub>S<sub>2</sub>] cluster that involve unfolding and subsequent refolding of the N-loop of the protein. To this end, the [Fe<sub>2</sub>S<sub>2</sub>] cluster has been parametrized in different oxidation states and simulations from both open and closed conformations at different redox states are produced. Our aMD simulations show that the FeSII is able to alter from the open to the closed conformation involving folding and unfolding of the N-loop through a series of intermediate states.

[1] P.R. Markwick, J.A. McCammon, *Phys. Chem. Chem. Phys.*, **13**, 20053 (2011)

[2] F. Feixas, S. Lindert, W. Sinko, J. A. McCammon, *Biophys. Chem.*, **186**, 31 (2014)

[3] Y. Miao, F. Feixas, C. Eun, J. A. McCammon, *J. Comp. Chem.*, **36**, 1536 (2015)

## Role of aromatic, aliphatic and backbone interactions in the stability of amyloids

**Dragan B. Ninković,<sup>1</sup> Predrag V. Petrović,<sup>1</sup> Dušan P. Malenov,<sup>2</sup> Michael B. Hall,<sup>3</sup> Edward N. Brothers,<sup>1</sup> and Snežana D. Zarić,<sup>1,2</sup>**

<sup>1</sup>*Science Program, Texas A&M University at Qatar, Texas A&M Engineering Building, Education City, Doha, Qatar.*

<sup>2</sup>*Department of Chemistry, University of Belgrade, 1000 Belgrade, Serbia.*

<sup>3</sup>*Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, USA.*

The amyloid fibrils have been studied very intensively because of their importance in Alzheimer's disease and other neurodegenerative diseases. The role of aromatic amino acids in formation of the amyloid fibrils is somewhat controversial. Aromatic amino acids are very frequent in natural amyloids, leading to idea that aromatic residues are essential for amyloid aggregation [1,2]. However, studies have shown that amyloid fibrils can be formed from peptides without aromatic amino acids [3].

In order to elucidate role of aromatic amino acids in aggregation of amyloids, in our work we applied DFT method to calculated interaction energies between amyloid  $\beta$ -sheets [4]. We performed calculations on two types of on model systems (1) with and (2) without aromatic amino acids. The model systems used in our work we made from crystal structures of amyloids. The two types of amyloids have similar interaction energies indicating that both types of amyloids can be formed, what is in agreement with experimental data.

In spite of similar stabilities, the analyses of the factors contributing to the amyloid stability shows that two types of amyloids are stabilized by different factors. In (1) amyloids with aromatic amino acids the main contribution to the interaction energies are interactions between side chains; the most important are interactions between aromatic and aliphatic groups followed by aromatic/aromatic interactions. In (2) amyloids without aromatic amino acids the main contribution are interactions of side chains with backbone and hydrogen bonds.

[1] M. Tena-Solsona, J. F. Miravet, B. Escude, *Chem. Eur. J.* **20**, 1023–1031 (2014)

[2] R. Cukalevski, B. Boland, B. Frohm, E. Thulin, D. Walsh, S. Linse, *ACS Chem. Neurosci.* **3**, 1008–1016 (2012).

[3] S. M. Tracz, A. Abedini, M. Driscoll, D. P. Raleigh, *Biochemistry*, **43**, 15901–15908 (2004).

[4] D. B. Ninković, D. P. Malenov P. V. Petrović, E. N. Brothers, S. Niu, M. B. Hall, M. R. Belić, S. D. Zarić, *Chem. Eur. J.* submitted.

**Design of AMPA receptor positive allosteric modulators: QSAR studies,  
virtual screening, and molecular dynamics simulations**

**Vladimir A. Palyulin, Dmitry S. Karlov, Mstislav I. Lavrov,  
Eugene V. Radchenko, Nikolay S. Zefirov**

*Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory, 1/3,  
Moscow 119991, Russia*

Glutamate is the major excitatory neurotransmitter in the CNS, and the malfunctioning of the glutamatergic system leads to serious neurological disorders and is associated with neurodegenerative diseases. The ionotropic glutamate receptors are ligand-gated ion channels that consist of four subunits forming the ion channel pore, the ligand-binding domains, and the amino-terminal domains. The positive allosteric modulators of an important type of glutamate receptors, AMPA receptors, are able to improve memory and cognition.

We have performed the molecular modeling of the ligand-receptor interactions and the QSAR studies for the AMPA receptor positive allosteric modulators (PAMs).

The molecular dynamics simulations for a series of AMPA receptor PAMs bound on the interface between two glutamate-binding domains have demonstrated a good correlation of the MM-GBSA and MM-PBSA binding energies with the experimental  $pEC_{50}$  values.

The Molecular Field Topology Analysis (MFTA) QSAR method developed by us was quite helpful in the modeling of ligand selectivity and multi-target activity in terms of local properties such as the atomic charges, group van der Waals radii, and local lipophilicity. In addition, the 3D QSAR and pharmacophore models of the AMPA receptor PAMs have been constructed.

The combination of these techniques as well as the virtual screening of large compound libraries allowed us to identify and design new scaffolds for PAMs and create the focused libraries of promising PAM structures. These modelling studies have lead to the development of positive AMPA receptor modulators with experimentally confirmed high potency in electrophysiological studies, which improve memory and cognition in animal models.

The advanced predictive models developed by us earlier for the important ADMET properties such as blood-brain barrier permeability, human intestinal absorption, and hERG affinity and activity were used as additional filters in the design of neuroprotective compounds.

This work was supported by the Russian Science Foundation (grant No.17-15-01455).

## AQUILES web server: open the eyes to blind docking

**José P. Cerón-Carrasco, José M. Cecilia and Horacio Pérez-Sánchez**

*Bioinformatics and High Performance Computing Research Group (BIO-HPC) Computer Engineering Department. Universidad Católica San Antonio de Murcia (UCAM), Spain*

The development of new drugs is an extremely expensive process that can be benefited from the use of a wide panel of theoretical tools including virtual screening, docking, molecular dynamics and *ab initio* computational chemistry approaches.

Our group has recently contributed to the design of novel molecules with real clinical applications by setting up an efficient blind docking workflow. Aiming to make this new technology accessible to any researcher, our protocol has been implemented in a blind docking server called AQUILES, which is already available via the Internet at

<http://bio-hpc.eu/software/blind-docking-server/>

In this contribution we discuss the potential use of AQUILES in the framework of anticoagulants, cancer, Parkinson, Fabry and Zika (see Figure 1).

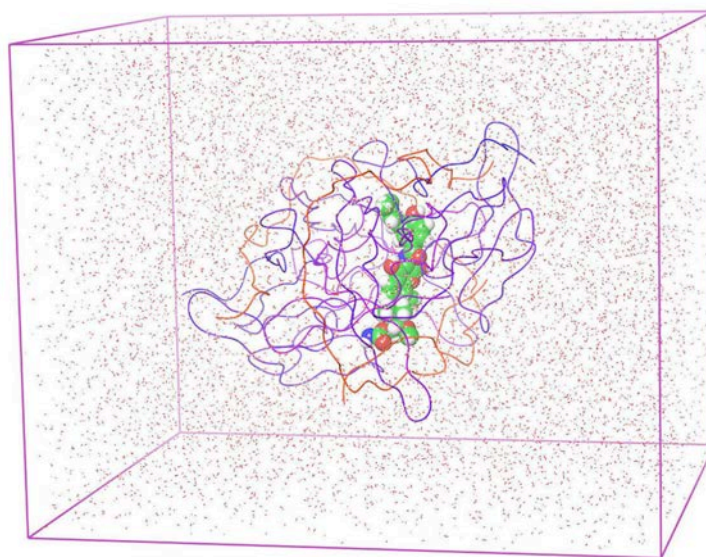


Figure 1: Chemical model of the new drug with a potent *in vivo* anti-Zika activity (invention currently under patent procedure) discovered with AQUILES.

## Thermodynamics of Self-Assembly of Perylene Derivatives

Jörg Baz<sup>1</sup>, Niels Hansen<sup>1</sup>

<sup>1</sup>*Institute of Thermodynamics and Thermal Process Engineering, University of Stuttgart, Pfaffenwaldring 9, D-70569 Stuttgart, Germany*

Functional organic materials composed of dye-based molecules that stack into various structures by non-covalent intermolecular forces have fascinating optical and mechanical properties. These novel materials are of increasing importance for many high-technology applications. Here is a need for a rational design of such materials based on the engineering of dye-dye interactions and the prediction of how these interactions impact the properties of nano- or bulk state materials. The required insight into the underlying physical processes can be derived from investigations on dye assemblies that constitute the intermediate state of matter between monomeric dyes and supramolecular materials. Perylene di-imide derivatives (PDIs) emerged as a prototype class of molecules for the elucidation of the transition from monomeric to bulk materials via the supramolecular state [1,2]. Their self-assembly into complex structures is determined by size and shape of the monomeric unit, system composition and thermodynamic boundary conditions. Given this diversity of factors, a molecular-level understanding of the various driving forces is essential for the rational material design.

In this project the free energy for the formation of dimers and higher aggregates are calculated for prototypical molecular building blocks carrying different functional groups in different solvent environments using molecular dynamics free-energy simulations based on force fields inherited from the area of biomolecular simulations. The temperature dependence of the free energy gives access to the entropic contribution while the change in potential energy during assembly provides the enthalpic contribution.

We discuss the influence of the molecular architecture and the solvent composition on the thermodynamic fingerprint of the aggregation and investigate the ability of classical molecular dynamics simulations to be used in rational materials design.

[1] F. Würthner, C. R. Saha-Möller, B. Fimmel, S. Ogi, P. Leowanawat, D. Schmidt, *Chem. Rev.* **116**, 962 (2016).

[2] E. Krieg, M. M. C. Bastings, P. Besenius, B. Rybtchinski, *Chem. Rev.* **116**, 2414 (2016).

## Solvation in 2D: Microsolvated Ions on Inert Surfaces

**János Daru, Prashant Kumar Gupta, Dominik Marx**

*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany*

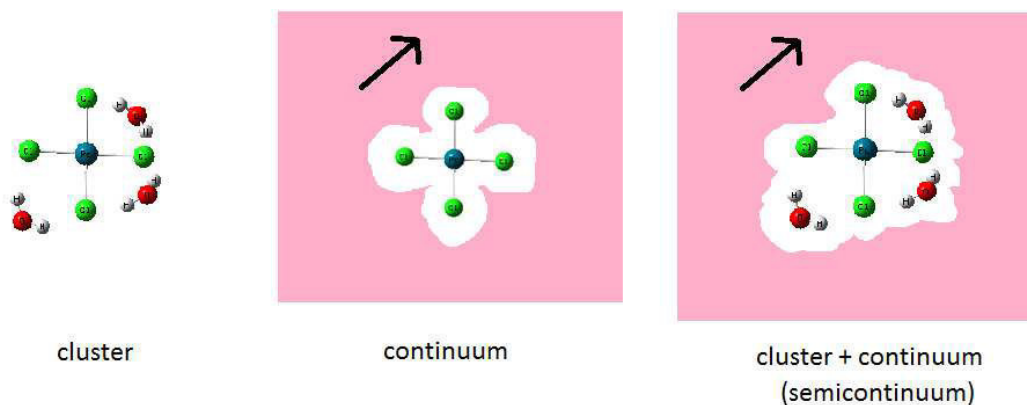
The present project aims to study the solvation process of alkali cations and halogen anions in the presence of weakly interacting surfaces. This investigation is a step forward toward understanding solvation in restricted environments. We have performed QM/MM simulations on solvatomers deposited on Xe layers on Cu(111) support. The system has been established in collaboration with our experimental partners in order to provide complementary results for STM studies of the same systems. The realistic description of surface polarization is achieved by including the neighboring Xe atoms into the QM subsystem and applying self-consistent image-charge interaction with the metal. In order to reduce finite size effects in our periodic model, the interaction between QM images are decoupled and the QM Xe atoms are embedded into the layers of their classical counterparts. Our computational approach has been thoughtfully tested in a related study of gas-phase ion solvation against high level *ab initio* benchmarks (with a special focus on treating dispersion interactions in this rather complex system) and converged path integral simulations. Our simulations provided remarkably different solvation structures in comparison with gas-phase solvatomers. The weak interaction with the surface can compensate for loss of water-water and water-ion interactions and therefore stabilize solvatomers that are unlikely or even unstable in gas phase. The sampled configurations of the performed NVT simulations will be used as initial conditions for future NVE trajectories. This ensemble of NVE simulations can be used for rigorous calculation of correlation functions and for obtaining (THz) spectra of the system being a direct probe of the hydrogen bond network dynamics.

## Aqueous Solution Thermodynamics: A Demonstration of Effective Use of the Semicontinuum (Cluster + Continuum) Idea

Allan L. L. East<sup>1</sup>

<sup>1</sup>*Department of Chemistry and Biochemistry, University of Regina, 3737 Wascana Parkway, Regina SK S4S0A2 Canada*

Modelling of solvation effects can be done with continuum-dielectric, explicit-solvent-cluster, or hybrid (“semicontinuum,” “cluster + continuum”) models. For aqueous solution thermodynamics, the first two methods can perform disastrously, but hybrid methods can effectively solve these problems. We present (i) the principles we have used for applying semicontinuum modelling, and (ii) several demonstrations of its utility: autoionization of water, coordination chemistry (ligand exchange), pK<sub>a</sub> of weak bases, carbamate ion stability, and mechanochemical speedup of peptide-bond solvolysis.





## Towards reliable computed thermodynamic data for aqueous metal ions: The case of cadmium.

Stefan Andersson<sup>2</sup>, Francesca L. Bleken<sup>1</sup>, Espen Sagvolden<sup>1</sup>, and Ole Swang<sup>1\*</sup>

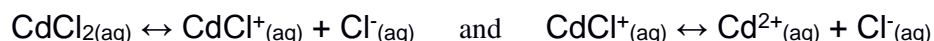
<sup>1</sup>SINTEF Materials and Chemistry, P. O. Box 124 Blindern, N-0314 Oslo, Norway.

<sup>2</sup>SINTEF Materials and Chemistry, P. O. Box 4760 Sluppen, N-7465 Trondheim, Norway.

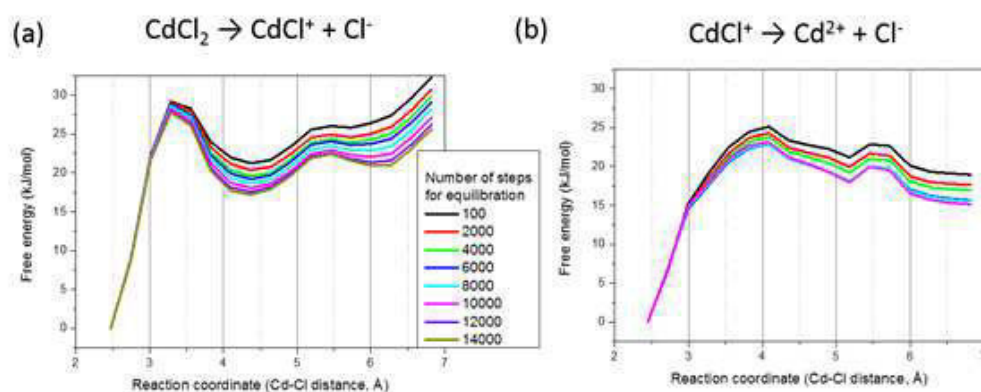
\*: Presenting author

Cadmium, due to its toxicity, it is increasingly being replaced by other materials. It is mostly produced as a by-product of the refining of other metals, notably zinc. It is an unwanted pollutant in many industrial processes, and technology for cadmium separation will probably continue to be important in the future, even if production should diminish. Both production and abatement of cadmium rely on aqueous processes. Atom-scale modelling of energetics for reactions in aqueous solution is done routinely for reactions involving many classes of species. Metal ions are demanding cases, and the goal of the present study is to investigate opportunities for reliable computed reaction energies for metal ions in aqueous solution.

We present reaction and activation energies for the reactions



as calculated using two different atom-scale dynamics approaches based on DFT and forcefields, respectively, followed by discussion on structures, mechanistic aspects, and opportunities for computational support in the development of improved metal-separation technology.



**Explicitly correlated *ab initio* benchmark study on water clusters (H<sub>2</sub>O)<sub>n</sub>, n=2–  
20: The right answer for the right reason?**

**Debashree Manna, Manoj Kumar Kesharwani, Nitai Sylvetsky,  
and Jan M. L. Martin**

<sup>1</sup>*Department of Organic Chemistry, Weizmann Institute of Science, 234 Herzl Street,  
7610001 Rehovot, Israel*

In a sequel to our recent revision[1] of the S66x8 noncovalent interactions benchmark, the BEGDB and WATER27 datasets of water cluster association energies have been re-examined at the MP2 and CCSD(T) basis set limit, with both conventional and explicitly correlated (F12) approaches. For the MP2 and CCSD–MP2 contributions, rapid basis set convergence is observed with explicitly correlated methods compared to conventional methods. However, conventional, orbital-based calculations are preferred for the calculation of the (T) term. For the CCSD-MP2 term, CCSD(F12\*) converges somewhat faster with the basis set than CCSD-F12b. The performance of various DFT methods is also evaluated: Head-Gordon's  $\omega$ B97X-V and  $\omega$ B97M-V functionals[2] are found to outperform all other DFT functionals. Counterpoise-corrected DSD-PBEP86 [3] and raw DSD-PBEPBE-NL also perform well. In the WATER27 dataset, the anionic (deprotonated) water clusters exhibit unacceptably slow basis set convergence with the regular cc-pVnZ-F12 basis sets, which only have diffuse s and p functions. To overcome this, we have constructed modified basis sets, denoted aug-cc-pVnZ-F12 or aVnZ-F12, which have been augmented with diffuse functions on the higher angular momenta.

Our best calculated dissociation energies can be reproduced through n-body expansion, provided one pushes to the basis set and electron correlation limit for the 2-body term: for the 3-body term, post-MP2 contributions (particularly CCSD-MP2) are important for capturing the 3-body dispersion effects. Terms beyond 4-body can be adequately captured at the MP2-F12 level.

- [1] B. Brauer, M.K. Kesharwani, S. Kozuch, J.M.L. Martin, *PCCP* **18**, 20905 (2016).
- [2] N. Mardirossian, M. Head-Gordon, *J. Chem. Phys.* **114**, 214110 (2016).
- [3] S. Kozuch, J.M.L. Martin, *J. Comput. Chem.* **34**, 2327 (2013).

## **GöBench: a joint initiative for experimental benchmarking of quantum chemical methods**

**Ricardo A. Mata<sup>1</sup>**

<sup>1</sup>*Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Tammannstr. 6, Göttingen, Germany*

In any computational study, one struggles in finding the best compromise between method accuracy and cost. Defining and committing to an approach requires some *a priori* knowledge of how the latter may fair in the envisioned application. Computational benchmarks can help with the task. Through the use of standardized tests, one can more effectively assess the ‘goodness’ of the method, and compare to the choices made by other research groups. They also often serve as a first quality check to newly developed quantum chemical methods, from DFT functionals to wave function based approaches.

For several reasons which have been pointed out elsewhere[1], we have grown accustomed to benchmarking theory results with other purely theory-based reference values. Although this is for the most part well justified, it can lead to some dangerous side effects. One example would be the neglect of molecular dynamics when only vertical electronic excitations are benchmarked. Furthermore, we tend to play it safe. We only benchmark systems and properties for which we can compute a ‘reliable’ (or so we think) value. My argument is that by leaving out experiment from our benchmarking practices, we are losing opportunities to advance quicker and more effectively our computational tools.

In this talk, I present this argument in light of experiments and calculations from small (triatomics) to large systems (a few hundred atoms), highlighting the benefit of experimental reference values and cross-semination of theoretical works. I will also present our local initiative GöBench at the University of Göttingen, which intends to bring together a suite of experimental groups to provide new and challenging experimental data for the benefit of the Theoretical Chemistry community.

[1] R. A Mata, M. Suhm, *Angew. Chem. Int. Ed.* DOI: 10.1002/anie.201611308

## Approaching CCSD(T)/CBS energies for large molecules with the linear-scaling local natural orbital CCSD(T) method

Péter R. Nagy<sup>1</sup>, Gyula Samu<sup>1</sup>, Bence Hégyel<sup>1</sup>, Dávid Mester<sup>1</sup>, Mihály Kállay<sup>1</sup>

<sup>1</sup>MTA-BME Lendület Quantum Chemistry Research Group, Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economic

Efficient, linear-scaling, local second-order Møller–Plesset (LMP2) and local natural orbital (LNO) coupled-cluster (CC) singles and doubles with perturbative triples [LNO-CCSD(T)] approaches are presented [1, 2, 3]. Using our highly optimized implementation correlation energies of the local scheme can be systematically improved towards the corresponding canonical CCSD(T) value within chemical accuracy for systems up to a few hundreds of atoms.

The error originating from the local approximations can be decreased in a simple, black-box manner using increasingly tighter, pre-defined threshold sets. The complete basis set (CBS) limit can be estimated, e.g., via extrapolation relying on triple- $\zeta$  and quadruple- $\zeta$  quality bases. In recent developments the redundancy in our local ansatz caused by the overlap of the fragments has been drastically decreased leading to an order of magnitude speedup in the integral transformation, and the MP2 and (T) amplitude evaluation steps [1, 2]. Extensions for the efficient evaluation of general order local CC and spin-scaled MP2 energies, and the perturbative terms of double-hybrid density functionals are also presented.

Benchmark calculations [1, 2] demonstrate that our implementation enables correlated calculations for realistic, three-dimensional molecules with more than 1000 atoms using at least triple- $\zeta$  basis sets (20000+ AOs) in a matter of days on a single processor (see Figure). Even better efficiency is achieved by utilizing our multi-layer scheme, where, e.g., LNO-CCSD(T) is employed for the most important, active part, while the environment is described at the LMP2 level [3].

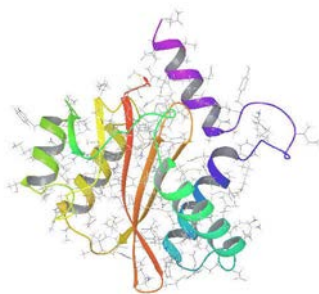


Figure 1: HIV-1 integrase catalytic domain (2380 atoms, 22621 AOs)

- [1] P. R. Nagy, M. Kállay. *J. Chem. Phys.*, **146**, 214106 (2017)
- [2] P. R. Nagy, G. Samu, M. Kállay. *J. Chem. Theory Comput.*, **12**, 4897 (2016)
- [3] B. Hégyel, P. R. Nagy, G. G. Ferenczy, M. Kállay *J. Chem. Phys.*, **145**, 064107 (2016)

## **Large-scale Valence Bond Applications: Excitons and Transition Metal Complexes**

**Graham D. Fletcher**

*Argonne Leadership Computing Facility, Argonne National Laboratory, 9700 S. Cass Ave., Lemont, USA*

Valence bond methods offer the advantage that the picture of electronic structure obtained is free from artifacts due to orthogonality, allowing the wave function to reflect the impact of physical effects unimpeded. This would be a great advantage in the study of excitons enabling us to ‘see’ the structure of the exciton. In addition, the localized nature of overlapping orbitals gives a clearer view of bonding and other important chemical ideas such as the octet rule and ligand field theory. Overlapping orbitals also have many advantages for computational scalability. A relatively new formulation of valence bond capturing all these advantages – Variational Subspace Valence Bond [1] – is described and its high scalability is demonstrated by application to excitons in lithium fluoride and complexes of copper oxide with carbon monoxide. All-electron calculations on systems with more than one hundred atoms using more than one million processes are presented.

[1] G. D. Fletcher, *J. Chem. Phys.*, 142, 134112 (2015).

## Scalable polarizable molecular dynamics using Tinker-HP: millions of atoms on thousands of cores

Jean-Philip Piquemal<sup>1,2,3</sup>,

<sup>1</sup>*Laboratoire de Chimie Théorique, Sorbonne Universités, UPMC Paris, France.*

<sup>2</sup>*Institut Universitaire de France, 75005, Paris, France.*

<sup>3</sup>*Department of Biomedical Engineering, the University of Texas at Austin, TX, USA.*

Tinker-HP is a CPU based, double precision, massively parallel package dedicated to long polarizable molecular dynamics simulations and to polarizable QM/MM. Tinker-HP is an evolution of the popular Tinker package (<http://dasher.wustl.edu/tinker>) that conserves its simplicity of use but brings new capabilities allowing performing very long molecular dynamics simulations on modern supercomputers that use thousands of cores. Indeed, this project gathers scientists from various fields including Chemistry, Applied Mathematics and Biomolecular Engineering and redefined completely the algorithmic of usual polarizable simulations package. The Tinker-HP approach offers various strategies using domain decomposition techniques for periodic boundary conditions in the framework of the (N)log(N) Smooth Particle Mesh Ewald or using polarizable continuum simulations through the new generation ddCosmo approach. Tinker-HP proposes a high performance scalable computing environment for polarizable force fields giving access to large systems up to millions of atoms. I will present the performances and scalability of the software in the context of the AMOEBA force field and show the incoming new features including the advanced SIBFA polarizable molecular mechanics approach and the density based GEM force field as well as newly available "fully polarizable" QM/MM capabilities. Various benchmarks and examples on biomolecular systems will be provided on several architectures showing that the approach is competitive with GPUs for small and medium size systems but allows addressing larger molecules on modern supercomputers. As the present implementation is clearly devoted to petascale applications, the applicability of such an approach to future exascale machines will be exposed and future directions of Tinker-HP discussed.

- [1] F. Lipparini, L. Lagardère, B. Stamm, E. Cances, M. Schnieders, P. Y. Ren, Y. Maday, J.-P. Piquemal, *J. Chem. Theory. Comput.* 10, 1638-1651 (2014).
- [2] L. Lagardère, F. Lipparini, E. Polack, B. Stamm, E. Cances, M. Schnieders, P. Y. Ren, Y. Maday, J.-P. Piquemal, *J. Chem. Theory. Comput.* 11, 2589 (2015).
- [3] F. Lipparini, L. Lagardère, C. Raynaud, B. Stamm, E. Cances, M. Schnieders, P. Y. Ren, B. Mennucci, Y. Maday, J.-P. Piquemal, *J. Chem. Theory. Comput.* 11, 623-634 (2015).
- [4] F. Aviat, A. Levitt, Y. Maday, B. Stamm, P. Y. Ren, J. W. Ponder, L. Lagardère, J.-P. Piquemal, *J. Chem. Theory. Comput.* 13, 180-190 (2017).
- [5] L. Lagardère, L.-H. Jolly, F. Lipparini, B. Stamm, G. A. Cisneros, N. Gresh, Y. Maday, J. W. Ponder, P. Y. Ren, J.-P. Piquemal, submitting (2017).

## Vibronic Boson Sampling

**Joonsuk Huh<sup>1</sup> and Man-Hong Yung<sup>2</sup>**

<sup>1</sup>*Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Korea*

<sup>2</sup>*Department of Physics, South University of Science and Technology of China, Shenzhen 518055, China*

The intrinsic nature of parallelism of quantum states is anticipated to give extraordinary computational power to quantum processors for certain problems. A linear optical network is one of the simplest quantum processors that it could reveal the (computational) quantum supremacy against classical machines. A photon-sampling problem in a linear optical network, so-called Boson Sampling, is a specially designed mathematical problem, which is expected to be intractable for any classical machine. Molecular vibronic spectroscopy, where the transitions involve non-trivial Bosonic correlation due to the Duschinsky Rotation, is strongly believed to be in a similar complexity class as Boson Sampling [1]. At finite temperature, the problem is represented as a Boson Sampling experiment with correlated Gaussian input states. Here we show that every instance of Gaussian Boson Sampling with an initial correlation can be simulated by an instance of Gaussian Boson Sampling without initial correlation, with only a polynomial overhead. We refer such a generalized Gaussian Boson Sampling motivated by the molecular sampling problem as Vibronic Boson Sampling [2].

[1] J. Huh, G. G. Guerreschi, B. Peropadre, J. R. McClean, and A. Aspuru-Guzik, *Nature Photon.*, **9**, 615 (2015).

[2] J. Huh and M.-H. Yung, Preprint: arXiv:1608.03731 (2016).

# PCMSolver: a modern, modular approach to include solvation in any Quantum Chemistry Code

Luca Frediani<sup>1</sup>, Roberto Di Remigio<sup>1</sup>

<sup>1</sup>*Centre for Theoretical and Computational Chemistry, Department of Chemistry, UiT, The Arctic University of Norway, Tromsø, Norway*

Many quantum chemistry packages are large collaborative efforts involving several communities with different expertise. The development and maintenance of the resulting codes is often a significant undertaking, and the inclusion of new features in a code becomes a challenging task, often requiring the knowledge of a large amount of code due to suboptimal design. In order to improve the efficiency of the code development work flow, and allow researchers to devote more efforts to the scientific discovery instead, a modular approach should be adopted.

A module can loosely be defined as a separate piece of code, providing a specific functionality through a library. In order to be widely deployable, a module needs several key-features such as: (1) a well defined Application Programming Interface; (2) unit- and regression-testing; (3) code development independent of the main Quantum Chemistry program.

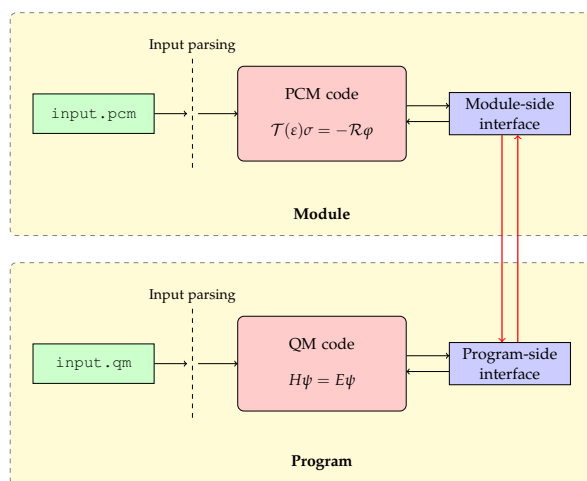


Figure 1: An illustration of the modular approach to solvation adopted by PCMSolver.

The inclusion of solvent effects in Quantum Chemistry is a clear example where such a modular approach can and should be adopted. The module provides the solvent reaction field, for a given potential of the molecular system. Most of the internals of the module (how the reaction field is obtained) are hidden inside the module, exposing to the main code only the functionality which is strictly required.

The advantage of such an approach is twofold: (1) once a new feature is available in the module, all codes which are interfaced to it could simply download the new version, largely reducing the coding efforts; (2) including solvation in a new code reduces to providing the in-

terface to the module, thus leveraging on the already available features of both the module and the main code.

Using this guiding principles, we have developed PCMSolver, which now provides continuum solvation functionality to several codes, such as Dalton, LSDalton, Dirac, Psi4 and Koala. In this contributions we will present PCMSolver, showing its features such as the different solvers and environments implemented, how it can be interfaced to any quantum chemistry code, and a few illustrative applications.



## Combining frozen-density embedding with the conductor-like screening model using Lagrangian techniques

Nils Schieschke<sup>1</sup>, Roberto Di Remigio<sup>2</sup>, Luca Frediani<sup>2</sup>, Johannes Heuser<sup>1</sup>,  
Sebastian Höfener<sup>1</sup>

<sup>1</sup>*Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), P.O. Box 6980,  
D-76049 Karlsruhe, Germany*

<sup>2</sup>*Department of Chemistry, Centre for Theoretical and Computational Chemistry, UiT, The  
Arctic University of Norway, N-9037 Tromsø, Norway*

We present the explicit derivation of an approach to the multiscale description of molecules in complex environments that combines frozen-density embedding (FDE) with the conductor-like screening model (COSMO). FDE provides an explicit atomistic description of molecule-environment interactions at reduced computational cost, while the outer continuum layer accounts for the effect of long-range isotropic electrostatic interactions. Our treatment is based on a variational Lagrangian framework, enabling a rigorous derivation of response properties. This method is used to compute Stokes shifts in the Tamm-Dancoff approximation (TDA). Using the second-order approximate coupled-cluster singles and doubles (RICC2) method for the subsystems, vertical excitation energies for some simplified protein models are computed, see Fig. 1. The interaction terms between the FDE subsystem densities and the continuum can influence excitation energies up to 0.3 eV and thus cannot be neglected for general applications.

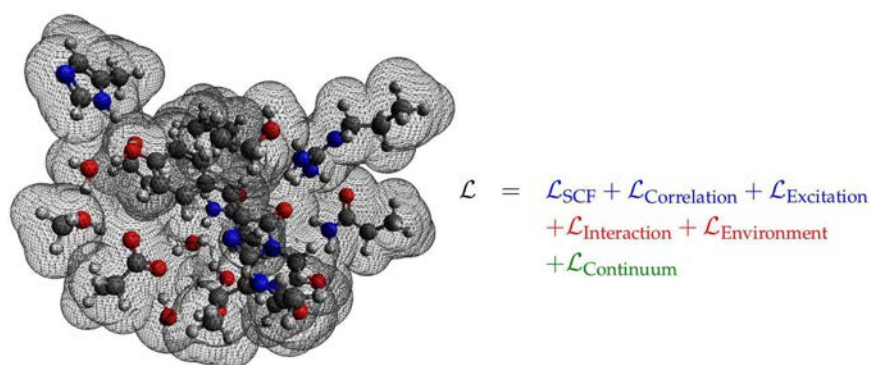


Figure 1: Symbolic COSMO surface of a simplified protein model (*left*) and the Lagrangian used for computing excited-state response properties from wavefunction FDE combined with COSMO (*right*).

- [1] N. Schieschke, R. Di Remigio, L. Frediani, J. Heuser, S. Höfener, *J. Comput. Chem.* published online, DOI: 10.1002/jcc.24813 (2017).

## Multiexcitons and strong correlation via single-excitation wavefunctions: applications and future directions

Nicholas J. Mayhall<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Virginia Tech, 900 West Campus Drive, Blacksburg, VA, USA*

Due to the possibility of improving in photovoltaic efficiencies, significant effort has been directed towards understanding the singlet fission mechanism. Although accurate quantum chemical calculations would provide a detail-rich view of the singlet fission mechanism, this is complicated by the multiexcitonic nature of one of the key intermediates, the  $^1(TT)$  state. Being described as two simultaneous and singlet-coupled triplet excitations on a pair of nearest neighbor monomers, the  $^1(TT)$  state is inherently a multielectronic excitation. This fact renders most single-reference quantum chemistry methods incapable of providing accurate results.

In this talk I will discuss our recently developed strategy in which single-spin flip calculations are mapped onto a spin-only Hamiltonian, which is then solved by exact diagonalization to yield the target low-energy biexciton states. In addition, new tensor-based techniques for solving the resulting spin-Hamiltonian will be discussed including numerical examples.

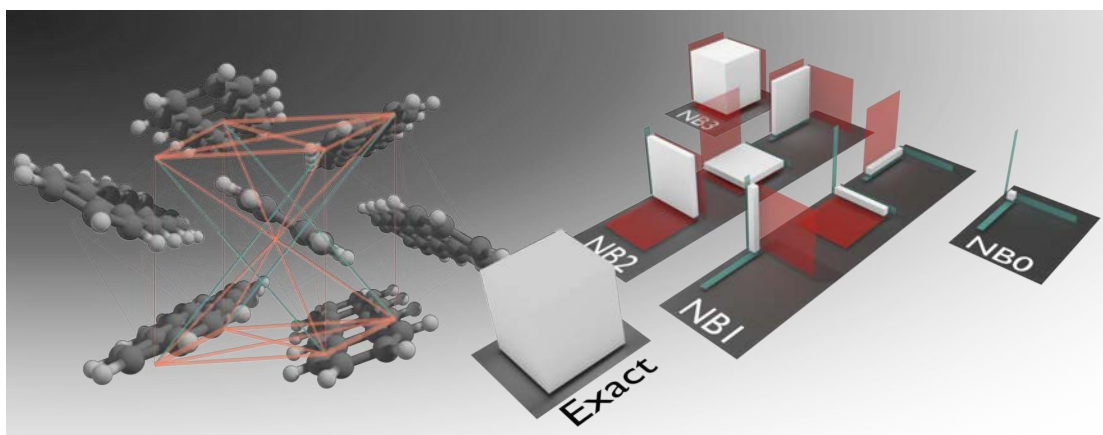


Figure 1: Schematic illustration of the  $n$ -body Tucker expansion for a 3-fragment system.

## The computation of dielectric constants

Selim Sami<sup>1</sup>, Riccardo Alessandri<sup>2,3</sup>, Ria Broer<sup>2</sup>, Remco W.A. Havenith<sup>1,2,4</sup>

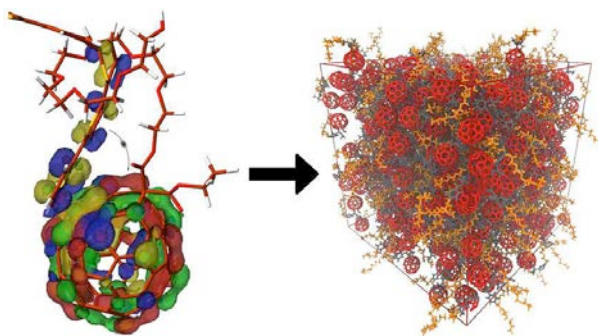
<sup>1</sup> Stratingh Institute for Chemistry, University of Groningen, The Netherlands

<sup>2</sup> Zernike Institute for Advanced Materials, University of Groningen, The Netherlands

<sup>3</sup> Groningen Biomolecular Sciences and Biotechnology Institute, University of Groningen, The Netherlands

<sup>4</sup> Department of Inorganic and Physical Chemistry, Ghent University, Belgium

The current generation of organic photovoltaic devices still lacks the required efficiency to be economically competitive. One proposed way to improve the efficiency is the use of materials with a high dielectric constant [1], thereby decreasing the exciton binding energy and facilitating electron-hole separation. In this presentation, a computational scheme, based on quantum chemical calculations and molecular dynamics simulations, to determine the dielectric constants for different frequency regimes is presented. The different contributions to the dielectric constant will be considered, together with the applicability of the method. For various fullerene derivatives, the dielectric constant is calculated and the applicability of these materials in organic solar cells is discussed. The results also point towards directions for the design of new organic materials with a high dielectric constant.



*A multiscale approach combining Quantum Mechanics and Molecular Dynamics*

[1] L. J. A Koster, S. E. Shasheen, J. C. Hummelen, *Adv. Energy Mater.* **2**, 1246 (2012).

## Organic photovoltaics with $p$ - $f$ - $n$ junctions: Computational study of ferroelectric columnar molecular clusters

Andrzej L. Sobolewski

*Institute of Physics, Polish Academy of Sciences, Warsaw, Poland*

*Al. Lotnikow32/46, PL-02668, Warsaw, Poland*

In the field of photovoltaics, in which manufacturing cost is essential, organics that can be solution-processed at low temperatures offer great advantages as compared to their inorganic counterparts [1]. Although a tremendous progress in the OPV technology has been achieved over the years, organic photovoltaic devices still suffer from several losses or bottlenecks – a major one of them being recombination of photogenerated electron-hole pairs. Generally, an external bias voltage is required to efficiently separate the electrons and holes in organic material and thus prevent their recombination.

In this contribution results of ab initio theoretical explorations of photophysical properties of ferroelectric molecular stacks will be presented. It will be show that in such systems the photogenerated, due to absorbed light, electrons and holes are driven by the polarization-induced internal electric field in opposite directions toward the cathode and anode, respectively, and thus directly contribute to the photovoltaic output without a need for construction of the  $p$ - $n$  junction [2]. This provides an intriguing possibility to replace of the ‘intrinsic’ ( $i$ ) layer in a  $p$ - $i$ - $n$ -type heterojunction architecture for organic solar cells [3] by the ferroelectric layer ( $f$ ). As the term  $p$ - $i$ - $n$  means the PV device where the photo-active layer is sandwiched between two doped wide-gap layers; a  $p$ -doped layer and  $n$ -doped layer, the term  $p$ - $f$ - $n$  is proposed for this new junction.

[1] W. Cao and J. Xue, Energy Environ. Sci., 2014, 7, 2123.

[2] A. L. Sobolewski, Phys. Chem. Chem. Phys. 2015, 17, 20580.

[3] B. Maennig et al., Appl. Phys. A 2004, 79, 1.

## Accurate Ionization Potentials, Electron Affinities, and Photoelectron Spectra of Molecules from First Principles

T. Körzdörfer

*AG Computational Chemistry, University of Potsdam, Institute of Chemistry, Karl-Liebknecht Straße 24-25, D-14476 Potsdam-Golm*

The accurate and computationally efficient prediction of ionization potentials (IPs), electron affinities (EAs), and full photoelectron spectra of molecules from first principles has been a long-standing challenge for computational materials science. In particular in the fields of molecular electronics and photovoltaics, the energetics of charged excitations are key factors determining the functionality and efficiency of devices. Hence, the ability to gain meaningful physical insight and to derive design rules for novel materials from first-principles calculations hinges on their ability to predict IPs and EAs with sufficient accuracy at bearable computational costs.

To assess the performance of different DFT and *GW* methods in the prediction of IPs and EAs, we recently benchmarked their vertical IPs and EAs for a test set of 24 organic acceptor molecules against CCSD(T) calculations in the complete basis set limit.[1, 2, 3] To further allow for a direct comparison of the calculated vertical IPs and EAs with experimental data from gas-phase photoelectron spectroscopy, we also implemented a scheme to calculate the full temperature-dependent, vibrationally resolved spectra based on DFT frequencies and a Franck-Condon multimode analysis.[4]

Not surprisingly, our benchmark study finds that those DFT and *GW* methods that employ a non-empirical, system-specific tuning procedure for determining an optimal amount of Hartree-Fock exchange in the exchange-correlation functional yield the most accurate results for IPs, EAs, and fundamental gaps. The downside of these functionals, however, is that they are not size-consistent. The severe consequences of this lack of size-consistency are demonstrated for the example of polyene chains of different lengths, for which we studied how the bond-length alternation, the IP, and the band-gap evolve with oligomer size and how this is influenced by using various different system-specific, non-empirically tuned DFT and *GW* methods.[5, 6]

- [1] L. Gallandi et al., *J. Chem. Theory Comput.* **2016**, *12*, 605.
- [2] J. W. Knight et al., *J. Chem. Theory Comput.* **2016**, *12*, 615.
- [3] L. Gallandi and T. Körzdörfer, *in preparation*.
- [4] L. Gallandi and T. Körzdörfer, *J. Chem. Theory Comput.* **2015**, *11*, 5391.
- [5] J. Bois and T. Körzdörfer, *J. Chem. Theory Comput.* **2016**, *12*, 1872.
- [6] J. Bois and T. Körzdörfer, *under review at JCTC*, **arXiv: 1706.00196**.

## Dissipation and dephasing for molecules close to plasmonic nanoparticles: an ab initio approach.

Emanuele Coccia<sup>1</sup>, Stefano Corni<sup>1,2</sup>

<sup>1</sup>*CNR Institute of Nanoscience, Via Campi 213/A, 41125 Modena, Italy*

<sup>2</sup>*Dept. Chemical Sciences, University of Padova, Via Marzolo 1, 35131, Padova, Italy*

Quantum decoherence is a fascinating property of matter occurring when a given system interacts with an external environment [1]. The theory of open systems is successful in describing decoherence in terms of loss of information of the system, for instance, as dissipation and dephasing. Here, we have exploited a computational protocol based on the real-time propagation of the time-dependent electronic wave function, expanded in configuration-interaction eigenstates of the molecular target [2]. Computational results in Ref. [2] have shown the enhancement in the optical properties of a chromophore induced by plasmonic effects, due to the presence of a metal nanoparticle. The molecule is treated at full quantum level, and the electron dynamics is influenced by the mutual polarization between molecule and nanoparticle.

Dissipation and dephasing effects are introduced in the framework of the stochastic Schrödinger equation (SSE) [3], which is fully equivalent to the master equation approach for the reduced density matrix [4]. We have implemented three different interaction channels with the environment (i. e., beside the metal nanoparticle): relaxation to the ground state by means of spontaneous emission, nonradiative relaxation through internal conversion and pure dephasing of the wave function. The propagation of the SSE has then been performed by using a quantum jump algorithm [5].

We have applied this ab initio approach to the study of the evolution of the electronic and optical properties of a model chromophore (LiCN) close to a metal nanoparticle, under the influence of an electromagnetic field, as a function of the distance between the molecule and the nanoparticle [6]. Moreover, the interplay among the different channels has been investigated.

[1] M. Schlosshauer, *Rev. Mod. Phys.* **76**, 1267 (2005).

[2] S. Pipolo, S. Corni, *J. Phys. Chem. C* **120**, 28774 (2016).

[3] R. Biele, R. D'Agosta, *J. Phys.: Condens. Matter* **24**, 273201 (2012).

[4] J. Dalibard, Y. Castin, K. Mølmer, *Phys. Rev. Lett.* **68**, 580 (1992).

[5] K. Mølmer, Y. Castin, J. Dalibard, *J. Opt. Soc. Am. B* **10**, 524 (1993).

[6] E. Coccia, S. Corni, in preparation.

## Microhydration induces qualitative changes in the photochemistry of biomolecular building blocks

Rafał Szabla<sup>1</sup>, Mikołaj Janicki<sup>2</sup>, Robert W. Góra<sup>2,3</sup>

<sup>1</sup>*Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland*

<sup>2</sup>*Department of Physical and Quantum Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370, Wrocław, Poland*

<sup>3</sup>*E-mail: robert.gora@pwr.edu.pl*

In the past few years we have been studying ultrafast photodeactivation processes of hypothetical abiotic precursors of ribonucleotides [1, 2, 3]. Our results indicate that the photochemistry of these heteroaromatic species is significantly altered in water solution. It is evident that due to direct interactions of water molecules with a chromophore, new deactivation channels become available, which are not present in the gas phase. All these processes seem to have a common signature. After excitation to a bright state and initial relaxation, the system may enter a dark charge-transfer state, in which the electron is either ejected from the chromophore towards the solvent (in  $^1\pi\sigma^*$  state) or the reverse process occurs (in  $^1n\pi^*$  state). The redistribution of electronic density is followed by proton transfer processes (often multiple) which may lead to formation of conical intersections or intersystem crossings that qualitatively change the photochemistry and photophysics of hydrated chromophores.

For instance, the electron-driven proton transfer (EDPT) along water wires induces the formation of  $^1\pi\sigma^*/S_0$  state crossing and provides a very efficient deactivation process, whose quantum yield may reach up to 60%, according to our nonadiabatic *ab initio* molecular dynamics simulations of microhydrated imidazole (Fig. 1a). On the other hand our calculations indicate that the long-lived dark state observed experimentally in cytidine, may be a  $^1n_N\pi^*$  state characterized by water-to-chromophore electron transfer (WCET) [4]. This may lead to formation of protonated cytidine and the hydroxyl anion among the photoproducts, and subsequent photohydration, C to U conversion, or oxazolidinone formation reactions (Fig. 1b). These are just a few examples of the EDPT and WCET processes that will be discussed during the presentation.

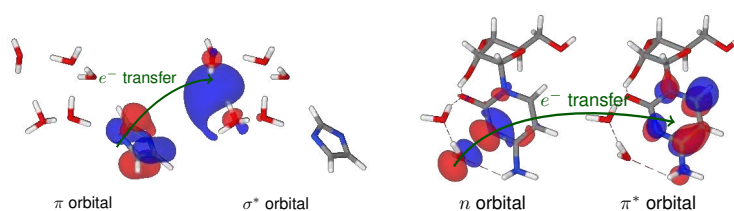


Figure 1: Electron-driven proton transfer in microhydrated imidazole (left) and water-to-chromophore electron transfer in the microhydrated 1-methylcytosine (right)

[1] R. Szabla, J. Šponer, R.W. Góra, *J. Phys. Chem. Lett.* **6**, 1467 (2015).

[2] R. Szabla, R.W. Góra, M. Janicki, J. Šponer, *Faraday Discuss* **195**, 237 (2016).

[3] J. Xu, et al. *Nat. Chem.* **9**, 303 (2017).

[4] M. Barbatti *J. Am. Chem. Soc.* **136**, 10246 (2014).



## Role of the environment in bioluminescence emission: QM/MM study

Isabelle Navizet<sup>1</sup>, Romain Berraud-Pache<sup>1</sup>, Cristina Garcia-Iriepe<sup>1</sup>

<sup>1</sup>Université Paris-Est, Laboratoire Modélisation et Simulation Multi Echelle, MSME UMR 8208 CNRS, 5 bd Descartes, 77454 Marne-la-Vallée, France

The emitting light in beetle and fireflies arises from the electronic relaxation of oxyluciferin, an organic compound resulting from the oxidation of the D-luciferin substrate inside an enzyme called luciferase. The protein environment plays a role in the colour modulation of the light emitted.

In order to theoretically study such systems [1,2], the use of quantum mechanical/molecular mechanical (QM/MM) methods is required. Accurate QM level is needed for dealing with electronic transition and charge transfer phenomena. Taking into account the surrounding protein at the MM level is essential in order to understand the colour modulation and influence of the enzyme. The presentation will discuss some of the results obtained on the bioluminescent system using the coupling of the programs MOLCAS (CASPT2/CASSCF) or G09 (DFT) and TINKER (AMBER force field).

Present results based on new resolved crystallographic structures of blue-shifted coloured and red-shifted coloured species were compared to the more conventional yellow-green emitted firefly systems. The prediction and rationalisation of the influence of the mutation of some residues inside the cavity of the light emitter will be explored with theoretical studies. I will also give last results on the influence of taking into account the water environment while comparing calculated results to the experimental studies of absorption and emission of the in-solution light emitter.

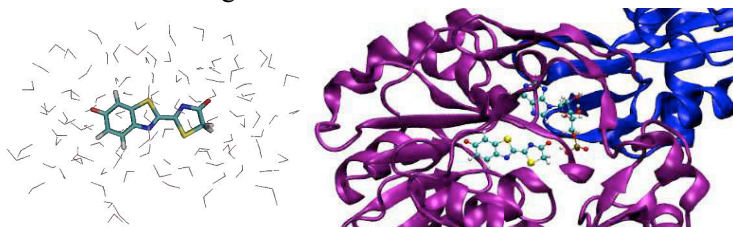


Fig: Oxyluciferin, the light emitter in different environment: water or luciferase protein

[1] Isabelle Navizet, Ya-Jun Liu, Nicolas Ferré, Hong-Yao Xiao, Wei-Hai Fang, Roland Lindh, Color-Tuning Mechanism of Firefly Investigated by Multi-Configurational Perturbation Method *J. Am. Chem. Soc.* **132**, 704-712 (2010).

[2] Romain Berraud-Pache and Isabelle Navizet, QM/MM calculations on a newly synthesised oxyluciferin substrate: new insights into the conformational effect, *PCCP*, **18**, 27460 – 27467 (2016).



## Investigation of optical probes for membrane phase recognition

**S. Osella, N. A. Murugan, N. K. Jena, S. Knippenberg**

*Division of Theoretical Chemistry and Biology, KTH Royal Institute of Technology,  
Stockholm, Sweden  
sknippen@kth.se*

Two sets of optically active probes for biological lipid bilayer tissues have been investigated as both Laurdan as well as azobenzene derivatives have been considered in a hybrid Quantum Mechanics-Molecular Mechanics approach. The differences in transition dipole moments between the probes in the various media are investigated and the influence of the media upon the probe's spectra in one photon absorption (OPA), two-photon absorption (TPA) and second harmonic generation (SHG) is discussed. It has also been shown that the applied theoretical approach enables novel simulations of fluorescence anisotropy decay experiments as well as fluorescence lifetime images.

For Laurdan and C-Laurdan, of which the latter is experimentally known to have a higher sensitivity to the membrane polarity at the lipid head-group region, a DOPC lipid bilayer at room temperature is considered. Throughout the simulations, a contrast in orientation for both probes has been found, which brings along differences in optical properties. The second harmonic generation (SHG) beta component is in this sense found to be twice as large for Laurdan with respect to C-Laurdan. The fluorescence anisotropy decay analysis confirms that Laurdan has more rotational freedom in the DOPC membrane, while C-Laurdan experiences a higher hindrance, making it a better probe for lipid membrane phase recognition [1].

Systems for which the change in properties of one component triggers the change in properties of the other are of utmost importance when 'on/off' states are needed. In an in silico study, a new derivative of the conformationally versatile azobenzene compound has therefore been considered [2]. Since the cis and trans conformers have different positions and orientations in the different lipid membranes (DOPC for the liquid disordered phase and DPPC for the gel phase), we found that the cis state is the 'on' state when the probe is inserted into the DOPC membrane, while it is in the 'off' state in the DPPC membrane. It has thus been seen that different environments will generate different responses on the same conformer of the probe.

[1] S. Osella, N. A. Murugan, N. K. Jena, S. Knippenberg, *J. Chem. Theory Comput.* **12**, 6169 (2016).

[2] S. Osella and S. Knippenberg, *J. Am. Chem. Soc.* **139**, 4418 (2017).

## Accurate treatment for ground and excited states of atoms and molecules in strong magnetic fields

Stella Stopkowicz<sup>1</sup>

<sup>1</sup>*Institut für Physikalische Chemie, Johannes Gutenberg-Universität Mainz,  
Duesbergweg 10-14, D-55128 Mainz, Germany*

For strong magnetic fields of around 1 atomic unit ( $1B_0 \approx 235000$  T), the magnetic and the Coulomb forces in an atom or molecule are equally important. Such extreme conditions exist for instance on some magnetic white dwarf stars. One may easily imagine that chemistry in these fields changes drastically. In fact, observational spectra from magnetic white dwarfs show a strong magnetic-field dependence, leading to a lot more complexity, i.e., different transition strengths, line-shifts, and splittings. For laboratory experiments, such magnetic fields strengths are completely out of reach such that theoretical predictions become crucial. Previous investigations using full configuration-interaction theory have already shown how different chemistry can be in strong magnetic fields. For instance, molecules may become bound by a bonding mechanism that has not been seen on Earth, the *perpendicular paramagnetic bonding*[1], which can stabilize molecules with a formal bond order of zero.

In order to retain the predictive capabilities and the high-accuracy in the wave function, but extending the applicability to systems with more than three electrons, an implementation of coupled-cluster (CC) theory for the treatment of atoms and molecules in strong magnetic fields has been presented[2]. Recently, the investigation of excited states in strong fields has also become possible via equation-of-motion (EOM) CC theory[3]. In EOM, excited open-shell states can be accessed without having to resort to a multireference treatment by starting from a well-behaved single-reference wave function. As such states, particularly high-spin states with high angular momenta, are stabilized in magnetic fields, the EOM-CC approach appears to be an ideal choice in this context. In this presentation, results for ground and excited states of atoms and molecules in strong magnetic fields are discussed that have been obtained at the CCSD(T) or EOM-CCSD level of theory[2, 3, 4]. In particular, the focus will be on the effect of the magnetic field on binding energies including cases with perpendicular paramagnetic bonding, total energies, the influence of electron correlation as well as the magnetic-field dependence of transition moments.

- [1] K. K. Lange, E. I. Tellgren, M. R. Hoffmann, and T. Helgaker, *Science* **337**, 327 (2012).
- [2] S. Stopkowicz, J. Gauss, K. K. Lange, E. I. Tellgren, and T. Helgaker, *J. Chem. Phys.* **143**, 074110 (2015).
- [3] F. Hampe and S. Stopkowicz, *J. Chem. Phys.* **146**, 154105 (2017)
- [4] S. Stopkowicz, *Int. J. Quantum Chem.*, DOI: 10.1002/qua.25391 (2017)

## Recent advances in theoretical spectroscopy from *ab initio* molecular dynamics

**Prof. Dr. Sandra Luber<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, University of Zurich, Winterthurerstrasse 190, Zurich, Switzerland*

Spectroscopy is extremely helpful for the analysis of materials. Besides experimental data, calculations provide important insight and allow the targeted study of specific structures, their dynamics and interactions.

We present innovative methods for the calculation of spectroscopic signatures based on density functional theory-based molecular dynamics with a focus on vibrational spectroscopy. Besides the study of solvation effects [1,2,3], efficient approaches for Infrared and Raman spectroscopy for condensed phase systems [4,5], relying e.g. on periodic subsystem density functional theory, have been presented. Other developments have dealt with Sum Frequency Generation and Raman Optical Activity spectroscopy [6,7]. This paves the way for the computationally efficient and accurate study of molecules on (semiconductor) surfaces/interfaces and in gas/liquid phase at ambient conditions with consideration of anharmonicity and realistic band shapes in the spectra. Among various investigated systems, chiral ionic liquids have recently been explored in detail [8].

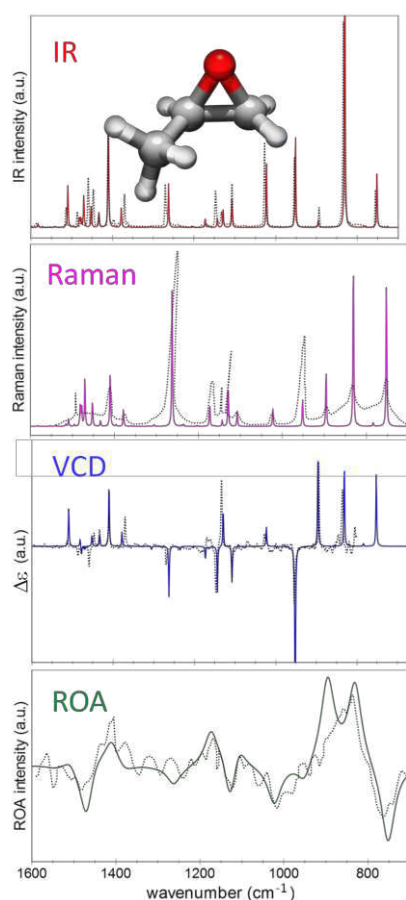
- [1] S. Luber, *J. Phys. Chem. A* **117**, 2760 (2013).
- [2] F. H. Hodel, S. Luber, *J. Chem. Theory Comput.* **113**, 947 (2017).
- [3] F. H. Hodel, P. Deglmann, S. Luber, *J. Chem. Theory Comput.* (2017), DOI:10.1021/acs.jctc.7b00214.
- [4] S. Luber, *J. Chem. Phys.* **141**, 234110 (2014).
- [5] S. Luber, M. Iannuzzi, J. Hutter, *J. Chem. Phys.* **141**, 094503 (2014).
- [6] S. Luber, *J. Phys. Chem. Lett.* **7**, 5183 (2016).
- [7] S. Luber, *J. Chem. Theory Comput.* **13**, 1254 (2017).
- [8] P. Oulevey, S. Luber, B. Varnholt, T. Bürgi, *Angew. Chem. Int. Ed.* **55**, 11787 (2016).

## Anharmonic Effects on Vibrational Spectra Intensities: Infrared, Raman, Vibrational Circular Dichroism, and Raman Optical Activity

Malgorzata Biczysko<sup>1</sup>, Julien Bloino<sup>2</sup>

<sup>1</sup>International Centre for Quantum and Molecular Structures, Shanghai University, 99 Shangda Road, Shanghai, China

<sup>2</sup>ICCOM-CNR, UOS Pisa, Italian National Research Council, Via G. Moruzzi 1, Pisa, Italy



An accurate comparison between simulated and experimental vibrational spectra requires going beyond the double-harmonic approximation, including anharmonic effects on vibrational energies, as well as on intensities. While the former are independent of the spectroscopy, the latter can only be done through property- and transition-specific developments, ideally taking into account the anharmonicity of both wave function and properties. This results in a proper account of the intensity of non-fundamental transitions and more accurate band-shapes. Recent developments on a comprehensive and robust generalized version of the second-order vibrational perturbation theory (GVPT2) for vibrational averages and transition properties have made possible the simulation of fully anharmonic infrared (IR), Raman spectra, as well as their chiral counterparts, namely vibrational circular dichroism (VCD) and Raman optical activity (ROA), for medium-to-large molecular systems [1-4]. We will show that a very good agreement between computed and experimental spectra, considering both band positions and their relative intensities, which define the overall spectral pattern, can be achieved, using methyloxirane as benchmark. We will also discuss on the extension of the approach toward larger and more complex molecular systems.

- [1] J. Bloino, A. Baiardi, M. Biczysko, *Int. J. Quant. Chem.* **116**, 1543 (2016)
- [2] J. Bloino, M. Biczysko, V. Barone, *J. Phys. Chem. A* **119**, 11862 (2015)
- [3] V. Barone, M. Biczysko, J. Bloino, *Phys. Chem. Chem. Phys.* **16**, 1759 (2014)
- [4] J. Bloino, V. Barone, *J. Chem. Phys.* **136**, 124108 (2012)

## Infrared absorption spectroscopy beyond the dipole approximation based on the multipolar Hamiltonian: Theory and application.

Takeshi Iwasa<sup>1,2</sup>, Masato Takenaka<sup>3</sup>, Tetsuya Taketsugu<sup>1, 2</sup>

<sup>1</sup>*Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Japan*

<sup>2</sup>*Elements Strategy Initiative for Catalysts and Batteries, Kyoto University, Kyoto, Japan*

<sup>2</sup>*Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo, Japan*

Recent advancements of vibrational spectroscopy combined with nano-optical techniques allow us to study molecular geometries, chemical reaction dynamics, or surface phonons at the scale down to the nanometer or even single molecule resolutions by adopting near field, i.e., a highly localized electromagnetic field around a metal tip or a small aperture. In these nano-spectroscopic measurements, molecules can interact with a nonuniform electric field because of the highly localized nature of near-field, requiring a theoretical method beyond the dipole approximation. One way to go beyond the dipole approximation is to consider a quadrupole interaction between molecule and near-field by considering the gradient of an electric field, especially in the study of surface enhanced Raman spectroscopy. It is not apparent, however, whether the interaction between a molecule and highly localized near-field can be described by first few terms of the multipole expansions. Also the spatial variation of electric fields depends on experimental setups, i.e., depends on the shape of a tip or aperture used. To study the near-field around nanostructures, researchers in computational nano-optics have developed a way to solve the Maxwell equation demonstrating that the field distribution is not unique at the nanometer scale.

Here we propose a theoretical method to account the full spatial variation of electric fields by using the multipolar Hamiltonian as our starting point [1]. The interaction between nonuniform electric fields and molecular vibrations is expressed as a vibrational normal-coordinate derivative of a spatial integral of the inner product of the total polarization of a molecule and an electric field so that the polarization is treated rigorously without invoking the conventional dipole approximation. The square of the derivative gives the infrared absorption intensity with an electric field with arbitrary shapes. The formulation is applied to small molecules. IR spectra with a model near field is clearly different from one obtained with uniform electric field (i.e., the dipole approximation). The peak intensities depend on the directions and intensity gradients of the applied electric field. As further applications, we compute an electric field around a metal nanoparticle by using computational electrodynamics techniques and use the computed near field to obtain IR spectra, giving excellent agreement with an experimental surface enhanced IR spectra. Our method thus allows us to combine computational electrodynamics and chemical calculations to study rapidly developing nano-spectroscopic measurements.

[1] T. Iwasa, M. Takenaka, and T. Taketsugu, J. Chem. Phys. 144, 124116 (2016).

## Toward the accurate simulation of vibrationally-resolved spectra for spin-forbidden transitions

Franco Egidi<sup>1</sup>, Alberto Baiardi<sup>1</sup>, Julien Bloino<sup>2</sup>, Marco Fusè<sup>1</sup>, Vincenzo Barone<sup>1</sup>

<sup>1</sup>*Scuola Normale Superiore, Piazza dei Cavalieri 7, Pisa, Italy*

<sup>2</sup>*Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti OrganoMetallici (ICCOM-CNR), UOS di Pisa, Via G. Moruzzi 1, 56124 Pisa, Italy*

Computational spectroscopy is nowadays routinely used as a predictive and interpretative tool to complement and support experimental results, provided the calculated results reach a sufficient level of accuracy. In this contribution, we present some of our recent developments for the simulation of vibrationally resolved electronic (vibronic) spectra for medium-to-large molecules, going beyond the simple Franck-Condon approximation.[1] In particular, we focus on transitions between states of different spin-multiplicity, which are forbidden under non-relativistic conditions.[2] The transition moments between such states cannot be obtained directly from most standard electronic structure calculations and a more accurate definition of the electronic Hamiltonian, including spin-orbit couplings, is needed.[3] Thanks to recent developments in non-collinear spin Density Functional Theory (DFT) [4, 6], scalar relativistic effects and spin-orbit couplings can be included within the electronic Hamiltonian variationally. Excited states and electronic transition energies and property moments can then be evaluated using two-component Time-Dependent DFT (2c-TDDFT).[5, 6] Furthermore, it is possible to go beyond the Franck-Condon approximation and obtain more accurate band-shapes by numerically differentiating the transition property moments, which are responsible for Herzberg-Teller effects. As an illustration of those aspects, the vibronic spectra of transition metal complexes can be simulated to study their photophysical properties as phosphorescent systems. The research leading to some of these results has been performed in the framework of the ERC Advanced Grant Project DREAMS “Development of a Research Environment for Advanced Modelling of Soft Matter”, GA No. 320951.

- [1] J. Bloino, A. Baiardi, M. Biczysko, *Int. J. Quantum Chem.* **116**, 1543 (2016).
- [2] G. Baryshnikov, B. Minaev, Hans Ågren, *Chem. Rev.* **117**, 6500 (2017).
- [3] T. Saue, *ChemPhysChem* **12**, 3077 (2011).
- [4] G. Scalmani, M. J. Frisch, *J. Chem. Theory Comput.* **8**, 2193 (2012).
- [5] F. Egidi, J. J. Goings, M. J. Frisch, X. Li, *J. Chem. Theory Comput.* **12**, 3711 (2016).
- [6] F. Egidi, S. Sun, J. J. Goings, G. Scalmani, M. J. Frisch, X. Li, *J. Chem. Theory Comput.* **Article ASAP**, (2017).

## Nuclear correlation effects in X-ray spectroscopy from a time-domain perspective

**Sven Karsten<sup>1</sup>, Sergey I. Bokarev<sup>1</sup>, Sergei D. Ivanov<sup>1</sup>, Oliver Kühn<sup>1</sup>**

<sup>1</sup>*Institute of Physics, Rostock University, Albert Einstein Str. 23-24, 18059 Rostock, Germany*

To date X-ray spectroscopy has become a routine tool that can reveal highly local and element specific information on the electronic structure of atoms in complex environments. Despite working on energy scales that are much larger than those corresponding to nuclear motions, taking nuclear dynamics and the associated nuclear correlations into account is shown to be of importance for X-ray spectroscopy in certain physical situations [1]. Here, we develop a rigorous time-correlation method employing ground state molecular dynamics simulations [1, 2]. The importance of nuclear correlation phenomena is demonstrated by comparison against the results from the conventional sampling approach for gas phase and bulk water. In contrast to the first-order absorption, second-order resonant inelastic scattering spectra exhibit pronounced fingerprints of nuclear motions. The developed methodology is not biased to a particular electronic structure method and, owing to its generality, can be applied to, e.g., X-ray photo-electron and Auger spectroscopies. General strategies for possible improvements to the method will be discussed and current results will be presented.

- [1] S. Karsten, S. D. Ivanov,\* S. G. Aziz, S. I. Bokarev,\* O. Kühn, *J. Phys. Chem. Lett.*, **8**, 992 (2017)
- [2] S. Karsten, S. I. Bokarev,\* S. G. Aziz, S. D. Ivanov,\* O. Kühn, arXiv:1611.05025 [physics.chem-phys] *Accepted in J. Chem. Phys.*, DOI:10.1063/1.4984930

## DFT calculations of NMR parameters of framework and extra-framework atoms in silicon-rich zeolites.

Stepan Sklenak<sup>1</sup>, Jiri Dedeczek<sup>1</sup>

<sup>1</sup>*J. Heyrovsky Institute of Physical Chemistry, The Czech Academy of Sciences,*

*Dolejskova 3, 182 23 Prague, Czech Republic*

Zeolites are crystalline microporous aluminosilicates that are important sorbents and catalysts. The determination of the positions of framework atoms and extra-framework cations is essential for the evaluation of the catalytic and sorption properties of silicon-rich zeolites. Multinuclear solid state NMR spectroscopy in tandem with periodic DFT calculations of the structure including extensive molecular dynamics conformational sampling of the siting of the cationic species and subsequent DFT cluster computations of the multinuclear NMR shielding values are shown to be a viable route to obtain the siting of framework atoms and extra-framework monovalent cations in silicon-rich zeolites. Periodic DFT calculations including extensive molecular dynamics conformational sampling of all possible Li<sup>+</sup>, Na<sup>+</sup>, and Cs<sup>+</sup> sites were performed employing the cp2k (Li and Na) and VASP (Cs) programs. The <sup>27</sup>Al, <sup>7</sup>Li, and <sup>23</sup>Na NMR shielding values were evaluated utilizing the Gaussian program and five or seven coordination shell clusters.[1-5] The <sup>133</sup>Cs NMR shielding for the Cs-zeolites was calculated using the relativistic Dirac-Kohn-Sham approach employing the ReSpect program.[6] Based on the comparison of our experimental MAS NMR results with the calculated ones, we reveal the siting of framework Al atoms and Li<sup>+</sup>, [7] Na<sup>+</sup>, and Cs<sup>+</sup> cations in silicon-rich zeolites.

[1] S. Sklenak, J. Dedeczek, C.B. Li, B. Wichterlova, V. Gabova, M. Sierka, J. Sauer, *Angew. Chem., Int. Ed.*, **46**, 7286 (2007).

[2] J. Dedeczek, S. Sklenak, C.B. Li, F. Gao, J. Brus, Q.J. Zhu, T. Tatsumi, *J. Phys. Chem. C*, **113**, 14454 (2009).

[3] S. Sklenak, J. Dedeczek, C.B. Li, B. Wichterlova, V. Gabova, M. Sierka, J. Sauer, *Phys. Chem. Chem. Phys.*, **11**, 1237 (2009).

[4] J. Dedeczek, M.J. Lucero, C.B. Li, F. Gao, P. Klein, M. Urbanova, Z. Tvaruzkova, P. Sazama, S. Sklenak, *J. Phys. Chem. C*, **115**, 11056 (2011).

[5] J. Brus, L. Kobera, W. Schoefberger, M. Urbanova, P. Klein, P. Sazama, E. Tabor, S. Sklenak, A.V. Fishchuk, J. Dedeczek, *Angew. Chem., Int. Ed.*, **54**, 541 (2015).

[6] S. Komorovsky, M. Repisky, K. Ruud, O.L. Malkina, V.G. Malkin, *J. Phys. Chem. A*, **117**, 14209 (2013).

[7] P. Klein, J. Dedeczek, H.M. Thomas, S.R. Whittleton, V. Pashkova, J. Brus, L. Kobera, S. Sklenak, *Chem. Commun.*, **51**, 8962 (2015).



## Elastic behavior of White Micas solid solutions as a function of the pressure

**A. Hernández Laguna<sup>1</sup>, C. I. Sainz-Díaz,<sup>1</sup> N. Hernández-Haro<sup>2</sup>, J. Ortega-Castro<sup>2</sup>, I. Vidal-Daza<sup>3</sup>, A. Sánchez-Navas<sup>3</sup>, C. Pérez del Valle<sup>4</sup>, D. Muñoz-Santiburcio<sup>5</sup>, and M. Mookherjee<sup>6</sup>**

<sup>1</sup>*Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Avda. Fuentenueva 4, 18100 Armilla, Granada, Spain*

<sup>2</sup>*Departament de Química, Universitat de les Illes Balears, Palma de Mallorca, Spain*

<sup>3</sup>*Faculty of Sciences, University of Granada, Granada, Spain.*

<sup>4</sup>*Département de Chimie Moléculaire, Université Grenoble Alpes, France*

<sup>5</sup>*Lehrstuhl für Theoretische Chemie, Ruh-Universität Bochum, 44780 Bochum, Germany*

<sup>6</sup>*Department of Earth, Ocean and Atmospheric Sciences, Florida State University, Tallahassee, FL, USA*

Phyllosilicates are found in igneous, metamorphic and sedimentary rocks in the Earth's crust and mantle. By subduction processes, these minerals help in bearing important amount of water in the Earth's interior. Muscovite (Ms) is the crossing point of two solid solutions (SS): one with Paragonite (Pg) and the other one with Phlogopite (Phl). In the first SS,  $\text{Na}^+$  and  $\text{K}^+$  are changing in the interlayer space; and in the second one, two  $\text{Al}^{3+}$  are changing with three  $\text{Mg}^{2+}$  in the octahedral sheet. These minerals are considered to be petrogenetic and Geobaro-thermo-meter indicators. So, the elastic behavior as a function of pressure (P) is an important issue to know.

Both SS can be described by the following ideal formula  $\text{K}_{1-x}\text{Na}_x\text{Al}_{2-y}\text{Mg}_{y+y*0.5}(\text{Si}_{4-z}\text{Al}_z)\text{O}_{10}(\text{OH})_2$ , when  $y = 0$ ,  $0 \leq x \leq 1$  and  $z \approx 1$  is the SS of Ms-Pg and when  $x = 0$ ,  $0 \leq y \leq 2$  and  $z \approx 1$  is the SS of Ms-Phl. Our calculations have been performed in the  $2M_1$  polytype. In this work, a DFT study of the crystal structure, polyhedral, atomic volume, elastic constants ( $C_{ij}$ ) and gap of solubility of the two SS as a function of the P is accomplished with the Siesta program. The Ms-Pg SS has been performed to 6 GPa, and the Ms-Phl to 9 GPa.

The  $c$  axis is compressed five time more than  $a$  and  $b$  axes. EoS' have been calculated. For the Ms, atomic compressibilities have been also calculated, finding  $\text{K}^+$  and O show the largest compressibility in the interlayer space. From the excess free energy due to volume, the gap of solubility of the Ms-Pg SS increases as a function of the P, and decreases in the Ms-Phl SS. In Ms-Pg SS,  $C_{ij}$  increases as a function of the P, showing different functional behavior; two regions of compression have been found out: at low P (to 1 GPa) and from 1 to 6 GPa. Different formulae  $C_{ij}=f(P)$  have been calculated in the different regions.

## Mixed valency and local hybrid functionals

Martin Kaupp<sup>1,\*</sup>, Simon Gückel<sup>1</sup>, Amir Karton<sup>2</sup>, Paul J. Low<sup>2</sup>

<sup>1</sup>*Technische Universität Berlin, Institut für Chemie, Theoretische Chemie, Sekr. C 7,  
Strasse des 17. Juni 135, D-10623 Berlin, Germany,*

<sup>2</sup>*School of Molecular Sciences, University of Western Australia, 35 Stirling Highway,  
Crawley, Perth 6009, Australia, \* email: martin.kaupp@tu-berlin.de*

The reliable prediction of mixed-valent (MV) systems close to the borderline between partially localized (class II of the Robin/Day description) and fully delocalized (class III) is a challenge for quantum-chemical methods, due to the need to accurately reproduce exchange and dynamical or non-dynamical correlation, and the often crucial role of environment (solvent, solid....) [1]. Using a pragmatic protocol [1] based on a custom-made global hybrid functional and suitable solvent models, we have been able to demonstrate the crucial role of conformation for electronic coupling and spectroscopy in organometallic MV systems [2,3], up to a break-down of the Robin-Day scheme due to a continuum of localized and delocalized conformations [3]. Application of the protocol to further systems, such as class II di-iron organometallics, has required an extension of our toolbox, as spin contamination and other limitations of the global-hybrid based scheme have been found. Here use of recent local hybrid functionals [4] with position-dependent exact-exchange admixture has been instrumental, in particular their recent TDDFT implementation in Turbomole [5]. Local hybrids allow to reproduce the inter-valence charge-transfer bands correctly, where global hybrids fail. Using a recent implementation of local hybrid gradients [6], similar functionals turn out to perform excellently for structure and energetics of gas-phase MV benchmark systems [7], where we may compare to virtually exact coupled-cluster data.

[1] M. Parthey, M. Kaupp, *Chem. Soc. Rev.* **43**, 5067 (2014).

[2] J. B. G. Gluyas, S. Gückel, M. Kaupp, P. J. Low, *Chem. Eur. J.* **22**, 16138 (2016); M. Parthey, J. B. G. Gluyas, P. A. Schauer, D. S. Yufit, J. A. K. Howard, M. Kaupp, P. J. Low, *Chem. Eur. J.* **30**, 9780 (2013).

[3] M. Parthey, J. B. G. Gluyas, M. A. Fox, P. J. Low, M. Kaupp, *Chem. Eur. J.* **20**, 6895 (2014).

[4] A. V. Arbuznikov, M. Kaupp, *J. Chem. Phys.* **136**, 014111 (2012).

[5] T. M. Maier, H. Bahmann, M. Kaupp, *J. Chem. Theor. Comput.* **11**, 4226 (2015); T. M. Maier, H. Bahmann, A. V. Arbuznikov, M. Kaupp, *J. Chem. Phys.* **144**, 074106 (2016).

[6] S. Klawohn, H. Bahmann, M. Kaupp, *J. Chem. Theor. Comput.* **12**, 4254 (2016).

[7] M. Kaupp, A. Karton, F. Bischoff, *J. Chem. Theor. Comput.* **12**, 3796 (2016).

## Double-hybrid density functionals: is there anything new to tell?

Lars Goerigk<sup>1</sup>

<sup>1</sup>*School of Chemistry, The University of Melbourne, Parkville, Victoria 3010, Australia*

Over the past years, we have seen tremendous improvements in the development of quantum-chemical procedures and we now have access to methods that allow the accurate treatment of systems with even hundreds of atoms. However, the large number of available methods also makes it hard for the computational-chemistry user to understand their benefits or potential risks. As a consequence, one can therefore observe the trend to stick to a few familiar — albeit sometimes older — levels of theory, such as the B3LYP or M06-2X density functional theory (DFT) approximations. Meanwhile, the DFT-developer community has acknowledged so-called double-hybrid density functionals (DHDFs) as established methods for treating electronic ground-state properties. Combined with London-dispersion corrections, DHDFs can even be considered as the currently most accurate DFT approximations for (main-group) thermochemistry, kinetics, noncovalent interactions, geometries, and frequencies; for a review, see Ref. [1].

In this presentation, I will first give a brief overview of the current state of double-hybrid DFT for electronic ground states, before I will discuss recent studies that explored strategies to further modify the current approximations [2,3].

Most researchers in the DFT community are probably unfamiliar with earlier work that has shown DHDFs to be accurate candidates for the calculation of excitation energies [1]. In the second part of my presentation, I will therefore review these previous findings, before I will outline our recent, successful efforts to expand relatively recent ground-state DHDFs within the time-dependent DFT framework [4].

[1] L. Goerigk, S. Grimme, *WIREs: Comput. Mol. Sci.* **4**, 576 (2014).

[2] B. Chan, L. Goerigk, L. Radom, *J. Comput. Chem.* **37**, 183 (2016).

[3] A. Najibi, L. Goerigk, *manuscript in preparation for J. Comput. Chem.*

[4] T. Schwabe, L. Goerigk, *manuscript submitted to J. Chem. Theory Comput.*

## Exchange-Correlation Potentials and Energy Densities in Spherically Confined Atoms

Sergei F. Vyboishchikov<sup>1</sup>

<sup>1</sup>*Institut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona, Carrer M. Aurèlia Capmany, 69, 17003 Girona, Spain*

One of the promising ways of developing density functionals lies in creating a simple physical system, in which accurate correlated electron densities are easily available and in which the amount of electron correlation can be tuned by varying a well-defined external parameter. To this end, we are using free atoms confined in a spherical cavity of a given radius  $R_c$  [1, 2]. The cavity radius  $R_c$  strongly influences the total atomic energy, the electron density, the exchange energy and density, and in some case the correlation energy and thus can be employed as the tuning parameter.

First, local exchange potentials corresponding to the Hartree–Fock electron density have been obtained using the Zhao–Morrison–Parr method [3] for a number of confined atoms. The exchange potentials obtained and the resulting density were compared to those given by the Becke–Johnson (BJ) model potential [4]. It is demonstrated that introducing a scaling factor to the BJ potential allows improving the quality of the resulting density. The optimum scaling factor increases with decreasing confinement radius [5].

We also studied correlation energies, correlated electron densities, and exchange-correlation potentials obtained from Configuration Interaction (CI) and DFT calculations in confined atoms. The variation of the correlation energy with  $R_c$  is relatively small for the He,  $\text{Be}^{2+}$ , and Ne systems. However, in the neutral Be atom the CI correlation energy increases markedly with decreasing  $R_c$ . This makes beryllium a very convenient system for developing and tuning correlation functionals [6].

Finally, we calculated pure correlation energy densities  $E_c^{\text{CI}}(r)$  from the CI wavefunction. To this end, we developed a method for obtaining  $E_c^{\text{CI}}(r)$  directly from CI coefficients, making use of Nesbet's theorem. Subsequently, the parameters of a model density functional  $E_c^{\text{M}}(\rho)$  were adjusted by the least-squares to reproduce  $E_c^{\text{CI}}(r)$ . The parameters depend on  $R_c$ , and this dependence was incorporated in  $E_c^{\text{M}}(\rho)$ . This strategy paves the way for a direct construction of local density functional from the correlated electron density.

- [1] E. V. Ludeña, *J. Chem. Phys.* **69**, 1770 (1978)
- [2] E. V. Ludeña, M. Gregori, *J. Chem. Phys.* **71**, 2235 (1979)
- [3] Q. Zhao, R. C. Morrison, R. G. Parr, *Phys. Rev. A*, **50**, 2138–2142 (1994)
- [4] A. D. Becke, E. R. Johnson, *J. Chem. Phys.*, **124**, 221101 (2006)
- [5] S. F. Vyboishchikov, *J. Comp. Chem.*, **36**, 2037–2043 (2015)
- [6] S. F. Vyboishchikov, *J. Comp. Chem.*, **37**, 2677–2686 (2016)

# Linked-cluster formulation of screened electron-hole interaction from explicitly-correlated geminal functions without using unoccupied states

Michael G. Bayne<sup>1</sup>, Ari Chakraborty<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Syracuse University, Syracuse, New York 13244, USA*

The electron-hole or quasiparticle representation plays a central role in describing electronic excitations in many-electron systems. For charge-neutral excitation, the electron-hole interaction kernel is the quantity of interest for calculating important excitation properties such as optical gap, optical spectra, electron-hole recombination and electron-hole binding energies. Accurate determination of the electron-hole interaction kernel remains a significant challenge for precise calculations of optical properties in the GW+BSE formalism. The inclusion of unoccupied states has long been recognized as the leading computational bottleneck that limits the application of this approach for large finite systems. In this work, we present an alternative derivation in real-space representation that avoids using unoccupied states to construct the electron-hole interaction kernel. The central idea of our approach is to treat electron-electron correlation for both ground and excited state wave functions using a two-body correlator operator which is local in real-space representation. We demonstrate using diagrammatic techniques that the frequency-dependent electron-hole kernel can be expressed in terms of connected closed-loop diagrams. We show that the cancelation of disconnected diagrams is a consequence of the linked-cluster theorem in real-space representation and the resulting renormalized operators are equivalent to infinite-order summations of particle-hole diagrams. The derived electron-hole interaction kernel was used to calculate excitation energies in atoms, molecules, clusters and quantum dots and the results for these systems were compared with CIS, TDHF, TDDFT, EOM-CCSD, and GW+BSE calculations.

- [1] Variational solution of the congruently transformed Hamiltonian for many-electron systems using a full-configuration-interaction calculation, J. M. Elward, J. Hoja, and A. Chakraborty, *Phys. Rev. A*, **86**, 062504 (2012).
- [2] Infinite-order diagrammatic summation approach to the explicitly correlated congruent transformed Hamiltonian, M. G. Bayne, J. Drogo, and A. Chakraborty, *Phys. Rev. A*, **89**, 032515 (2014).
- [3] Construction of R12 geminal-projected particle-hole creation operators for many-electron systems using diagrammatic factorization approach, M. G. Bayne, Y. Uchida, J. Eller, C. Daniels, and A. Chakraborty, *Phys. Rev. A*, **94**, 052504 (2016).
- [4] Derivation of time-dependent transition probability for 2e–2h generation from 1e–1h state in the presence of external electromagnetic field, M. G. Bayne and A. Chakraborty, *arXiv:1704.02428* (2017)

## Local Spins

**István Mayer**

*Research Centre for Natural Sciences, Hungarian Academy of Sciences,  
Magyar tudósok körútja 2, Budapest, Hungary*

It is known that for singlet systems the spin density vanishes everywhere. Nonetheless, there are systems (*e.g.*, antiferromagnets, singlet diradicals) for which the physics indicates that the overall singlet state is resulting from singlet coupling of non-vanishing *local spins*. In order to study these local spins on the wave function level, one has to decompose the expectation value  $\langle \hat{S}^2 \rangle$  of the total spin-square operator  $\hat{S}^2$ . But  $\langle \hat{S}^2 \rangle$  is a single number, for its meaningful decomposition additional conditions should be considered.

A long quest resulted in a set of requirements that permit to decompose  $\langle \hat{S}^2 \rangle$  in a unique and physically relevant manner. In the lecture these requirements will be described and the derivation of the resulting formulas for single determinant and correlated wave functions will be discussed, along with some numerical examples and some further aspects of the formalism.

## Spin-Orbit Coupling Effects of Open-Shell Systems with Coupled-Cluster Theory

Zhanli Cao<sup>1</sup>, Zhifan Wang<sup>1</sup> and Fan Wang<sup>1</sup>

<sup>1</sup>*Institute of Atomic and Molecular Physics, Sichuan University, No. 24 South Section,  
Yihuan Road, Chengdu, P. R. China*

A coupled-cluster approach has been implemented at the CCSD and CCSD(T) levels to account for spin-orbit coupling (SOC) effects of closed-shell systems[1], where SOC is included in post self-consistent field (SCF) treatment. This SOC-CC approach is quite efficient due to the use of real spin-orbitals particularly for molecules with low symmetry. It has been shown to be able to describe SOC effects of even superheavy-element molecules with high accuracy using relativistic effective core potentials, since single excitation amplitudes can account for orbital relaxation effectively. To deal with open-shell systems, the equation-of-motion (EOM) approaches based on the SOC-CCSD method for ionized[2], electron-attached[3], and double ionized states[4] with a closed-shell reference have been developed.

EOM-CCSD for double electron attachment based on this SOC-CC approach with closed-shell reference will be reported. Rather accurate SOC splitting is achieved with this approach. Furthermore, this SOC-CC is extended to spatially non-degenerate open-shell systems in this work[5]. The unrestricted Hartree-Fock determinant corresponding to the scalar relativistic Hamiltonian is employed as the reference. Due to broken of time-reversal symmetry and spatial symmetry, this open-shell SOC-CC approach is rather expensive compared with the closed-shell SOC-CC approach. The open-shell SOC-CC approach is applied to some open-shell atoms and diatomic molecules with  $s^1$ ,  $p^3$ ,  $\sigma^1$ , or  $\pi^2$  configuration. Our results indicate that reliable results can be achieved with the open-shell SOC-CCSD(T) approach for these systems.

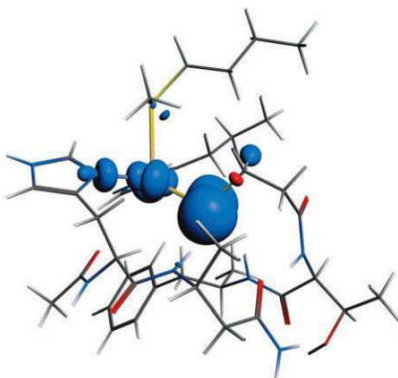
- [1] Z. Y. Tu, D. D. Yang, F. Wang, and J. Guo, *J. Chem. Phys.* **135**, 034115 (2011).
- [2] Z. Y. Tu, F. Wang, and X. Y. Li, *J. Chem. Phys.* **136**, 174102 (2012).
- [3] D. D. Yang, F. Wang, and J. W. Guo, *Chem. Phys. Lett.* **531**, 236 (2012).
- [4] Z. F. Wang, S. Hu, F. Wang, and J. W. Guo, *J. Chem. Phys.* **142**, 144109 (2015).
- [5] Z. Cao, F. Wang and M. Yang, *J. Chem. Phys.* **146**, 134108 (2017).

## Can Spin-State Energetics of Transition Metal Complexes be Accurate at Single Reference Level?

Mikael P. Johansson

*Department of Chemistry, University of Helsinki, P.O. Box 55, FI-00014 Helsinki, Finland*

The molecular spin state has a potentially crucial effect on the chemical properties of transition metal complexes. Thus, the difficulty in accurately predicting even the ground-state configuration, not to mention quantitative spin-state energy differences, is one of the great challenges faced by computational quantum chemistry [1, 2]. With the exception of a few density functional approaches [3], accurate quantum chemical methods for describing spin have long been restricted to relatively small systems [4], due to the many facets of electron correlation having to be properly described in order to obtain reliable results. Recently, the domain based local pair natural orbital coupled cluster theory with single-, double-, and perturbative triple excitations, DLPNO-CCSD(T), by Neese and co-workers [5] was augmented with the ability to treat open-shell systems. The set of open-shell complexes treatable at the CCSD(T) level of theory has thus grown immensely. However, is single-reference CCSD(T) accurate enough?



- [1] M. Radoń, K. Gąssowska, J. Szklarzewicz, E. Broclawik, *J. Chem. Theory Comput.* **12**, 1592 (2016).
- [2] K. Pierloot, Q. M. Phung, A. Domingo, *J. Chem. Theory Comput.* **13**, 537 (2017).
- [3] M. Swart, M. Solà, F. M. Bickelhaupt, *J. Chem. Phys.* **131**, 094103 (2009).
- [4] M. P. Johansson, D. Sundholm, *J. Chem. Phys.* **120**, 3229 (2004).
- [5] C. Riplinger, P. Pinski, U. Becker, E. F. Valeev, F. Neese, *J. Chem. Phys.* **144**, 024109 (2016).



## Specific Ion Interactions with Biomolecules: Molecular Dynamics Simulations and Energy Decomposition Analysis

Ran Friedman<sup>1\*</sup>, Emma Ahlstrand<sup>1</sup>, Kersti Hermansson<sup>2</sup>

<sup>1</sup>Computational Chemistry and Biochemistry Group, Department of Chemistry and Biomedical Sciences, Linnaeus University, 391 82 Kalmar, Sweden

<sup>2</sup>Ångström Laboratory, Department of Chemistry, Uppsala University, Lägerhyddsvägen 1, 751 21 Uppsala, Sweden

\*Presenting author, WATOC life member

Specific effects of ions depend not only on the charge of the ions but also on their other properties (such as size, polarisability and structure of hydrated complexes). The effects of salts on protein precipitation were studied by Hofmeister already at the 19th century, and led to the development of the famous Hofmeister series. Computer simulations have been very useful in the study of specific ion effects. The development of force-field parameters for simulations of ions was very instrumental in this respect. A realistic representation of interactions between ions and solutes in water, however, remains a challenge, because of the need to account for ion-solute, ion-water and solute-water interactions at the same time and with the same set of parameters. Here, we will discuss our recent applications of computer simulations to study the interactions between alkali cations and tetraether membranes or bovine serum albumin. Using computer simulations, we could develop a model to explain how certain microorganisms are able to withstand solutions with strikingly low concentrations of sodium and potassium [1]. We could also show that, unlike other proteins, bovine serum albumin does not have a clear preference to sodium over potassium [2]. Finally, using QM-based energy decomposition analysis we have found that the binding of  $\text{Li}^+$  (and to a smaller extent also that of  $\text{Na}^+$  and  $\text{K}^+$ ) to protein ligands is not purely electrostatic, and involves an unnegligible contribution from polarisation. The consequences of this to computer simulations will be discussed. Finally, we will also discuss the potential to simulate proteins together with  $\text{Zn}^{2+}$  [3], which is a very common protein cofactor.

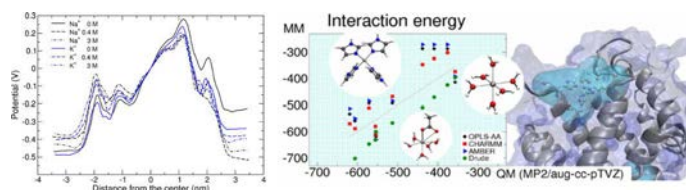


Figure 1: **Specific ion interactions - examples of effects and challenges.** Specific ion interactions can modify the potential of membranes (left) and proteins in a concentration-dependent manner. Forcefield accuracy remains an issue when it comes to a correct quantitative description of such interactions (right).

- [1] Pineda De Castro, L., Dopson, M., and Friedman, R., *J. Phys. Chem. B*, **120**, 10628–10634 (2016)
- [2] Beconi, O., Ahlstrand, E., Salis, A., and Friedman, R. *Isr. J. Chem.*, **In Press** (2017)
- [3] Ahlstrand, E. and Hermansson, K. and Friedman, R. *J. Phys. Chem. A*, **In Press** (2017)

## Computational Insights into Sulphur Isotopic Fractionation in Carbonate-Associated Sulphate

**Mark A. Iron**

*Computational Chemistry Unit, Department of Chemical Research Support,  
Weizmann Institute of Science, Rehovot, Israel*

Sulphate incorporated into calcium carbonate minerals, or carbonate-associated sulphate (CAS), is a promising proxy for the sulphur isotope composition of seawater sulfate over Earth's history. However, the isotopic fractionation of sulphur between dissolved sulphate and CAS has not yet been systematically investigated, neither experimentally nor theoretically. In a set of carbonate precipitation experiments at variable sulphate concentration we find an intriguing dependence of sulphur isotope fractionation on the sulphate-carbonate ratios in solution (and the concentration of CAS). As sulphate is incorporated into the carbonate lattice at concentrations of hundreds to thousands of ppm, it is conceivable that it affects the energetics of the crystal lattice sufficiently to influence the equilibrium sulphur isotope fractionation.

Isotopic fractionation ( $\alpha$ ) can be calculated using the vibrational frequencies ( $\omega_i$ ) of each species:

$$\alpha = \beta_{CAS} / \beta_{solution}$$

$$\beta = \frac{Q_H}{Q_L} = \prod_{i=1}^{3N-6} \frac{u_{H_i}}{u_{L_i}} \cdot \frac{\exp\left(-\frac{u_{H_i}}{2}\right)}{\exp\left(-\frac{u_{L_i}}{2}\right)} \cdot \frac{1 - \exp(-u_{L_i})}{1 - \exp(-u_{H_i})}$$

where  $N$  is the number of atoms,  $Q$  is the partition function, H and L denote the heavy and light isotopes, respectively, and  $u_i = \frac{h \cdot c \cdot \omega_i}{k_B \cdot T}$ . [1]

We investigated this possibility by density functional theory and considered various factors affecting the calculations. We will present the dependence of sulphur isotopic fractionation between dissolved sulphate and CAS on the concentration of sulphate in the carbonate lattice. We will also evaluate CAS as a proxy for seawater sulphate isotopic composition.

[1] (a) H. C. Urey, *J. Chem. Soc.* 562-581 (1947). (b) M. Méheut, M. Lazzeri, E. Balan, F. Mauri, *Geochim. Cosmochim. Acta* **71**, 3170-3181 (2007). (c) S. D. Domagal-Goldman, J. D. Kubicki, *Geochim. Cosmochim. Acta* **72**, 5201-5216 (2007). (d) J. R. Rustad, P. Zarzycki, *Proc. Nat. Acad. Sci. USA* **105**, 10297-10301 (2008).

## Tailoring Resonance Assisted Hydrogen Bonds

**Gerard Pareras,<sup>1</sup> Marcin Palusiak,<sup>2</sup> Miquel Solà,<sup>1</sup> Miquel Duran,<sup>1</sup> and Sílvia Simon<sup>1</sup>**

<sup>1</sup> *Institut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona, C/ Maria Aurèlia Capmany 6, 17003 Girona, Catalonia, Spain*

<sup>2</sup> *Department of Theoretical and Structural Chemistry, Faculty of Chemistry, University of Łódź, Pomorska 163/165, 90-236 Łódź, Poland*

Intramolecular Resonance Assisted Hydrogen Bond (RAHB) brings extra-stabilization to a molecule due to the creation of a *quasi*-ring, which can resemble a benzene ring. In a recent review<sup>1</sup> it was highlighted the involvement of RAHB as a driving force in the synthesis of organic, coordination and organometallic compounds. The extra-stabilization of the *quasi*-ring depends on different factors, being the availability of  $\pi$  electron within the new *quasi*-ring one of the more important ones. Thus, when RAHB is linked to one or more benzene rings (sharing a CC bond) the *ipso*-ring aromaticity influences the RAHB distance: the lower the aromaticity of benzene ring the shorter the HB distances, so stabilizing the system.<sup>2-3</sup>

In this work we will discuss two different ways of designing RAHB with different HB distances; (a) substituents effect<sup>4</sup> and (b) topology and number of benzene rings in the structure. For the first case, we study all possible mono- and di-substitutions in the 3 and 4 position of o-hydroxybenzaldehyde considering three electron donating groups (EDG: NH<sub>2</sub>, OH, and F) and three electron withdrawing groups (EWG: NO<sub>2</sub>, NO, and CN). We show that it is possible to tune the HB bond distance in the RAHB by locating different substituents in given positions of the aromatic ring. A second way of tailoring the HB distance is adding benzene rings using different topologies, that is, linear and kinked chains. Following Clar's aromatic  $\pi$  rules, polycyclic aromatic hydrocarbons (PAH) have quite different aromaticity if they are in a linear or a kinked topology,<sup>5</sup> so presenting more or less available  $\pi$  electron for sharing with a *quasi*-ring. In that case, not only the influence if the topology is taken into account, but also the number of benzene rings added.

- [1] Mahmudov, K. T.; Pombeiro, A. J. L., *Chemistry – A European Journal* **2016**, 22 (46), 16356-16398.
- [2] Palusiak, M.; Simon, S.; Sola, M., *J. Org. Chem.* **2009**, 74 (5), 2059-2066.
- [3] Palusiak, M.; Simon, S.; Sola, M., *J. Org. Chem.* **2006**, 71 (14), 5241-5248.
- [4] Pareras, G.; Palusiak, M., Solà, M.; Duran, M.; Simon, S. *Org. Chem. Front. Submitted*
- [5] Solà, M., *Frontiers in Chemistry* **2013**, 1, 2

## Effect of Biradical Character of Organic Molecules on Opto Electronic Properties

Ulrike Salzner

*Department of Chemistry, Bilkent University, Ankara, Turkey*

Most organic molecules and polymers used in organic electronics have closed-shell singlet ground states. Certain donor-acceptor systems, however, are open-shell singlet biradicals.[1] Presence of biradicals leads to close packing in crystals as intramolecular and intermolecular electron coupling compete with each other. As a result conductivity along stacking directions is particularly strong for crystals of biradicals.[2] Another important characteristic of biradicals is that they are prone to intramolecular singlet fission.[3] Singlet fission is a process during which the absorption of one photon leads to formation of two triplet states.[4] Intermolecular singlet fission was first observed in tetracene crystals[5] but in donor-acceptor systems[3] intramolecular singlet fission[6] has been demonstrated. Although direct formation of triplet states from singlet ground states is spin forbidden, quantum yields can reach almost 200%. In this presentation the effect of open-shell character of building blocks for organic electronics will be explored based on time-dependent density functional theory calculations.

- [1] a) M. Karikomi, C. Kitamura, S. Tanaka, Y. Yamashita, *J. Am. Chem. Soc.* **1995**, *117*, 6791-6792;  
b) U. Salzner, O. Karalti, S. Durdagi, *J. Mol. Model.* **2006**, *12*, 687-701.
- [2] J. D. Yuen, M. Wang, J. Fan, D. Sheberla, M. Kemei, N. Banerji, M. Scarongella, S. Valouch, T. Pho, R. Kumar, E. C. Chesnut, M. Bendikov, F. Wudl, *Journal of Polymer Science Part A: Polymer Chemistry* **2015**, *53*, 287-293.
- [3] E. Busby, J. Xia, Q. Wu, J. Z. Low, R. Song, J. R. Miller, X. Y. Zhu, L. M. Campos, M. Y. Sfeir, *Nat. Mater.* **2015**, *14*, 426-433.
- [4] M. B. Smith, J. Michl, *Chemical Reviews* **2010**, *110*, 6891-6936.
- [5] W. M. Moller, M. Pope, *The Journal of Chemical Physics* **1973**, *59*, 2760-2761.
- [6] E. G. Fuemmeler, S. N. Sanders, A. B. Pun, E. Kumarasamy, T. Zeng, K. Miyata, M. L. Steigerwald, X. Y. Zhu, M. Y. Sfeir, L. M. Campos, N. Ananth, *ACS Central Science* **2016**, *2*, 316-324.

## Computationally Driven Design of Efficient Photosensitizer for Dye-sensitized Solar Cell Applications

Hong-Xing Zhang<sup>1</sup>

<sup>1</sup> *Institute of Theoretical Chemistry, Jilin University, Changchun, China*

**Abstract:** In this talk, I will present some of our recent works on development of high-efficiency sensitizers for dye-sensitized solar cell application, which is a hot topic for solar energy conversion and utilization. The performance of dyes is very relevant to its atomistic details. Using density functional theory/time-dependent density functional theory calculations and semiempirical quantum dynamics simulations in conjugation with extended Huckel theory, our results showed that replacement of ancillary ligands of Ru(II) complexes dye with square-planar quadridentate ligands can efficiently extend the light-harvesting region to longer wavelength range, the interface electron transfer rate is improved due to the enhanced donor-acceptor coupling. Our results also demonstrated that the performance of dyes can be regulated via the controlled charged states. The addition of anionic ancillary ligands in cyclometalated Ru(II) complexes can efficiently improve the electron-donating ability, raise the occupied orbitals energy levels, enlarge the light-harvesting ability, increase the electron donor-acceptor coupling, and finally promote the interface charge separation. We also examined the role of anchoring group for DSSC applications. The hydroxamate anchoring group might be an alternative to the existing carboxylic acid anchors. This theoretical study explores the new configurations and design strategies of dyes for efficient light harvesting device.

[1] T.F. Lu, W. Li, et al, *Phys. Chem. Chem. Phys.* 18, 29591 (2016)

[2] W. Li, F.Q. Bai, et al., *J. Power Sources* 275, 207 (2015)

[3] W. Li, L. G. C. Rego, et al., *J. Phys. Chem. Lett.* 5, 3992 (2014)

[4] W. Li, J. Wang, et al., *Phys. Chem. Chem. Phys.* 16, 9458 (2014)

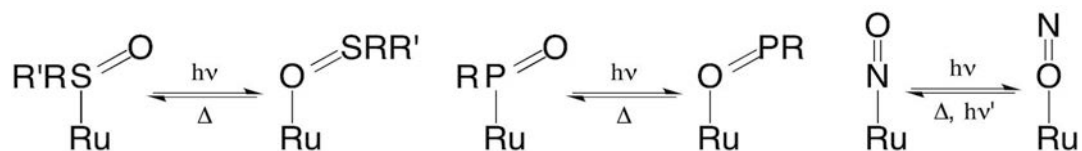
## Computational Studies of the Photoswitching Mechanisms in Photochromic Ruthenium Complexes

F. Talotta<sup>1,2</sup>, F. Alary<sup>1</sup>, I. M. Dixon<sup>1</sup>, J.-L. Heully<sup>1</sup>, L. González<sup>2</sup>, M. Boggio-Pasqua<sup>1</sup>

<sup>1</sup> *Laboratoire de Chimie et Physique Quantiques, UMR 5626, IRSAMC, CNRS et Université Toulouse 3, 118 route de Narbonne, 31062 Toulouse, France*

<sup>2</sup> *Institut für Theoretische Chemie, Universität Wien, Währinger Str. 17, 1090 Vienna, Austria*

Photochromism represents an increasing area of research in photochemistry because of its actual and potential applications in nanosciences, biology, and photonic or optoelectronic devices. The vast majority of light-activated molecular switches displaying photochromic properties rely on organic compounds (e.g., diarylethenes, spiropyrans, fulgides...). However, transition metal complexes have also been designed to display photochromic properties. These systems are often based on linkage isomerizations between the metal center and various ambidentate ligands such as nitrosyl (NO), sulfoxide (RR'SO) and sulfur dioxide (SO<sub>2</sub>). While all these photochromic systems have been scrutinized from an experimental point of view, sometimes completed by theoretical studies, the underlying photoswitching mechanisms are far from being fully understood. Computational photochemistry is an essential tool in order to rationalize the photochemical behavior of such compounds. Many computational studies have been reported for organic photochromic compounds but analogous studies of photochromic metal complexes are few. In this presentation, we report some of our recent theoretical results on the linkage photoisomerization mechanisms in photochromic ruthenium complexes Ru-RR'SO,<sup>[1,2]</sup> Ru-RPO,<sup>[3]</sup> and Ru-NO<sup>[4]</sup> (see figure below) using density functional theory and multiconfigurational second-order perturbation theory. In particular, we will show that both adiabatic and nonadiabatic mechanisms are expected to compete, but also that triplet states of different natures can be involved along the photoisomerization pathways.



[1] A. J. Göttle et al., *J. Am. Chem. Soc.* **133**, 9172 (2011).

[2] A. J. Göttle et al., *Inorg. Chem.* **53**, 6752 (2014).

[3] O. P. J. Vieuxmaire et al., *J. Phys. Chem. A* **117**, 12812 (2013).

[4] J. Sanz García et al., *Inorg. Chem.* **54**, 8310 (2015).

## Photosensitizing properties of functionalized thiolate-protected gold nanoclusters: insights from theory.

Aurélie Perrier<sup>1,2</sup>

<sup>1</sup>Université Paris Diderot, Sorbonne Paris Cité, 75205 Paris, France

<sup>2</sup>Institut de Recherche de Chimie de Paris, Chimie Paris Tech, PSL Research University, 11 rue Pierre et Marie Curie, 75005 Paris, France

In the course of developing electro- or photoactive devices, the integration of molecular systems with the unique opto-electronic properties of gold nanoparticles (NPs) has attracted a growing attention. The challenge consists in controlling and understanding the interactions between the NPs and the molecules to design new functional materials presenting emerging properties. Recent works have considered the opportunity of using thiolate-protected gold nanoclusters (GNC)  $\text{Au}_x(\text{SR})_y$  where R is an organic ligand. In that vein, GNCs functionalized with glutathione groups have recently been incorporated as photosensitizers in photovoltaic cells, "Metal-Cluster-Sensitized Solar Cells" (MCSSCs), and in photoelectrochemical cells for water splitting [1]. Consequently, there is today a great challenge to understand the electronic properties of these hybrid organic- inorganic systems and the possible electron and/or energy transfer between a photoactive ligand and the GNC.

Within this framework, theoretical tools constitute a powerful complement to design more efficient hybrid architectures. An accurate computational strategy for studying the structural, redox and optical properties of thiolated GNCs using (Time-Dependent) Density Functional Theory [TD-DFT] will be presented. These three properties are of fundamental importance for both "photosensitizer" devices and optoelectronic applications. We will expose how it is possible to (i) to describe with a comparable precision both the GNC and the ligands' properties, (ii) rationalize the effects of the coating on the GNC properties and (iii) analyze the photoinduced energy/charge transfer between the GNC and the ligands [2-4]. Finally, for larger gold NP functionalized with photoactive ligands, we will analyse the interaction between the NP plasmon and the excitation of the molecule with the help of a Quantum Mechanics (QM) /Electrodynamics (ED) computational scheme. [5]

- [1] Y.-S. Chen, H. Choi, P. V. Kamat, *J. Am. Chem. Soc.* **135**, 8822 (2013) ; Y.-S. Chen, P. V. Kamat, *J. Am. Chem. Soc.* **136**, 6075 (2014).
- [2] A. Fihey, F. Maurel, A. Perrier *J. Phys. Chem. C* **118**, 4444 (2014).
- [3] A. Fihey, F. Maurel, A. Perrier *Phys. Chem. Chem. Phys.* **16**, 26240 (2014).
- [4] C. Azarias, C. Adamo, A. Perrier *Phys. Chem. Chem. Phys.* **18**, 7737 (2016).
- [5] A. Fihey, F. Maurel, A. Perrier *J. Phys. Chem. C* **119**, 9995 (2015).

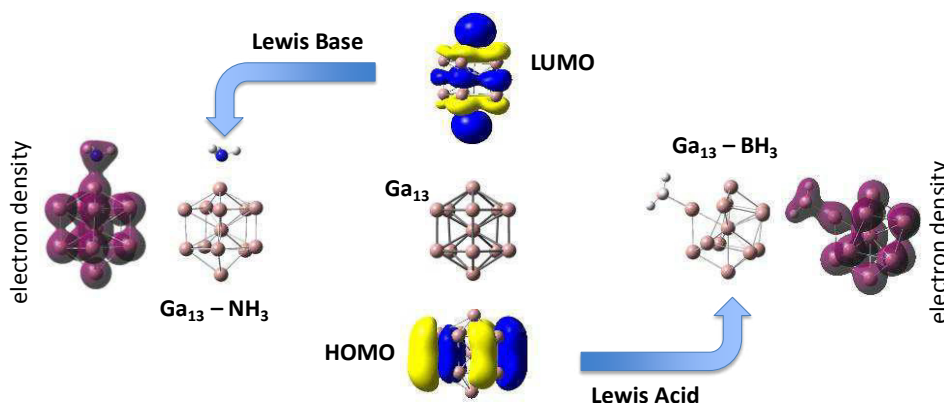


## Modifying the Reactivity of Gallium Nanoclusters with Ligands

David J. Henry

*Chemical and Metallurgical Engineering and Chemistry, Murdoch University, Western Australia 6150, Australia*

Doped gallium clusters ( $\text{Ga}_{12}\text{X}$ ,  $\text{X} = \text{B}, \text{C}, \text{N}, \text{Al}, \text{Si}, \text{P}, \text{Ga}, \text{Ge}, \text{and As}$ ) exhibit interesting electronic and structural variations as a function of the dopant [1-4]. To fully realise the potential of these nano-clusters for catalysis it is necessary to explore in detail the interaction of these species with a range of small molecules. This research uses *ab initio* and Density Functional Theory methods to determine the reactivity of novel gallium-based clusters with small molecules and identifies the structures and stabilities of cluster-molecule complexes. Adsorption of hydrogen, [5] Lewis acids and Lewis bases is found to be energetically favourable but there is significant isomerization with respect to the adsorption site. Consequently, adsorption energies vary not only with valence electronic configuration but also with the adsorption site. Regioselectivity of these interactions is analyzed in terms of cluster bonding and orbital interactions. The cluster-hydrogen interaction is strongly governed by the location and shapes of the frontier orbitals.



Ligand coordination modifies the electronic structure of the cluster, leading to an enhancement of reactivity. In particular,  $\text{NH}_3$  coordination was found to lower the energy barrier for  $\text{H}_2$  chemisorption by 10% and  $\text{BH}_3$  coordination led to reduction of the barrier by 20%. These results demonstrate the potential for ligand coordination as a means of accelerating reactions on cluster surfaces.

- [1] L. Guo, *Comput. Mater. Sci.* **45**, 951 (2009).
- [2] H. Wang, Y. J. Ko, K. H. Bowen, et al., *J. Phys. Chem. A* **114**, 11070 (2010).
- [3] D.J. Henry, *J. Phys. Chem. C*, **116**, 24814 (2012).
- [4] D.J. Henry, K. Ichikawa, H. Nozaki, A. Tachibana, *Comput. Mater. Sci.* **115**, 145 (2016).
- [5] D.J. Henry, *J. Phys. Chem. C*, **117**, 26269 (2013).



## Hydrolysis of (germano)silicates: a new low-barrier mechanism from biased ab initio molecular dynamics.

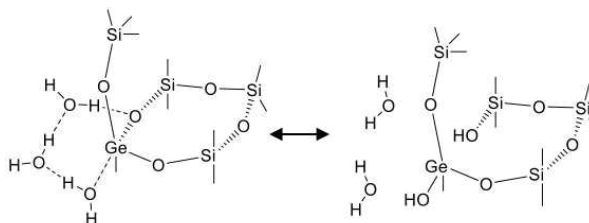
Lukáš Grajciar, Pengbo Lyu, Miroslav Položij and Petr Nachtigall

<sup>1</sup>*Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Hlavova 2030, Prague 2, 12800, Czechia*

The silicates, based on a tetrahedron-shaped anionic  $\text{SiO}_4^{4-}$  group, is one of the most abundant classes of compounds on Earth being heavily used in industry. However, the silicates, and in particular silicates doped with aluminum or germanium, are often being degraded and eventually destroyed upon prolonged exposure to humidity. On the contrary, a well-directed hydrolysis can be beneficial leading to synthesis of new materials such as hierarchical layered silicates with micro- and meso-porosity [1].

Therefore, with a goal to hinder or direct the silicate hydrolysis, numerous first principle studies have focused on understanding the hydrolysis mechanism. However, they were limited to static calculations not properly accounting for both the water dynamics in a fully solvated material and temperature effects [2]. In this study, we employed a (biased) ab initio molecular dynamics to accurately incorporate temperature effects and most importantly to allow for explicit treatment of water molecules in interaction with a (germano)silicate.

A new hydrolysis path has been found, which includes proton-transfer through a chain of surrounding water molecules (see Figure). This new mechanism has two- to three-times smaller reaction barrier ( $\sim 50\text{--}90 \text{ kJ}\cdot\text{mol}^{-1}$ ) than the most stable mechanism proposed previously using limited solvation model [2] and should be thus a preferred mechanism if water is in abundance. In addition, the new mechanism can help explain the possibility of directed hydrolysis for some silicates; the lowest barriers ( $\sim 50 \text{ kJ mol}^{-1}$ ) are found for well accessible exposed  $\text{SiO}_4^{4-}/\text{GeO}_4^{4-}$  tetrahedra whereas markedly larger barriers ( $\sim 90 \text{ kJ mol}^{-1}$ ) were calculated for less exposed silicate surfaces. Although, the current study considered a specific (germano)silicate, the UTL zeolite, we expect the new mechanism to be of importance for other (germano)silicates as well.



[1] W. J. Roth, P. Nachtigall, R. E. Morris, J. Čejka, *Chem. Rev.* **114**, 4807 (2014).

[2] S. Malola, S. Svelle, F. Bleken, O. Swang, *Angew. Chem. Int. Ed.* **51**, 652 (2012).

## Aromaticity from the point of view of the Vorticity of the Current Density Tensor.

José E. Barquera-Lozada<sup>1</sup>

<sup>1</sup>*Chemistry Institute, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán, C.P. 04510, CdMx, Mexico.*

The induced current density vector field ( $\mathbf{j}(\mathbf{r})$ ) has been extensively used for the study of aromaticity [1–4]. However, it has the disadvantage that the direction of the magnetic vector must be choose a priori without the information about the direction of the most important currents. This does not represent a drawback for plane molecules because the main currents are parallel to the molecular plane and the magnetic vector must be perpendicular to it, but, for non-planar aromatic systems, such as polyhedral boranes and fullerenes, the main currents are not in a single plane. Therefore, the analysis of  $\mathbf{j}(\mathbf{r})$  is cumbersome. The anisotropy of the current induced density (ACID) has overcome this problem by compressing the information of the induced current density tensor ( $\mathbf{J}(\mathbf{r})$ ) in a scalar quantity [5,6]. However, it cannot differentiate between anti/aromatic compounds by itself. The vorticity of the induced current density ( $\nabla \times \mathbf{j}(\mathbf{r})$ ) compress the information of  $\mathbf{j}(\mathbf{r})$  in mainly one direction [4]. Here, we analyze the topology of the trace of the vorticity of  $\mathbf{J}(\mathbf{r})$  ( $\text{tr}(\nabla \times \mathbf{J}(\mathbf{r}))$ ). This scalar field do not need an arbitrary magnetic vector to be define and because of that it can be used to study 3D aromaticity. Its analysis shows that the topology of an aromatic and antiaromatic molecules are significantly different. It also can distinguish the most aromatic rings in polyaromatic compounds. Since  $\text{tr}(\nabla \times \mathbf{J}(\mathbf{r}))$  is a scalar, its analysis is significantly easier than for  $\mathbf{j}(\mathbf{r})$  and contrary to ACID scalar field, it can differentiate anti/aromatic systems by itself.

[1] Fliegl, H.; Sundholm, D.; Taubert, S.; Jusélius, J.; Klopper, W. *J. Phys. Chem. A* **2009**, *113* (30), 8668.

[2] Lazzeretti, P. *Phys. Chem. Chem. Phys.* **2016**.

[3] Sundholm, D.; Fliegl, H.; Berger, R. J. F. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2016**, n/a.

[4] Keith, T. A.; Bader, R. F. W. *J. Chem. Phys.* **1993**, *99* (5), 3669.

[5] Geuenich, D.; Hess, K.; Köhler, F.; Herges, R. *Chem. Rev.* **2005**, *105* (10), 3758.

[6] Fliegl, H.; Jusélius, J.; Sundholm, D. *J. Phys. Chem. A* **2016**, *120* (28), 5658.

## Cesium cation- $\pi$ interactions: DFT and QTAIM studies

**Fabio Pichierri**

*Department of Applied Chemistry, Graduate School of Engineering, Tohoku University,  
Sendai 980-8579, Japan*

In a recent analysis of the Cambridge Structural Database (CSD) we have identified several crystal structures of cesium complexes which are stabilized by multiple  $\text{Cs}^+$ - $\pi$  interactions [1]. We have therefore decided to investigate a selected number of such complexes so as to unravel the nature of the  $\text{Cs}^+$ - $\pi$  interaction with the aid of both density functional theory (DFT) and Bader's quantum theory of atoms in molecules (QTAIM). These combined DFT and QTAIM studies are useful in the design of macrocyclic receptors and chemosensors [2,3] with high selectivity toward radiocesium ( $\text{Cs-137}$ ). This radionuclide represents an environmental hazard ( $t_{1/2}$ ~30 years) which results from nuclear power plant accidents as well as from the use of radioactive materials.

Acknowledgments. The present research is supported by the Japan Society for the Promotion of Science (JSPS) "Grants-in-Aid for Scientific Research" and by the Graduate School of Engineering of Tohoku University.

- [1] F. Pichierri, *J. Radioanal. Nucl. Chem.* **311**, 1251 (2017).
- [2] F. Pichierri, *Theor. Chem. Accts.* **135**, 1 (2016).
- [3] F. Pichierri, *Dalton. Trans.* **42**, 6083 (2013).

## Hypervalency and reactivity from Wannier orbitals

András Stirling<sup>1</sup>

<sup>1</sup>*Institute of Organic Chemistry, Research Centre for Natural Sciences, Budapest, Hungary*

Compounds said to be hypervalent are very useful reactants in organic chemical syntheses where their remarkable reactivity is tacitly associated with their hypervalency. Hypervalent iodonium compounds are prototypes of these main-group compounds. In this presentation I focus on the hypervalency and reactivity of iodonium compounds.

QMMM simulations of selected iodonium compounds in solvent DCM have been done. Electron structure analysis of the trajectories has been performed to discern the valency of iodonium. Maximally localized Wannier orbitals have been generated and their spatial extensions and the distribution of their centers have been scrutinized. Wannier description provides a chemically meaningful picture that is particularly useful for describing bonding situations because it follows a strict definition of valence with 2 electrons, connecting in this way the traditional MO and Lewis pictures. The analysis reveals that the iodonium is not hypervalent in these compounds. The reactivity of these compounds can then be ascribed to the strong unquenched charge separation present in these molecules which represents a compromise between Coulomb interaction and the resistance of iodonium toward hypervalency.

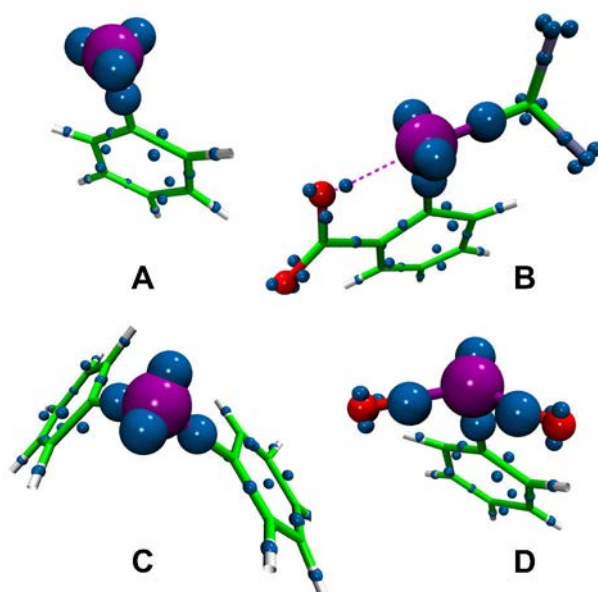


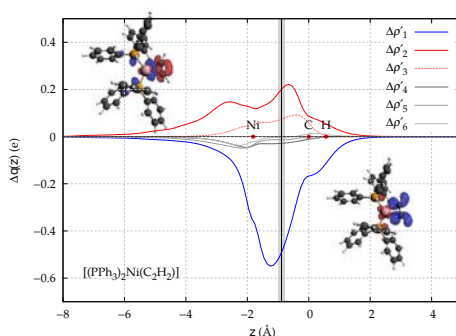
Figure 1: Typical structures taken from QMMM trajectories with the centers of the maximally localized Wannier functions. Centers in close vicinity of iodine are highlighted.

## Charge-displacement analysis: a simple tool to reveal charge transfer effects throughout the whole periodic table (from Helium to Oganesson).

Leonardo Belpassi<sup>1</sup>

<sup>1</sup>*Institute of Molecular Science and Technologies (CNR-ISTM), c/o Department of Chemistry, Biology and Biotechnology, University of Perugia, Italy*

Charge-displacement (CD) analysis was introduced almost ten years ago in order to characterize the chemical bond between noble-gas (Xe) and a noble metal (Au) in Xe-AuF [1]. It is a simple yet powerful tool to reveal and quantify the charge transfer component of the interaction in chemical regimes, from gas phase water's van der Waals complexes, electronic excited states to the super-heavy elements chemical characterization. The method is based on a partial progressive integration of the electron density changes that accompanies intermolecular interactions. Recently, charge-displacement analysis has been employed to analyze on quantitative grounds the Dewar-Chatt-Duncanson components of transition metal coordination complexes [2]. The CD method provides clear-cut measures of donation and back-donation charges that show a stringent correlation with selected experimental observables [3, 4]. The method has been extended to the relativistic four-component Dirac formulation and some preliminary results of this new implementation will be presented.



- [1] L. Belpassi, I. Infante, F. Tarantelli, L. Visscher, *J. Am. Chem. Soc.* **2008**, *130*, 1048–1060.
- [2] G. Bistoni, S. Rampino, F. Tarantelli, L. Belpassi, *J. Chem. Phys.* **2015**, *142*, 084112.
- [3] G. Bistoni, L. Belpassi, F. Tarantelli, *Angew. Chem. Int. Ed.* **2013**, *52*, 11599–11602.
- [4] G. Bistoni, S. Rampino, N. Scafuri, G. Ciancaleoni, D. Zuccaccia, L. Belpassi, F. Tarantelli, *Chem. Sci.* **2016**, *7*, 1174–1184.

**The nature of the chemical bond in Be containing molecules:****Apostolos KALEMOS**

*Department of Chemistry,  
National and Kapodistrian University of Athens,  
Athens 15771, HELLAS*

The present study focuses on the  $\text{Be}_2^+$ ,  $\text{Be}_2$ ,  $\text{Be}_2^-$ ,  $\text{Be}_3$  [1] and  $\text{BeO}^{0,-}$ ,  $\text{BeOBe}^{+,0,-}$  [2] species with the aim to unveil their bonding pattern. The ground states of the above molecules are examined mainly through single and multi reference correlation methods. Previous work is scrutinized with an eye to the instability problems inherent in various Hartree–Fock schemes. Under this point of view, we rationalize previous findings and put them in a unified context of what and why should be done in similar hard to crack cases. In all these species excited and/or ionized atomic states participate in a resonant way making chemically possible molecules that have been termed hypervalent and explains also the “incompatible” geometrical structure of some species.

[1] A. Kalemios, *J. Chem. Phys.* **145**, 214302 (2016).

[2] A. Kalemios, *J. Chem. Phys.* **146**, 104307 (2017).

## Theoretical Investigation of a strong cis-effect in an imidazole-imidazolium substituted alkene

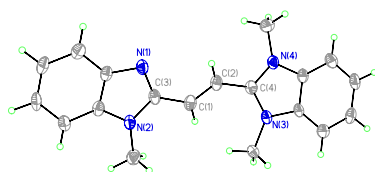
**David J. Wilson<sup>1</sup>, Jason L Dutton<sup>1</sup>, Evan J. Bieske<sup>2</sup>, Conor F. Hogan<sup>1</sup>**

<sup>1</sup>*La Trobe Institute for Molecular Science, La Trobe University, Melbourne, Australia*

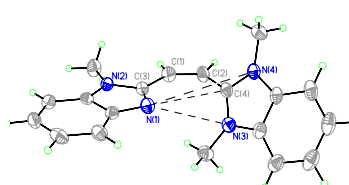
<sup>2</sup>*School of Chemistry, University of Melbourne, Australia*

We report the first example of an alkene with two carbon-bound substituents (imidazole and imidazolium rings) where the Z-isomer has a greater thermodynamic stability than the E-isomer that persists in both the gas phase and in solution [1]. Theoretical calculations, solution fluorescence spectroscopy and gas-phase ion mobility mass spectrometry studies confirm the preference for the Z-isomer, the stability of which is traced to a non-covalent interaction between the imidazole lone pair and the imidazolium ring.

Theoretical calculations up to DLPNO-CCSD(T) are required, including solvent effects, to correctly identify the preference for the Z-isomer. A combination of MO, NBO, QTAIM and I-SAPT analyses provide an underlying rationale for the preference for the Z-isomer, which arises from non-covalent (electrostatic) interactions between the N lone pair of the benzimidazole cation and the central C of the benzimidazolium, and an increased localization of the central C=C double bond in the Z-isomer for the cation.



E-isomer



Z-isomer (most stable)

[1] D. C. Georgiou, M. A. Haghighatbin, C. F. Hogan, M. S. Scholz, J. N. Bull, E. J. Bieske, D. J. D. Wilson, J. L. Dutton, *Angew. Chemie Int. Ed.*, 2017, DOI 10.1002/anie.201702287.

## Fragment Attributed Molecular System Energy Change (FAMSEC) in the study of interactions and molecular stability.

**Ignacy Cukrowski<sup>1</sup>, Daniel M. E. van Niekerk<sup>1</sup>, Jurgens H. de Lange<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, University of Pretoria, Lynnwood Rd, Pretoria, South Africa*

FAMSEC [1] performs a dedicated energy partitioning of a molecular system without breaking existing bonds. By making use of IQA/IQF concepts, it allows monitoring energy of molecular fragments as well as their contribution to molecular energy on a structural change from an initial to a final state of a molecule (or molecular system). Consequently, most (i) (de)stabilized fragments and (ii) (de)stabilizing a molecule fragments in the final molecular state can be identified and their energetic contributions computed. Furthermore, the origin, on a fundamental level, of the energy contributions can be explored.

Usefulness of FAMSEC will be briefly demonstrated in identifying the origin of (i) increased energy of *cis*-2-butene [2] and *in-in* Xylene conformers (with the CH--HC contact) relative to respective equilibrium structures and (ii) relative stability of amino-acid  $\beta$ -alanine conformers: the lowest energy one with the red-shifted O-H $\cdots$ N and the higher energy conformer with the blue-shifted N-H $\cdots$ O intramolecular hydrogen bond [3]. Importance of using 4-atom fragments in exploring intramolecular interactions (bonds) and their contribution to molecular energy will be explained.

It is commonly accepted that reliability of the IQA data depends on how well molecular energy is recovered by use of IQA-defined energy terms. It will be shown that this is indeed the case in the direct evaluation of IQA data except HF and B3LYP for which  $E(\text{IQA}) = E$  but large errors in the computed self-atomic and diatomic interaction energies are present. For post-HF levels (*e.g.*, MP2) and when a comparative approach is used, such as in FAMSEC, a new criterion is proposed to assess quality of IQA data for comparative analyses,  $\Delta E(\text{IQA}) \approx \Delta E$ , where  $\Delta E(\text{IQA})$  and  $\Delta E$  stand for IQA and electronic energy differences, respectively, between a final and initial-state of a molecular system. The closer  $\Delta E(\text{IQA})$  approaches  $\Delta E$  the closer FAMSEC data approaches values obtained at the CCSD/BBC1 level, regardless of the level of theory/approximation combination used [4].

- [1] I. Cukrowski, *Comp. Theory Chem.* 1066, 62 (2015).
- [2] I. Cukrowski, F. Sagan, M. P. Mitoraj, *J. Comp. Chem.* **37**, 2783 (2016).
- [3] I. Cukrowski, D. M. E. van Niekerk, Jurgens H. de Lange, *Struct. Chem.* (2017), DOI: 10.1007/s11224-017-0956-5.
- [4] I. Cukrowski, P. M. Polestshuk, *Phys. Chem. Chem. Phys.* (2017), DOI: 10.1039/C7CP02216F.



## Efficiently modeling the electronic circular dichroism of amino and nucleic acids ensembles

Hugo Gattuso<sup>1</sup>, Marco Marazzi<sup>1</sup>, Cristina García-Iriepa<sup>2</sup>, Angelo Spinello<sup>3</sup>, Xavier Assfeld<sup>1</sup>, Giampaolo Barone<sup>4</sup> and Antonio Monari<sup>1</sup>

<sup>1</sup> *Université de Lorraine, Nancy, Theory-Modeling-Simulation, SRSMC, Boulevard des Aiguillettes 54506, Vandoeuvre-les-Nancy, France*

<sup>2</sup> *Laboratoire de Modélisation et Simulation Multi Echelle, 5, Boulevard Descartes 77454, Marne-la-Vallée, France*

<sup>3</sup> *CNR-IOM-Democritos National Simulation Center, Trieste, Italy*

<sup>4</sup> *Università di Palermo, Dipartimento di Scienze Biologiche, Chimiche e Farmaceutiche, Viale delle Scienze, Palermo, Italy*

Modeling spectroscopic signals (absorption and circular dichroism) of biomacromolecular systems such as DNA and proteins, is far from being straightforward since it requires the computation of excited states for a relatively high number of atoms and coupled chromophores. So far, only few methodologies have been developed to model nucleic/amino acids ECD spectra and the systems that have been already efficiently tackled are B-DNA [1,2,3], G-quadruplexes [2,4] and peptides [5]. Moreover these methodologies are either computationally costly [2] or lack environmental effects [1]. In our case, we developed a protocol based on the coupling between the Frenkel exciton theory and a QM/MM description of the excited states. Moreover, the conformational space of the system and its dynamic behavior are explored using classical molecular dynamics simulations. The Frenkel excitons theory allows an approximation of the excited states of large molecular systems based on the excited states of relatively smaller QM partitions (coupled chromophores of the system), reducing considerably the computational cost. In the present contribution I will present our promising protocol combining the previously presented features and the results obtained so far on DNA [3], G-quadruplexes[4] and peptides [5].

[1] P. Norman, J.Parello, P. L. Polavarapu and M. Linares, *Phys. Chem. Chem. Phys.*, **17**, 21866-21879 (2015).

[2] D. Loco, S. Jurinovich, L. Di Bari and B. Mennucci, *Phys. Chem. Chem. Phys.*, **18**, 866-877 (2016).

[3] H. Gattuso, A. Xavier, A. Monari, *Theo. Chem. Acc.*, 2015, **134**, 225-232 (2015).

[4] H. Gattuso, A. Spinello, A. Terenzi, X. Assfeld, G. Barone, A. Monari, *J. Phys. Chem. B*, **120**, 3113-3121 (2015).

[5] H. Gattuso, C. García-Iriepa, D. Sampedro, A. Monari, M. Marazzi, *J. Chem. Theo. Comp.*, accepted.



# POSTER SESSION 1



## **Systematic Evaluation of Optimization Strategies Used to Investigate Organic Reaction Mechanisms in Solvent**

**Gavin O. Jones<sup>1</sup>, Brian Levandowski<sup>2</sup>, Julia E. Rice<sup>1</sup>, Ashay Patel<sup>2</sup>, Gonzalo Jimenez-Oses<sup>2</sup>, K. N. Houk<sup>2</sup>**

*<sup>1</sup>IBM Research – Almaden, 650 Harry Rd, San Jose, CA 95120, USA*

*<sup>2</sup>Department of Chemistry and Biochemistry, University of California Los Angeles, 607 Charles E. Young Drive East, Los Angeles, CA 90095, USA*

Two major strategies have traditionally been utilized to account for solvent effects on organic reaction mechanisms: structures have either been fully optimized in an intrinsic solvent using solvent models such as CPCM, SMD, etc., or structures have been first optimized in gas-phase prior to calculation of single-point solvation energies using intrinsic solvent models. Of the two, the second strategy is arguably the more popular method because optimizations are faster, and there is typically no loss in accuracy. However, the accuracy of computed trends and energies obtained by gas-phase optimizations/single-point energy solvent calculations may be affected by the type of solvent, as well as by the type of mechanism.

Investigations have been performed with various density functional methods to investigate how these two types of solvation procedure predicts mechanisms, energies and reactivity trends for a variety of reactions. We believe that these investigations will provide useful guidelines for when both strategies would be suitable for the investigation of reaction mechanisms.

## Developing a DFT/TD-DFT Method for Designing BODIPY Based Anion Sensors and for their Mechanism Demonstration

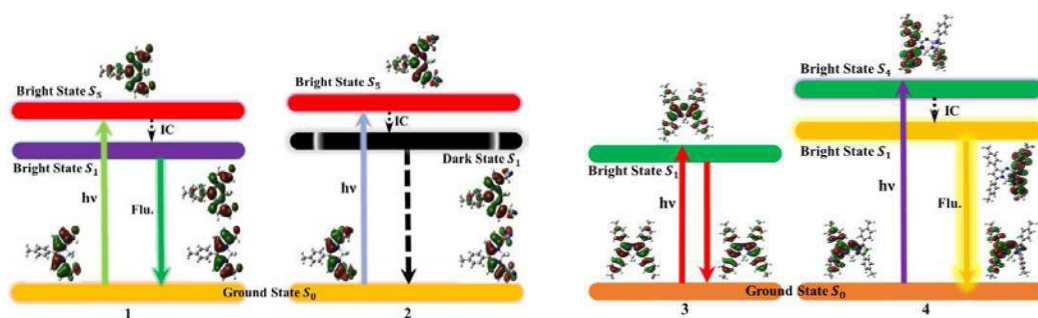
**Haamid R. Bhat<sup>1</sup>, Prakash C. Jha<sup>2</sup>**

<sup>1</sup> Computational Chemistry Laboratory, School of Chemical Sciences, Central University of Gujarat, Gandhinagar, India, 382030.

<sup>2</sup> Centre for Applied Chemistry, Central University of Gujarat, Gandhinagar, India, 382030.

### Abstract

We examined the cyanide anion ( $\text{CN}^-$ ) sensing mechanism of 3,5-diformyl-borondipyrromethene (**1**) by calculating the photophysical properties of **1** and **2** (cyano addition product of **1**) with density functional theory (DFT) and time dependent-density functional theory (TD-DFT) methods using Gaussian 09 programs package. The negative values of energy changes ( $\Delta E$ ) and the free energy changes ( $\Delta G$ ) confirmed the feasibility of  $\text{CN}^-$  addition. The blue-shifted UV-vis spectra calculated for **1** and **2** show a good agreement with earlier reported results [1]. **1** and **2** show different excited state deactivation process as predicted by TD-DFT computations which designate the first excited state of **1** as a coplanar local excited state with  $\pi\text{-}\sigma^*$  transition. A slight charge separation character in the first excited state of **2** and loss of coplanarity at the formyl groups pave the pathway for non-radiative deactivation of the excited state and under their synergistic effect, the fluorescence of **1** after the  $\text{CN}^-$  addition is quenched notably. Thus, the different excited state features of **1** and **2** play a role in the  $\text{CN}^-$  sensing mechanism of **1**. Furthermore, it is experienced that out of the functionals employed here in this contribution (i.e., PBEPBE, CAM-B3LYP, M06-2X and LSDA) [2-5] DFT and TD-DFT computations performed at PBEPBE/6-311+G(2d,p)//PBEPBE/6-311G(2d,p) and CAM-B3LYP/6-311+G(2d,p)//CAM-B3LYP/6-311G(2d,p) levels respectively are adequate for reproducing the excitation and fluorescence energies with a fine accuracy. Using this methodology, we designed an aza-BODIPY (**3**) which shows a fluorescence enhancement on cyanide binding (**4**) involving intramolecular charge transfer and partial configurational changes and it is for the synthetic chemists now to synthesize the designed molecule **3** for cyanide sensing in particular. This employed method can again be utilized for calculating the absorption and emission spectra of BODIPYs and its derivatives and it may pave a way for the designing of new potential BODIPY based anion sensing molecular candidates.



### References

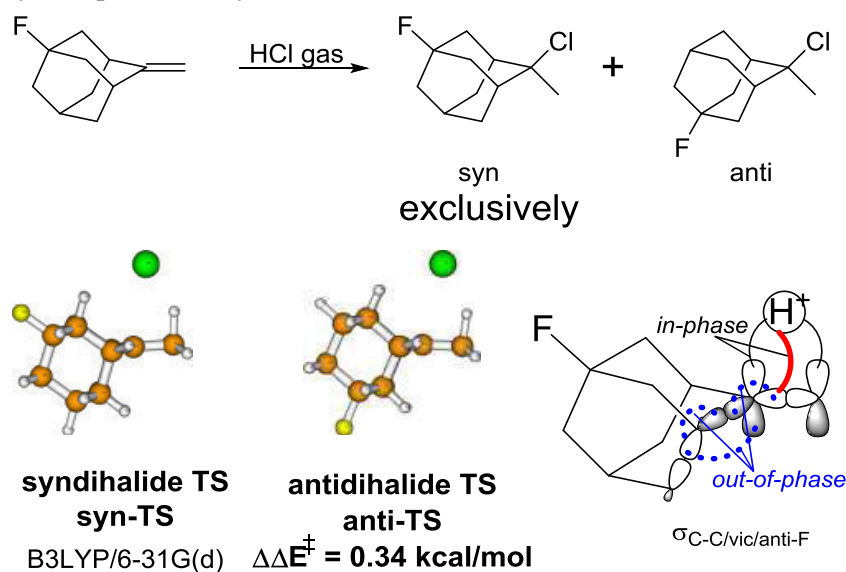
- 1) S. Madhu, S. K. Basu, S. Jadhav and M. Ravikanth, *Analyst*, **138**, 299, (2013).
- 2) D. Jacquemin, A. Planchat, C. Adamo and B. Mennucci, *J. Chem. Theory Comput.*, **8**, 2359, (2012).
- 3) F. Santoro and D. Jacquemin, *WIREs Comput. Mol. Sci.*, 1–27, (2016).
- 4) D. Jacquemin and E. A. Perpe, *J. Chem. Theory Comput.*, **5**, 2420, (2009).
- 5) M. J. Peach, P. Benfield, T. Helgaker and D. J. Tozer, *J. Chem. Phys.*, **128**, 1, (2008).

## Orbital Phase Theory in Diastereoselectivity of Electrophilic Addition to 4-Fluoro-1-methylenadamantane

Yuji Naruse

Department of Chemistry and Biomolecular Science, Gifu University, 1-1 Yanagido, Gifu, 501-1193 Japan

Recently we have shown that the cyclic orbital interaction including the geminal bond participation controls the diastereoselectivity in electrophilic addition [1]. We applied this idea to rationalize the diastereoselectivity in electrophilic addition to 4-fluoro-1-methylenadamantane [2]. The vicinal C-C bonds anti to the fluoro group should be more electron-donating than those syn to the fluoro group due to the antiperiplanar effect with the fluoro group. Thus, the cyclic orbital interaction among  $\psi^*_{\text{H}^+} - \pi_{\text{C}=\text{C}} - \sigma_{\text{C}-\text{C}/\text{vic}/\text{anti-F}} - \sigma_{\text{C}-\text{C}/\text{gem}} - \sigma_{\text{C}=\text{C}} -$  should be more effective to stabilize the TS, i.e., the electrophile should approach in direction syn to the fluoro group. We performed the theoretical calculations of the model [3], which were subjected to the bond model analysis [4] to confirm the idea numerically and quantitatively.



- [1] Y. Naruse, Y. Hasegawa, K. Ikemoto, *Tetrahedron Lett.* **57**, 2029 (2016).
- [2] S. Srivastava, W. J. le Noble, *J. Am. Chem. Soc.* **109**, 5874 (1987); J. H. Chu, W. S. Li, I. Chao, W. S. Chung, *Tetrahedron* **60**, 9493 (2004).
- [3] Gaussian09, Rev. D 01. Gaussian, Inc.
- [4] Bond Model Analysis, ver 1.1. S. Inagaki, H. Ikeda, T. Ohwada, T. Takahama, 1996-2013.

# Radiative Association of $^{36}\text{Ar}$ and $^{38}\text{Ar}$ with Ionic Hydrogen

Fatima Talhi<sup>a\*</sup>, Moncef Bouledroua<sup>b</sup>

<sup>a</sup> Laboratoire de physique des rayonnements , Université Badji Mokhtar, Annaba, Algérie

<sup>b</sup> Laboratoire de physique des rayonnements , Université Badji Mokhtar, Annaba, Algérie

\* email : f.talhi.phys@gmail.com

## Abstract

In a recent paper written by Barlow et al. [Science 342, 1343 (2013)], the  $\text{ArH}^+$  ionic system has been detected in the Crab Nebula. We accordingly propose in this work to examine the radiative association of the argon atoms  $^{36}\text{Ar}$  and  $^{38}\text{Ar}$  with ionic hydrogen  $\text{H}^+$  and to calculate the related temperature dependent rate coefficients. To do so, we have to construct the potential energy curves via which both Ar and  $\text{H}^+$  species approach each other and the permanent dipole moments. The corresponding data points are borrowed from the recent and reliable results of Stolyarov and Child [PCCP 7, 2259 (2005)]. Once the curves are constructed, the rate coefficients are computed quantum mechanically and analyzed in the temperature range 1 – 10000K.

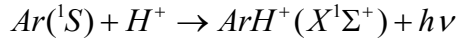
**Keywords :** Radiative Association, Transition Dipole Moments, Potential Energy Curves, The Radiative Association Rate coefficients.

## 1. Introduction

Barlow et al. reported in Ref. [1] detection in the Crab Nebula of traces of the argonium cation  $^{36}\text{ArH}^+$ . Their interpretations of spectra obtained with the Herschel Space Observatory enabled them to demonstrate the presence of the first noble gas in space and diffuse interstellar medium.

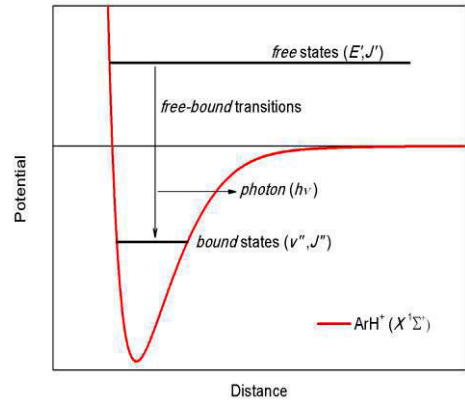
## 2 Radiative Association

The formation of the ground ionic species  $\text{ArH}^+$  starts by considering the following radiative association (RA) process :



The RA rate coefficient :

$$\alpha(T) = \left(\frac{8}{\pi\mu}\right)^{1/2} \left(\frac{1}{k_B T}\right)^{3/2} \int_0^\infty \varepsilon' Q(\varepsilon') \exp\left(-\frac{\varepsilon'}{k_B T}\right) d\varepsilon'$$



## 3. Conclusion

This theoretical work computes the radiative association rate coefficients of the ionic systems  $^{36}\text{ArH}^+$  and  $^{38}\text{ArH}^+$  and examines their behavior with temperature. To do so, the  $X^1\Sigma^+$  potential-energy curve and permanent dipole moment have been constructed from recent and reliable data points. The accuracy of both constructed curves is checked by determining the rovibrational levels and comparing their values with those available in literature.

## Références / References

[1] Barlow et al. [Science 342, 1343 (2013)].

[2] Stolyarov and Child [PCCP 7, 2259 (2005)].

## Thermal Activation of Methane by a Concerted Double C–H Bond Insertion: Charge-Induced Catalysis

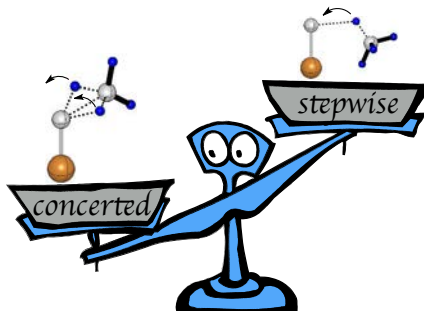
Jilai Li<sup>1,2,\*</sup>, Helmut Schwarz<sup>1,\*</sup>

<sup>1</sup>*Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany*

<sup>2</sup>*Institute of Theoretical Chemistry, Jilin University, Changchun 130023, PR China*

\*Correspondence should be addressed to H.S. ([Helmut.Schwarz@tu-berlin.de](mailto:Helmut.Schwarz@tu-berlin.de)), or to J.L. ([Jilai.Li@campus.tu-berlin.de](mailto:Jilai.Li@campus.tu-berlin.de))

**Abstract:** In the context of methane C–H bond activation mediated by metal complexes under ambient conditions, classical hydrogen-atom transfer,<sup>1,2</sup> proton-coupled electron transfer,<sup>3,4</sup> as well as hydride transfer<sup>5</sup> scenarios have been proposed, and many of the key factors that control the reactivity have also been clarified. We report herein an unprecedented, mechanistically unique Cu<sup>+</sup>-mediated insertion of a carbon atom into two C–H bonds of methane to form ethylene in a single, barrier-less step. In addition, arguments are provided showing that the copper atom in the ethylene forming reaction of [Cu–C]<sup>+</sup> with methane, can be replaced by an oriented external electric field of a positive point charge. Thus, the term “charge-induced catalysis” is suggested.<sup>6</sup>



### Reference:

- (1) Li, J.; Wu, X.-N.; Schlangen, M.; Zhou, S.; González-Navarrete, P.; Tang, S.; Schwarz, H. *Angew. Chem. Int. Ed.* **54**, 5074 (2015).
- (2) Dietl, N.; Schlangen, M.; Schwarz, H. *Angew. Chem. Int. Ed.* **51**, 5544 (2012).
- (3) Li, J.; Zhou, S.; Zhang, J.; Schlangen, M.; Usharani, D.; Shaik, S.; Schwarz, H. *J. Am. Chem. Soc.* **138**, 11368 (2016).
- (4) Li, J.; Zhou, S.; Zhang, J.; Schlangen, M.; Weiske, T.; Usharani, D.; Shaik, S.; Schwarz, H. *J. Am. Chem. Soc.* **138**, 7973 (2016).
- (5) Li, J.; Zhou, S.; Schlangen, M.; Weiske, T.; Schwarz, H. *Angew. Chem. Int. Ed.* **55**, 13072 (2016).
- (6) Geng, C.; Li, J.; Weiske, T.; Schlangen, M.; Shaik, S.; Schwarz, H. *J. Am. Chem. Soc.* **139**, DOI: 10.1021/jacs.6b12514 (2017).

## Optimizing Water Oxidation with Hematite by Simulations

Xueqing Zhang<sup>1</sup>, M.C.M van de Sanden<sup>1,2</sup>, Anja Bieberle-Hütter<sup>1</sup>

<sup>1</sup>*Electrochemical Materials and Interfaces, Dutch Institute for Fundamental Energy Research, De Zaale 20, Eindhoven, the Netherlands*

<sup>2</sup>*Plasma and Materials Processing, Department of Applied Physics, Eindhoven University of Technology (TU/e), De Zaale, Eindhoven, the Netherlands*

X.Zhang@diffen.nl; A.Bieberle@diffen.nl

The design of highly efficient electrodes for photo-electrochemical water splitting is of both fundamental and practical importance [1-3]. We show in this presentation that the water splitting activity with hematite can be enhanced strongly by modification of the structure and the local chemistry [1, 2, 4, 5]. We will discuss the effects of surface orientation, active surface sites, presence of surface steps, lateral interaction, and oxygen vacancies in the subsurface layer on the oxygen evolution reaction (OER) activity [4, 5]. Particularly, the presence of oxygen vacancies is found to be efficient to control the OER activity. Figure 1 shows the free energies of intermediate species calculated for the (110) surface with/without oxygen vacancies (a), and the comparison of the calculated overpotentials with the literature (b) [7, 8]. An OER overpotential of as low as 0.47 V was obtained for an optimal oxygen vacancy concentration of 1.26/nm<sup>2</sup>. The obtained results are used to calculate the rate constants of the OER steps which will serve as input for state-space modeling [6] to simulate electrochemical impedance data that can be directly compared to experiments. We choose hematite as a model system. In general, this method helps in identifying reaction rate limiting parameters and optimizing OER materials.

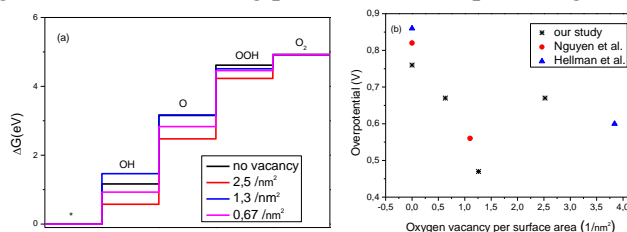


Figure 1 a) free energy diagram, b) Overpotential as a function of oxygen vacancy concentration.

- [1] X. Zhang, A. Bieberle-Hütter, *ChemSusChem*, **9**, 1223 (2016).
- [2] J. Rossmeisl, Z.W. Qu, H. Zhu, G.J. Kroes, J.K. Nørskov, *J. Electroanal. Chem.*, **607**, 83(2007).
- [3] R. van de Krol, Y. Liang, J. Schoonman, *J. Mater. Chem.*, **18**, 2311 (2008).
- [4] X. Zhang, P. Klaver, R. van Santen, M.C.M. van de Sanden, A. Bieberle-Hütter, *J. Phys. Chem. C*, **120**, 18201 (2016).
- [5] X. Zhang, C. Cao, A. Bieberle-Hütter, *J. Phys. Chem. C*, **120**, 28694 (2016).
- [6] A. Bieberle, L.J. Gauckler, *Solid State Ionics*, **146**, 23 (2002).
- [7] M.-T. Nguyen, S. Piccinin, N. Seriani, R. Gebauer, *ACS Catal.*, **5**, 715 (2015).
- [8] A. Hellman, B. Iandolo, B. Wickman, H. Grönbeck, J. Baltrusaitis, *Surf. Sci.*, **640**, 45 (2015).



## Study of surface reactivity of high index platinum surfaces

**Gabriele Tomaschun<sup>1</sup>, Thorsten Klüner<sup>1</sup>**

*<sup>1</sup>IfC, CvO University of Oldenburg, Carl-von-Ossietzky-Str. 9-11, 26129 Oldenburg, Germany*

The main challenges of the catalysis are to investigate and improve efficient, waste reducing and environmentally friendly processes. This can be realized by changing the composition of the chemical process or by tuning the shape of the catalyst itself. [1] The Pt nanoparticles as catalysts for instance show different catalytic reactivity by varying the surface shape and structure. [2] It has been established, that the higher density of atomic steps and kinks leads to more active sites on the surface. This might lead to an increasing reactivity for these stepped platinum surfaces.

In the present study we will analyze the dependence of the catalytic reactivity and selectivity of the industrially relevant reactions, such as condensation of light alcohols, on the kinked and stepped of Pt nanoparticles. These Pt surfaces provide thereby a lot of active sites for the mentioned reactions, thus detailed insight in the reaction mechanisms can be obtained. The theoretical calculations of the catalytic surface reactions will be performed using the exchange-correlation functional PBE [3] implemented in the Vienna ab initio simulation package (VASP) [4]. The analysis of the adsorption and coadsorption sites, adsorption energies, transition states and the favorable reaction paths of the investigated reactions will be the key objective of this research.

[1] K. An, G. A. Somorjai, *ChemCatChem* **4**, 1512 (2012).

[2] S. Motoo, N. Furuya, *Electroanal Chem* **172**, 339 (1984).

[3] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

[4] G. Kresse, J. Hafner, *Phys. Rev. B* **49**, 14251 (1994).

## Hybrid Algorithm based on *Tabu Search Method* for the Synthesis of Macromolecular Compounds with Imposed Properties

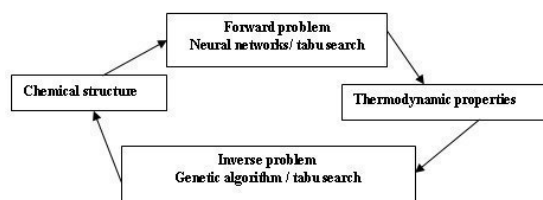
Teodora Rusu<sup>1</sup>, Oana Marilena Gogan<sup>2</sup>

<sup>1</sup>*P. Poni Institute of Macromolecular Chemistry, Iasi, Romania*

<sup>2</sup>*ARTINFO SRL, Iasi, Romania*

One of the most promising applications of Artificial Intelligence Methods (AI) is the computer-aided molecular design (CAMD). The CAMD can achieve the design of totally new molecules with desired properties according to our needs. In CAMD, two things must be known to some extent: the properties that are desired and how they relate to a molecule's structure. The structure–activity relationship is needed to both determine the necessary properties and build a molecule that has those properties. Artificial intelligence algorithms have paved the way for a multitude of applications, and the use of neural networks is increasing in the field of chemistry and biochemistry. The models of neural networks (NN) and their potential applications of classification, modeling, association, and mapping make them as a good partner in the CAMD. Usually the CAMD implies the use of combined artificial methods.

Our paper deals with a system build from Neural Network combined with a hybrid evolutionary algorithm Genetic Algorithm (GA). In order to improve the combinatory property of the GA path a Tabu Search algorithm was attached.



**Scheme 1. Hybrid algorithm**

In the present study, we pursue two research themes in the genetic design framework. One is to investigate the efficacy of genetic design for problems with much larger and more complex design spaces. The second theme is to extend the original genetic algorithmic framework by incorporating higher-level chemical knowledge to better handle constraints such as chemical stability and molecular complexity by use of a *Multiobjective Tabu Search*. The fitness function of the system has been evaluated.

**Acknowledgment:** This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI – UEFISCDI, project number PN-III-P3-3.6-H2020- 2016-0011, within PNCDI III

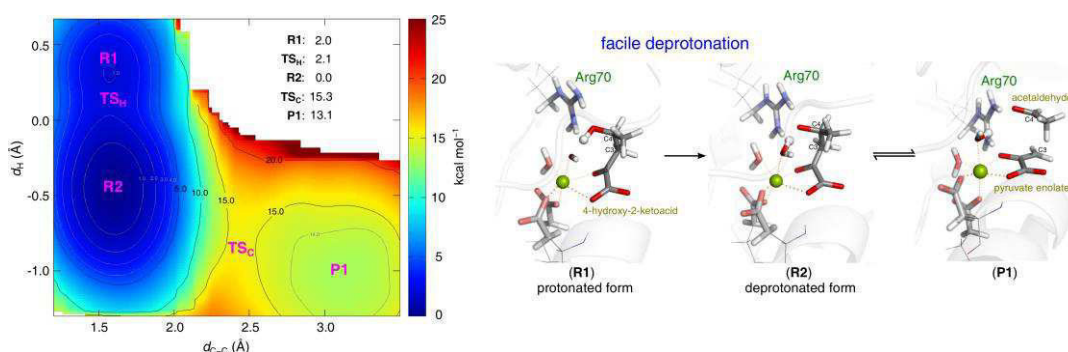
## Catalytic Roles of Metal-bound Hydroxide and Arginine in Pyruvate Class II Aldolase Investigated by QM/MM Metadynamics

Gou-Tao Huang<sup>1</sup>, Jen-Shiang K. Yu<sup>1,2,\*</sup>

<sup>1</sup> Department of Biological Science and Technology, National Chiao Tung University,  
No.75 Po-Ai St, Hsinchu City 300, Taiwan

<sup>2</sup> Institute of Bioinformatics and Systems Biology, National Chiao Tung University, No.75  
Po-Ai St, Hsinchu City 300, Taiwan

The retro-aldol reaction catalyzed by pyruvate class II aldolase is investigated with the QM/MM metadynamics. This enzyme consisting divalent metal ions as catalytic cofactors catalyzes the aldol cleavage of 4-hydroxy-2-ketoacid into pyruvate enolate and aldehydes, where the former binds to the metal ion. Aldol cleavage is mechanistically initialized by the deprotonation of the hydroxyl group of the substrate 4-hydroxy-2-ketoacid by the metal-bound hydroxide. The simulation demonstrates a small barrier of around 0.1 kcal mol<sup>-1</sup> during the deprotonation, which suggests a practically barrierless process. The deprotonated form is then stabilized by the vicinal positively-charged arginine, facilitating the subsequent aldol cleavage. The C–C bond cleavage leads to the release of the aldehyde molecule, and the pyruvate enolate binds to the metal ion. The barrier for the C–C bond cleavage is estimated at approximately 15.3 kcal mol<sup>-1</sup>, which reasonably agrees with the experimental rate constant ( $k_{\text{cat}}$ ) of 205.4 s<sup>-1</sup>. In addition to the metal cation coordinated by the pyruvate enolate in a chelating form, the arginine also contributes to stabilize the enolate oxyanion. In the overall catalytic process, the metal-bound hydroxide functions to deprotonate the reactant, which converts into the active form that continues on the C–C bond cleavage in the aldol cleavage reaction. The role of the arginine is to stabilize the deprotonated form of the reactant as well as the pyruvate enolate moiety by hydrogen bonding and electrostatic interactions.



[1] M. Coincon,; W. Wang, J. Sygusch, S. Y. K. Seah, *J. Biol. Chem.* **287**, 36208 (2012).

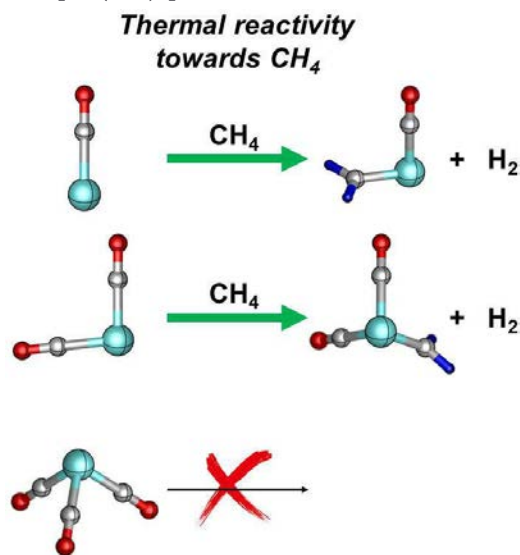
# On the Origin of Reactivity Enhancement/Suppression Upon Sequential Ligation: the $[\text{Re}(\text{CO})_x]^+/\text{CH}_4$ ( $x = 0 - 3$ ) Couples

Shaodong Zhou<sup>1</sup>, Jilai Li<sup>1,2</sup>, Maria Schlangen<sup>1</sup>, Helmut Schwarz<sup>1</sup>

<sup>1</sup>*Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany*

<sup>2</sup>*Institute of Theoretical Chemistry, Jilin University, Changchun, 130023, People's Republic of China*

**Abstract:** The thermal gas-phase reactions of the rhenium carbonyl complexes  $[\text{Re}(\text{CO})_x]^+$  ( $x = 0 - 3$ ) with methane have been explored by using FT-ICR mass spectrometry complemented by high-level quantum chemical calculation. While it had been concluded that addition of closed-shell ligands in general decreases the reactivities of metal ions[1], the current work provides an exception: the previously demonstrated inertness of atomic  $\text{Re}^+$  towards methane is completely changed upon ligation with CO. Both,  $[\text{Re}(\text{CO})]^+$  and  $[\text{Re}(\text{CO})_2]^+$ , bring about efficient dehydrogenation of the hydrocarbon at ambient condition. However, addition of a third ligand to form  $[\text{Re}(\text{CO})_3]^+$  quenches completely the reactivity. While the former reactivity enhancing effect can be traced back to a change of spin multiplicities of the metal center and the involvement of multi-state reactivity scenarios, the inertness of the latter is ascribed to the presence of a stable, closed-shell electronic configuration of  $^1[\text{Re}(\text{CO})_3]^+$ .



[1] D. Schröder, H. Schwarz, *Proc. Natl. Acad. Sci. U. S. A.* **105**, 18114 (2008).

## Theoretical study of Co(II/III)-complex catholytes used Li-ion redox flow batteries

Ji Young Park<sup>1,2</sup>, Georgios Nikiforidis<sup>2,3</sup>, Chunzhen Yang<sup>3</sup>, Mu-Hyun Baik<sup>1,2</sup>, Hye-Ryung Byon<sup>2,3,4</sup>

1. Center for Catalytic Hydrocarbon Functionalizations, Institute for Basic Science (IBS), Daejeon 34141, Republic of Korea.

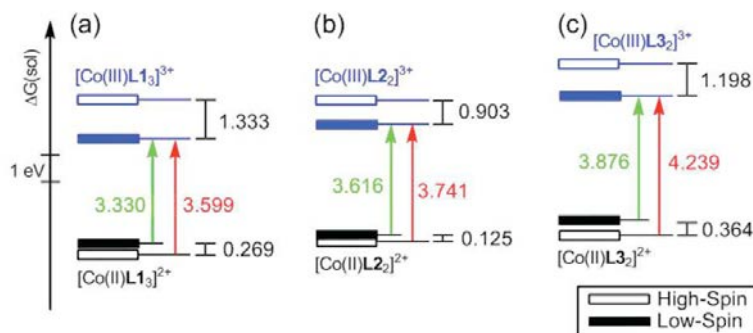
2. Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea

3. Byon Initiative Research Unit (IRU), RIKEN, Saitama 351-0198, Japan

4 KAIST Institute NanoCentury, Daejeon 34141, Republic of Korea

In the recent material chemistry field, redox battery with non-aqueous electrolyte is one of the hottest issue<sup>1,2</sup>. Different from electrolyte study, catholyte study have not be done much yet. Byon's group suggested transition metal include 6-coordinate compound as a catholyte of Li-ion redox flow battery system.

Herein we analyze the performance of suggested Co(II/III)-complex catholyte in Li-ion redox flow batteries. Spin-crossover<sup>3</sup> and entropy penalty are successfully describe experimental data. One step further, we suggest novel materials which show higher redox potential and capacity theoretically.



- [1] B. Dunn, H. Kamath, J.-M. Tarascon, *SCIENCE* **334**, 928(2011).
- [2] Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon, J. Liu, *Chem. Rev.* **111**, 3577 (2011).
- [3] J. England, E. Bill, T. Weyhermüller, F. Neese, M. Atanasoc, K. Wieghardt, *Inorg. Chem.* **54**, 12002 (2015).
- [4] C. Yang, G. Nikiforidis, J. Y. Park, Y. Luo, L. Zhang, Z. Hou, M.-H. Baik, Y. Lee, H.-R. Byon, *Nature Energy* (2017) in preparation

## Stochastic Basis Set Approach to Density Functional Theory

**Marcel David Fabian<sup>1</sup>, Ben Shpiro<sup>1</sup>, Eran Rabani<sup>2</sup>, Daniel Neuhauser<sup>3</sup>, Roi Baer<sup>1</sup>**

<sup>1</sup>*Fritz Haber Center for Molecular Dynamics, Institute of Chemistry, The Hebrew University of Jerusalem, 91904, Israel*

<sup>2</sup>*Department of Chemistry, University of California and Lawrence Berkeley National Laboratory, Berkeley, California, 94720, USA*

<sup>3</sup>*Department of Chemistry and Biochemistry, University of California, Los Angeles, California, 90095, USA*

Although density functional theory (DFT) is routinely used to study the properties of a wide range of molecular and crystal systems, its utility for studying large systems in materials science and biology is limited. This is due to the fact that the DFT computational effort, in terms of memory and CPU time, typically scales quadratically with system-size. While linear-scaling methods have been developed by several groups, these are often of limited applicability due to the non-locality of the density matrix in many types of large systems. An alternative approach has been developed [1, 2] which circumvents the calculation of the density matrix and the Kohn-Sham (KS) orbitals using stochastic orbitals. These stochastic orbital methods are useful for orthogonal basis-sets, such as plane-waves and grids. In this work we extend the methods to non-orthogonal basis sets which are common in quantum chemistry. The greatest hurdle is to bypass the need to invert the overlap matrix and this we accomplish by using the preconditioned conjugate gradient method. The projection of orbitals on the occupied space is carried out using Chebyshev propagators. Various observables are treated as random variables with mean equal to the deterministic KS values and variance which drops when the number of random orbitals is increased in accordance with the central limit theorem. Results for the calculation of silicon clusters are shown.

[1] R. Baer, D. Neuhauser and E. Rabani, *Phys. Rev. Lett.* **111**, 106402 (2013).

[2] D. Neuhauser, R. Baer and E. Rabani, *J. Chem. Phys.* **141**, 041102 (2014).

## Thermal properties of organic solids from the quasi-harmonic approximation

**Jan Gerit Brandenburg**<sup>1,2,3</sup>

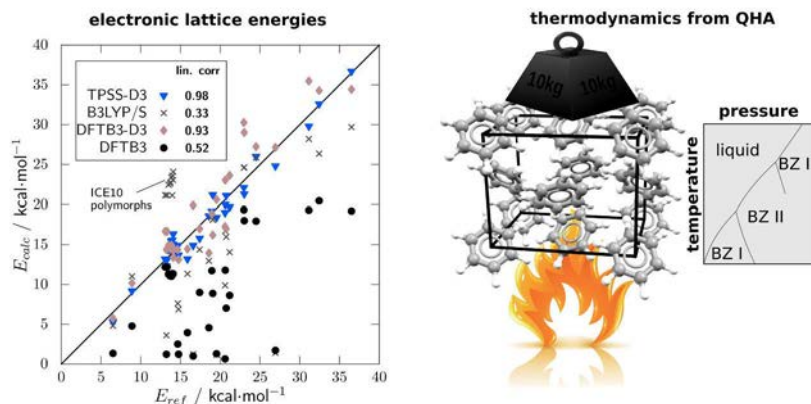
<sup>1</sup>Department of Chemistry, University College London, 20 Gordon Street, London, UK.

<sup>2</sup>London Centre for Nanotechnology, University College London, 17-19 Gordon Street, London, UK.

<sup>3</sup>Thomas Young Centre, University College London, Gower Street, London, UK.

Kohn-Sham density functional theory and tight-binding approximations are the method of choice for efficient electronic structure calculations. Especially when reliable geometries and thermodynamic properties are needed, this will continue to be the case in the foreseeable future. In the past years the standard semi-local methods have been improved to incorporate non-local correlation effects leading to the omnipresent van der Waals interaction. Thus, their area of applicability has been extended to the important class of molecular crystals.[1]

I will present a combination of modern dispersion corrected tight-binding methods with a quasi-harmonic treatment of lattice dynamics to efficiently describe thermodynamic properties of organic crystals.[2, 3] The discussed systems range from the small and mostly rigid squaric acid to larger and more flexible pharmaceuticals like naproxen and carbamazepine. While the focus will be on structural features, the impact on relative free energies is discussed. This is of major importance for the control and prediction of polymorphism, which is highlighted by results from the 6<sup>th</sup> blind test for organic crystal structure prediction.[4, 5, 6]



### Key references

- [1] S. Grimme, A. Hansen, J. G. Brandenburg, C. Bannwarth, *Chem. Rev.* **116**, 5105-5154 (2016).
- [2] J. G. Brandenburg, S. Grimme, *J. Phys. Chem. Lett.* **5**, 1785-1789 (2014).
- [3] J. G. Brandenburg, E. Caldeweyher, S. Grimme, *Phys. Chem. Chem. Phys.* **18**, 15519-15523 (2016).
- [4] J. G. Brandenburg, S. Grimme, *Top. Curr. Chem.* **354**, 1-23 (2014).
- [5] J. G. Brandenburg, S. Grimme, *Acta. Cryst. B* **72**, 502-513 (2016).
- [6] S.L. Price, J. G. Brandenburg, *Molecular Crystal Structure Prediction*, Eds. G. DiLabio, A. Otero-de-la-Roza, Elsevier Australia, Melbourne, Australia (2017).

[www.gerit-brandenburg.de](http://www.gerit-brandenburg.de)

## Ethylene glycole decomposition on a Palladium subnanometric cluster: a graph theory based approach

Remedios Cortese<sup>1</sup>, Roberto Schimmenti<sup>1</sup>, Antonio Prestianni<sup>1</sup>, Dario Duca<sup>1</sup>

<sup>1</sup>*Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, Viale delle Scienze ed. 17, Palermo, Italy*

In the context of biomass feeds reforming [1, 2], ethylene-glycol ( $C_2$ ) was selected as oxygenates model species and its decomposition on a subnanometric Pd cluster was investigated by means of DFT. Studies dealing with the reactivity of this molecule are of interest both to enhance practical goals of hydrogen production and to provide fundamental insights into the underlying competition among C–H, O–H, C–C, and C–O bond cleavages in polyols. The size of the catalytic system above, involving a small Pd cluster ( $Pd_{12}$ ) and the simple  $C_2$  species, allowed one to explore by computational techniques almost all the reactive routes associated to the ethylene-glycol decomposition. This determined the generation of a large grid of possible events, useful to deepen the energetic ordering of different reaction pathways that in principle would let to unravel the whole reaction mechanism, involving many and complexly tangled molecular events. So, to effectively analyze the decomposition path it is necessary to accurately characterize not only the elementary steps involved in the reaction network but also their sequences. The protocol followed for the reaction network analysis was organized into three

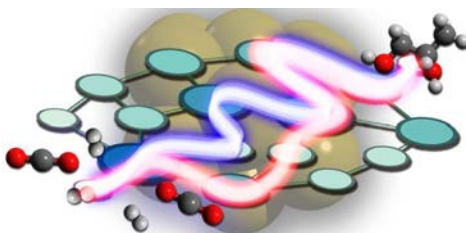


Figure 1: Paths found to be favoured, in ethylene-glycol decomposition on  $Pd_{12}$ .

steps: i) *ab-initio* calculation of the activation barriers and presieving of the possible molecular events, ii) organization of the graph representing the final reaction network, iii) analysis of the possible pathways and characterization of the final graph with centrality indexes. The analysis of the resulting network was performed considering that, as stated in the frame of the graph theory (GT) approach, a path is a walk in which no vertex occurs more than once. The differently long pathways found were ordered taking into account the total energy content (TEC), defined as the summation of all the activation barriers involved in the development of a given route.

[1] R. D. Cortright, R. R. Davda, J. A. Dumesic, *Nature* **418**, 946 (2002).

[2] G. A. Deluga, J. R. Salge, L. D. Schmidt and X. E. Verykios, *Science* **303**, 993 (2006).

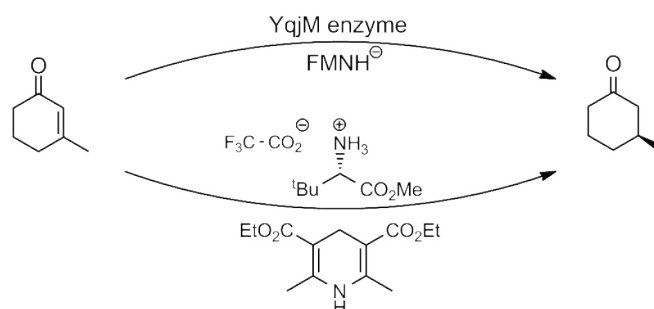


## A comparative study of hydrogen bond and iminium mechanisms in organocatalytic and enzymatic reduction

Dávid Ferenc , Ádám Kovács , Ádám Madarász

Research Center for Natural Sciences, Hungarian Academy of Sciences, Magyar Tudósok  
Körútja 2, H-1117 Budapest, Hungary

Reduction of  $\alpha,\beta$  unsaturated ketones can be carried out via enzymatic or organocatalytic reactions. They have high importance in synthetic organic chemistry, since both yield chiral products.



In the organocatalytic scheme an iminium activated reaction mechanism is considered to be the most favored and was examined by Gutierrez *et al.*[1] On the other hand in the enzyme catalyzed case a hydrogen bond activated mechanism is advised and was studied by QM/MM methods.[2] However with a lysine amino acid present in the active center of the enzyme an iminium activated mechanism can be envisioned in the biocatalytic case as well.

In the present work the two possible mechanisms were examined for both the organocatalytic and enzymatic routes by DFT calculations, using the  $\omega$ B97X-D functional. In the biocatalytic case the so called “Quantum chemical cluster” approach was applied, which means, that model systems, including the most important residues and ligands around the active center, have been built where the chain ends of the amino acids were frozen in their X-ray structure position. This approach also has the advantage that the biocatalytic pathways can be compared directly in free energies. QM/MM calculations were also performed to investigate the mechanisms in more details. Our results indicate that the iminium activation is more plausible than the hydrogen bond mechanism for both the enzyme and organocatalyst. These new insights can help to improve the efficiency of the organocatalytic reduction.

[1] O. Gutierrez, R. G. Iafe, K. N. Houk, *Org. Lett.* **11**, 4298–4301 (2009).

[2] R. Lonsdale, M. T. Reetz, *J. Am. Chem. Soc.* **137**, 14733–42 (2015).

## Improved Accuracy of Hybrid Atomistic/Coarse-Grained Simulations Using Reparametrised Interactions.

**Annick Renevey<sup>1</sup>, Sereina Riniker<sup>1</sup>**

<sup>1</sup>*Department of Chemistry and Applied Biosciences, Laboratory of Physical Chemistry, ETH Zürich, Vladimir-Prelog-Weg 2, Zürich, Switzerland*

Reducing the number of degrees of freedom in molecular models, by so-called coarse-graining, is a popular approach to increase the accessible time scales and system sizes in molecular dynamics (MD) simulations. It involves, however, a loss of information. In order to retain a high accuracy in the region of interest, hybrid methods that combine two levels of resolution in a single system are an attractive trade-off. Hybrid atomistic (AT)/coarse-grained (CG) simulations have previously been shown to preserve the secondary structure elements of AT proteins in CG water but to cause an artificial increase in intramolecular hydrogen bonds due to the lack of hydrogen-bonding capacity of CG water, resulting in a reduced flexibility of the proteins.[1] Recently, it was found that the AT-CG interactions employed in these simulations were too favourable for apolar solutes and not favourable enough for polar solutes.[2] Here, the AT-CG interactions are reparametrised to reproduce the solvation free energy of a series of AT alkanes and side-chain analogues in CG water, while retaining the good mixing behaviour of AT water with CG water. The new AT-CG parameters are tested in hybrid simulations of four proteins in CG water. Structural and dynamic properties are compared to those obtained in fully AT simulations and, if applicable, to experimental data. The results show that the artificial increase of intramolecular hydrogen bonds is drastically reduced, leading to a better reproduction of the structural properties and flexibility of the proteins in atomistic water.

[1] S. Riniker, W. F. van Gunsteren, *J. Chem. Phys.* **137**, 044120 (2012).

[2] A. Kuhn, S. M. Gopal, L. V. Schäfer, *J. Chem. Theory Comput.* **11**, 4460 (2015).

**Binding isotope effects as a tool to detecting HIV-1 RT binding sites.****Agnieszka Krzemińska<sup>1</sup>, Piotr Paneth<sup>1</sup>***<sup>1</sup>Institute to Applied Radiation Chemistry, Faculty of Chemistry, Lodz University of Technology, ul. Stefana Żeromskiego 116, 90-924 Łódź, Poland.*

HIV-1 reverse transcriptase (RT) is one of three enzymes involved in the human immunodeficiency virus (HIV-1) replication cycle. Half of 26 antiretroviral approved drugs target RT at allosteric cavity or RNase H active site. Resistance of RT mutants to current therapies prompted us to explore computationally binding inhibitors not only to the allosteric cavity and RNase H active site but also to other, recently identified Knuckles, NNRTI Adjacent and Incoming Nucleotide Binding sites.

Our computational protocol was evaluated based on nine, FDA approved RT nucleoside (NRTI) and non-nucleoside (NNRTI), inhibitors.[1] According to our theoretical[2] and experimental[3] studies we have recently shown that N-(2-chloro-4-sulphamoylphenyl)-2-((4-(2,4-dimethyl-phenyl)-5-(thiophen-2-yl)-4H-1,2,4-triazol-3-yl)sul-phenyl)-acetamide, L-1, is an inhibitor of HIV-1 RT that binds in the hydrophobic allosteric pocket via van de Waals interactions and even more strongly to the RNase H active site using electrostatic attraction. Using promising L-1 scaffold, additional three triazole-based derivatives (L-2, L-3 and L-4) have been developed and docked to the allosteric cavity, the RNase H active site, the Knuckles, the NNRTI Adjacent, and the Incoming Nucleotide Binding sites. Complexes of the ligand with the protein have been obtained after long QM/MM MD simulations. Heavy-atom (<sup>13</sup>C, <sup>15</sup>N and <sup>18</sup>O) binding isotope effects, BIEs, have been analyzed in the context of distinguishing between binding sites. Specific interactions between the ligands and RT binding sites have been characterized.

- [1] A. Krzemińska, P. Paneth, V. Moliner, K. Świderek, *J. Phys. Chem.B.* **119**, 917 (2015).
- [2] A. Krzeminska, K. Świderek, P. Paneth, *Phys. Chem. Chem. Phys.* **18**, 310 (2016).
- [3] T. Fraczek, A. Paneth, R. Kaminski, A. Krakowiak, P. Paneth, *J. Enzym. Inhib. Med. Chem.* **31**, 481 (2015).

## Simulation of reversibly interlocked SWCNTs

**Sebastian Gsänger<sup>1</sup>, Bernd Meyer<sup>1</sup>**

*<sup>1</sup>Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center,  
Friedrich-Alexander-Universität Erlangen-Nürnberg,  
Nägelsbachstraße 25, 91052 Erlangen, Germany*

In chemical functionalization of single-walled carbon nanotubes (SWCNTs), usually one has to compromise between altering the structure of the nanotube via covalent attachment of the adsorbates or by forming rather fragile supramolecular complexes. An alternative, which combines having only non-covalently bound species but leads to very stable structures, is the concept of mechanically interlocking the CNT inside the adsorbate molecule. Specifically, we explore adsorbates which allow for a reversible ring closure in the rotaxane-forming step, therefore promising greater yields and a better control of the target structure. By performing molecular dynamics simulations with the generalized AMBER force field, we identified suitable structures and geometries and analyzed their behaviour under different reaction conditions.

## Indirect-to-Direct Band Gap Crossover in Few-Layer Transition Metal Dichalcogenides

Yajing Sun , Dong Wang <sup>\*</sup>, Zhigang Shuai <sup>\*</sup>

*Department of Chemistry, Tsinghua University, Beijing, China*

**Abstract:** Layered transition metal dichalcogenides (TMDs) have been found to exhibit the indirect-to-direct band gap transition when they are thinned to a single monolayer. We disclose that the indirect-to-direct band gap crossover in TMDs is essentially a competition between the spin-orbit coupling and inter layer electronic coupling. For MoS<sub>2</sub>, MoSe<sub>2</sub> and WS<sub>2</sub>, the indirect-to-direct band gap transition occurs in the monolayer where interlayer interactions completely vanish. The spin-orbit coupling effect of WSe<sub>2</sub> is so large that the indirect-to-direct band gap crossover takes place in the trilayer, and for WTe<sub>2</sub> such a crossover even happens in the tetralayer. The valley degeneracy of the band edges and the valley-dependent optical transitions in few-layer TMDs have opened up the way to manipulate their valley degree of freedom for valleytronics and spintronics.

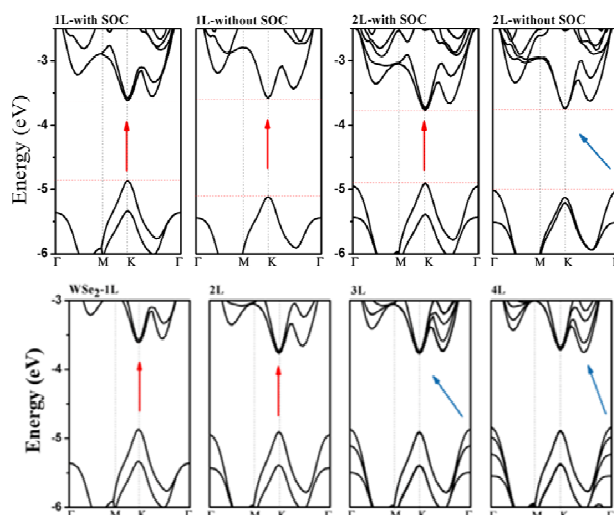


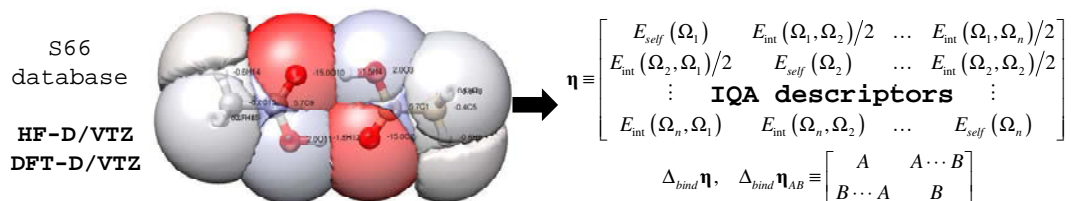
Fig.1 Top panel displays band structures for monolayer and bilayer of WSe<sub>2</sub> for with and without spin orbital coupling (SOC). The bottom is the band structure of WSe<sub>2</sub> as a function of the layer thickness. The indirect-to-direct band gap crossover in TMDs is essentially a competition between the spin-orbit coupling and inter layer coupling effects: SOC favors direct band gap while interlayer dispersion favors indirect gap.

## Interacting Quantum Atoms Approach Applied to the S66 Database of Noncovalent Complexes

Dimas Suárez,<sup>1</sup> Natalia Díaz<sup>1</sup>, Evelio Francisco,<sup>1</sup> Angel Pendás<sup>1</sup>

<sup>1</sup>*Departamento de Química Física y Analítica. Universidad de Oviedo.  
Avda. Julián Clavería 8. 33006. Oviedo. Spain.*

The interacting quantum atoms (IQA) method [1] decomposes the total energy of a molecular system in terms of physical components that are ultimately divided into one- and two-center (atomic) contributions within the context of the quantum theory of atoms in molecules. In principle IQA can assess, systematically and in great detail, the strength and physics of covalent and noncovalent interactions in biomolecular systems. Similarly, molecular mechanics (MM) potentials and QM-MM treatments could be assessed in terms of IQA descriptors. However, IQA is computationally expensive due to six-dimensional numerical integrations over the irregularly-shaped atomic basins that involve the first and second order density matrices. In addition, numerical errors may also affect the accuracy of the QM energy reconstructed by IQA. These factors still limit the size of molecular systems and the choice of QM methods that can be treated with IQA. Both methodological and technical advances are needed to extend the applicability of IQA to biomolecules comprising ~100 “QM atoms”, but gaining further computational experience on smaller systems is also necessary. Hence, we examine the S66 database [2] of benchmark geometry and binding energies relevant to biomolecular models. For all the structures, we perform single-point and geometry optimizations using HF and selected DFT methods with triple- $\zeta$  basis sets followed by full IQA calculations. Pairwise dispersion energies are accounted for by the DFT-D3 method. We analyze the goodness of the HF & DFT binding energies, the magnitude of numerical errors, the relative weight of intra- and intermolecular interactions, the mode of binding, the similarities and differences depending on the level of theory, etc. Considering all the information, we make recommendations of model chemistries and IQA settings for larger systems.



[1] M.A. Blanco, A. Martín-Pendás, E. Francisco. *J. Chem. Theory Comput.* **1**, 1096 (2005).

[2] J. Řezáč, K.E. Riley, P. Hobza. *J Chem. Theory. Comput.* **7**, 2427 (2011).

## Probing the Feasibility Limits of Coupled Cluster Theory: Highly Accurate Activation Barriers of Unexpected Reactions for Energetic Materials

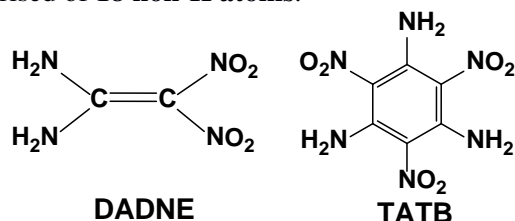
**Vitaly G. Kiselev,<sup>1,2</sup> Nina P. Gritsan<sup>1,2</sup>**

<sup>1</sup>*Novosibirsk State University, 2, Pirogova Str., Novosibirsk, Russia*

<sup>2</sup>*Institute of Chemical Kinetics and Combustion, 3, Institutskaya Str., Novosibirsk, Russia*

Kinetics and mechanism of thermal decomposition are crucial for enhancing safety and performance of energetic materials (EM). While direct kinetic experiments with EM are hindered due to numerous fast exothermic reactions occurring simultaneously, quantum chemical calculations are often a convenient alternative to experiment. However, the accuracy of routinely used DFT methods is often not sufficient to provide convincing evidence on the thermolysis mechanism of EM. To achieve reliable chemical accuracy on the activation barriers ( $\sim 1$  kcal/mol), the expensive high-level coupled cluster computations are always desirable. Unfortunately, the CCSD(T) calculations with the basis set of quadruple zeta quality are feasible for the systems with at most 7-8 atoms like C, N, O. However, the explicitly correlated CCSD(T)-F12 modifications allow for significant reduction of the basis set while retaining the proper accuracy. In our previous extensive benchmark studies for a series of energetic nitro species, we showed that even CCSD(T)-F12/VDZ-F12 thermochemistry is generally of the CCSD(T)/CBS(3,4) quality [1].

Here we present the two instructive examples of the highly accurate CCSD(T)-F12 computations for decomposition mechanisms of widely used high-performance insensitive EM: 1,1-diamino-2,2-dinitroethylene (DADNE, FOX-7) and triamino-trinitrobenzene (TATB). In particular, we managed to perform CCSD(T)-F12/VDZ-F12 calculations for TATB, which is comprised of **18 non-H atoms**.



For both species, CCSD(T)-F12 computations provided new important insights into the decomposition mechanism. In the case of DADNE, the calculations suggested the two competing primary reaction channels never discussed before: viz., the H-transfer (enamino-imino tautomerization) followed by radical decomposition (effective activation barrier  $\sim 48$  kcal/mol) and intramolecular cyclization to oxazete-N-oxide, which is prone to fast subsequent molecular decomposition (overall activation barrier  $\sim 55$  kcal/mol). In the case of TATB, the accurate CCSD(T)-F12 activation barriers of the three channels: viz., intramolecular cyclization followed by decomposition reactions, nitro-aci-nitro isomerization with subsequent cyclization and water elimination, and nitro-nitrite rearrangement, are very close to each other ( $\sim 59$  kcal/mol). All these findings were possible only with CCSD(T) convincing evidence, the DFT values were notably scattered.

[1] V. G. Kiselev, *Chem. Phys. Phys. Chem.* **17**, 10283 (2015).

## On the nature and reactivity of the Substrate/Dioxygen Bound Intermediate in Tyrosinase: QM/MM Study Correlated with Spectroscopic Data.

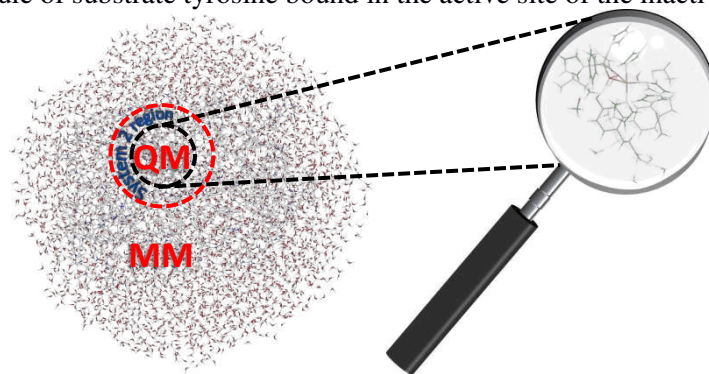
**Prokopis C. Andrikopoulos<sup>1</sup>, Ryan E. Cowley<sup>2</sup>, Jake Ginsbach<sup>2</sup>, Gregory L. Schneider<sup>2</sup>, Ioannis Kipouros<sup>2</sup>, Edward I. Solomon<sup>2</sup>, Lubomir Rulíšek<sup>1</sup>**

<sup>1</sup>*Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, Flemingovo nám. 2, 16610 Prague, Czech Republic*

<sup>2</sup>*Department of Chemistry, Stanford University, Stanford, CA 94305-5080, USA*

Tyrosinase is an enzyme controlling the production of melanin by converting phenols to quinones. The active site responsible for the transformation is a “diamond” Cu<sub>2</sub>O<sub>2</sub> core formed by the binding of dioxygen to the dinuclear copper center of the enzyme.

QM/MM calculations were employed to study the structure and reactivity of the ternary complex (**Figure 1**), based on the available crystal structure of -zinc substituted- tyrosinase with the molecule of substrate tyrosine bound in the active site of the inactive enzyme [1].



**Figure 1** Representation of the Quantum (QM) and Molecular Mechanics (MM) region of Tyrosinase.

After reproducing the main features of the Zn<sub>2</sub>/tyrosine crystal structure by the QM/MM calculations, thus verifying the reliability of the computational setup, the native form of the enzyme with the Cu<sub>2</sub>O<sub>2</sub> core was studied. Reactant complexes were constructed and their spectroscopic features and reactivity were checked with respect to available experimental evidence on enzyme as well as model systems [2].

Despite the fact that accurate quantum chemical treatment of the Cu<sub>2</sub>O<sub>2</sub> core is a highly challenging problem [3], the QM/MM(-DFT) calculations yielded a plausible description of the Tyrosinase reaction mechanism.

[1] M. Goldfeder, M. Kanteev, S. Isaschar-Ovdat, N. Adir, A. Fishman, *Nat. Commun.* **4505**, 1 (2014).

[2] M. F. Qayyum, R. Sarangi, K. Fujisawa, T. D. P. Stack, K. D. Karlin, K. O. Hodgson, B. Hedman, E. I. Solomon *J. Am. Chem. Soc.* **135**, 17417 (2013).

[3] Y. Kurashige, J. Chalupský, T. N. Lan, T. Yanai *J. Chem. Phys.* **141**, 174111 (2014).



## Explicitly Correlated N-Electron Valence State Perturbation Theory (NEVPT2-F12)

**Yang Guo<sup>1</sup>, Kantharuban Sivalingam<sup>1</sup>, Edward F. Valeev<sup>2</sup> and Frank Neese<sup>1</sup>**

<sup>1</sup>*Max Planck Institut für Chemische Energiekonversion, Stiftstr. 34-36, D-45470  
Mülheim an der Ruhr, Germany*

<sup>2</sup>*Department of Chemistry, Virginia Tech, Blacksburg, VA 24061, USA*

Explicitly correlated second order N-electron valence state perturbation theory (NEVPT2-F12) has been implemented in ORCA. Our NEVPT2-F12 algorithm is based on a fully internally contracted (FIC) wave function and includes the correction of semi-internal excitation subspaces. The basis set incompleteness correction for the CASSCF energy is considered as well. For all relative energies calculated in this work, the errors with respect to the complete basis set (CBS) limit for NEVPT2-F12 method are within 1 kcal/mol. If the number of active MOs is considered as a constant, the overall scaling of the computational effort is  $O(N^5)$ . The algorithm exploits the resolution of identity (RI) approximation to improve the computational efficiency. The computational cost of a RI-NEVPT2-F12 correlation energy calculation for each root is comparable to a closed-shell RI-MP2-F12 calculation on the same system.

- [1] Y. Guo, K. Sivalingam, E. F. Valeev, and F. Neese, *J. Chem. Phys.* Submitted
- [2] F. Neese, *WIREs Comput. Mol. Sci.* **2**, 73 (2011).
- [3] L. Kong, and E. F. Valeev, *J. Chem. Phys.* **133**, 174126 (2010).
- [4] T. Shiozaki, and H.-J. Werner, *J. Chem. Phys.* **133**, 141103 (2010).

## Elucidation of the Singlet Fission Mechanism: A Theoretical Insight

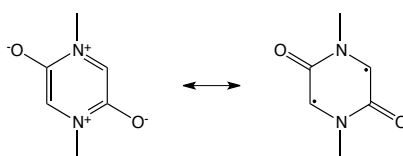
Meilani Wibowo<sup>1,2</sup>, Ria Broer<sup>1</sup>, Maurizio Persico<sup>2</sup>, and Remco W. A. Havenith<sup>1,3</sup>

<sup>1</sup>Theoretical Chemistry, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

<sup>2</sup>Dipartimento di Chimica e Chimica Industriale, Università di Pisa, v. Risorgimento 35, I-56126 Pisa, Italy

<sup>3</sup>Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen The Netherlands, and Ghent Quantum Chemistry Group, Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 (S3), B-9000 Gent, Belgium

Singlet fission (SF) is a fast (sub-ps) process in which the lowest excited singlet state of one molecule transfers parts of its energy to a neighbouring molecule resulting in two (local) triplets that are coupled into a singlet (<sup>1</sup>TT). It can be beneficial for the improvement of organic photovoltaic cells since it exploits a high-energy photon with minimal thermal energy loss and it generates multiple excitons for charge separation. The elucidation of SF mechanism is crucial for the development of new and highly efficient SF chromophores. With the aid of theoretical chemistry and computational modelling, parameters that determine the SF efficiency as well as the states that are involved in the transition process from the lowest (diabatic) excited spin singlet state to the <sup>1</sup>TT state can be deduced. The SF efficiency can be determined by calculations of the SF rate and the rates of other competing processes. In the Fermi's golden rule approximation, the SF rate is proportional to the electronic coupling between the initial and final diabatic states [1]. We have developed a nonorthogonal configuration interaction approach to calculate this electronic coupling directly with a clear chemical interpretation of the photoexcited states involved [2,3], and in addition, we explore the potential energy surfaces (PESs) of the relevant excited states using nonadiabatic dynamics simulations [4]. Here, we present the details of our approach for calculating the electronic coupling and the preliminary results of the PESs of the relevant excited states of a biradicaloid molecule (see Figure 1), which has been previously investigated as a promising candidate for a SF chromophore [5].



**Figure 1.** The resonance structures of the biradicaloid molecule

### References

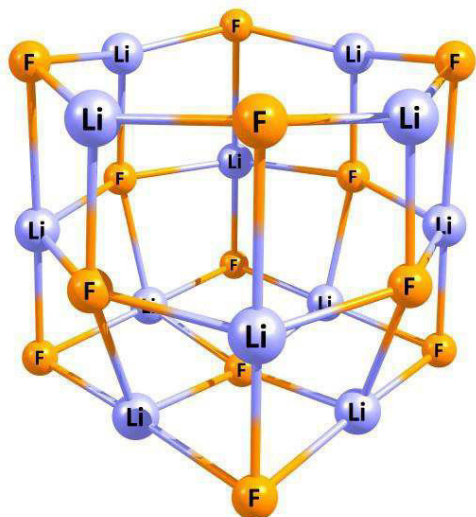
- [1] M.B. Smith, J. Michl, *Chem. Rev.* **110**, 6891 (2010).
- [2] R.W.A. Havenith, H.D. de Gier, R. Broer, *Mol. Phys.*, **110**, 2445 (2012).
- [3] M. Wibowo, R. Broer, R.W.A. Havenith (in preparation).
- [4] M. Persico, G. Granucci, *Theor. Chem. Acc.* **133**, 1526 (2014).
- [5] A. Akdag, Z. Havlas, J. Michl, *J. Am. Chem. Soc.* **134**, 14624 (2012).

## Polynuclear $\text{Li}_{12}\text{F}_{13}^-$ superhalogen anion as a steric shielding agent with respect to selected metal ions

Marcin Czapla<sup>1</sup>

<sup>1</sup>Laboratory of Quantum Chemistry, Faculty of Chemistry University of Gdańsk  
Wita Stwosza 63, 80-308 Gdańsk, Poland

Polynuclear superhalogen anion  $\text{Li}_{12}\text{F}_{13}^-$  and its ionic complexes formed by the interaction with selected metal cations (i.e.,  $\text{Li}_{12}\text{F}_{13}^-\text{Na}^+$ ,  $\text{Li}_{12}\text{F}_{13}^-\text{K}^+$ ,  $\text{Li}_{12}\text{F}_{13}^-\text{Mg}^{2+}$ , and  $\text{Li}_{12}\text{F}_{13}^-\text{Zn}^{2+}$ ) were proposed and investigated on the basis of ab initio calculations [1]. The thermodynamic stability, vertical excess electron detachment energy, and binding energies between ionic components were examined and discussed.



The  $\text{Li}_{12}\text{F}_{13}^-$  anion has been proved stable against fragmentation and its vertical electronic stability was found to approach 10 eV. Due to its specific equilibrium structure that resembles a molecular basket, the  $\text{Li}_{12}\text{F}_{13}^-$  anion was found capable of trapping positively charged metal ions inside to form strongly bound ionic complexes. The large values of binding energies predicted for the  $\text{Li}_{12}\text{F}_{13}^-\text{Na}^+$ ,  $\text{Li}_{12}\text{F}_{13}^-\text{K}^+$ ,  $\text{Li}_{12}\text{F}_{13}^-\text{Mg}^{2+}$ , and  $\text{Li}_{12}\text{F}_{13}^-\text{Zn}^{2+}$  systems and their specific equilibrium structures indicate that the  $\text{Li}_{12}\text{F}_{13}^-$  anion can be useful as a steric shielding agent which protect the metal ions from the interaction with the surroundings.

**Acknowledgements:** This work was supported by the Polish Ministry of Science and Higher Education (Grant Number: DS 530-8375-D499-16). The calculations have been carried out using resources provided by Wrocław Centre for Networking and Supercomputing (<http://wcss.pl>) Grant No. 350.

[1] M. Czapla, *Theor. Chem. Acc.* **135**, 231 (2016).

## Analytic Hyperpolarizability and Polarizability Derivative with Fractional Occupation Numbers for Large Extended Systems

Yoshio Nishimoto<sup>1</sup>

<sup>1</sup>*Fukui Institute for Fundamental Chemistry, Kyoto University, 34-4 Takano Nishibiraki-cho, Sakyo, Kyoto 606-8103, Japan*

A problem in the calculation for large extended systems is the steep increase of the computational cost, but another problem is the difficulty of SCF convergence because of a small HOMO–LUMO gap. This problem may be attributed to the fact that the orbital occupation number is integer and may be avoided by employing the fractional occupation number (FON) with reasonable computational cost.

In computing second- and higher-order derivatives, coupled-perturbed (CP) equations are usually solved. In the conventional CP equation, an explicit computation for dependent pairs can be avoided (non-canonical approach). However, with FON, one additionally has to consider the response term in partially occupied orbitals. The response term may be extremely large when degenerated orbitals are partially occupied, and the convergence of CP equations is then challenging. In an earlier study [1], we solved the problem in the first-order CP equation and made it possible to compute a second-order geometrical derivative. In the present study [2], we derived and implemented analytic third-order derivatives (hyperpolarizability and polarizability derivative) with FON. The expression obtained here employs limit values when the difference of orbital energies is small and is therefore applicable to the computation of third-order derivatives for the system with degenerated orbitals. The derived equations for the density-functional tight-binding (DFTB) method were implemented into GAMESS-US. We verified that calculated spectra with the implementation are accurate.

The developed method was applied to a series of zigzag-type graphene nanoribbon (ZGNR). By performing a parallel calculation for a ZGNR consisting of 1012 atoms using four E5-1650 v3 calculation node (24 CPU cores in total), a computation of energy, gradient, Hessian, dipole derivative, hyperpolarizability, and polarizability derivative of the ZGNR finished in 7.55 hours. The scaling of the computational cost was 3.98 with respect to the number of atoms. We expect that the developed method is useful in simulating infrared and non-resonance Raman spectra of large extended systems.

### References

- [1] Y. Nishimoto, S. Irle, *Chem. Phys. Lett.* **667**, 317–321 (2017).
- [2] Y. Nishimoto, *J. Chem. Phys.* **146**, 084101 (2017).

## Trends in catalytic activity of Ni-based electrodes for the hydrogen evolution reaction

Hannah Schlott<sup>1</sup>, Marc Ledendecker<sup>2</sup>, Markus Antonietti<sup>3</sup>, Bernd Meyer<sup>1</sup>,  
Menny Shalom<sup>4</sup>

<sup>1</sup>*Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center,  
Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*

<sup>2</sup>*Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany*

<sup>3</sup>*Max-Planck-Institute of Colloids and Interfaces, Potsdam, Germany*

<sup>4</sup>*Chemistry Department, Ben Gurion University of the Negev, Israel*

Metallic binary compounds have emerged in recent years as highly active and stable electrocatalysts toward the hydrogen evolution reaction. The origin of their high activity from a theoretical and experimental point of view is elucidated. Different metallic ceramics ( $\text{Ni}_3\text{S}_2$ ,  $\text{Ni}_3\text{N}$ , and  $\text{Ni}_5\text{P}_4$ ) are grown directly on Ni support in order to avoid any contaminations. DFT calculations were performed to obtain a deeper understanding of possible active adsorption sites and the observed catalytic stability. It is found that the heteroatoms P, S, and N actively take part in the reaction. Due to the anisotropic nature of the materials, a variety of adsorption sites with highly coverage-dependent properties exist, leading to a general shift in hydrogen adsorption free energies  $\Delta G_{\text{H}}$  close to zero. Extending the knowledge gained about the here described materials, a new catalyst is prepared by modifying a high surface Ni foam, for which current densities up to  $100 \text{ mA cm}^{-2}$  at around 0.15 V are obtained.

- [1] M. Ledendecker, H. Schlott, M. Antonietti, B. Meyer, M. Shalom, *Adv. Energy Mater.*, 1601735 (2016).

## Improving the thermodynamics and transferability of coarse-grained models

Thomas D. Potter<sup>1</sup>, Mark R. Wilson<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Durham University, South Road, Durham, United Kingdom*

Coarse-grained (CG) simulations are becoming increasingly important for the modelling of soft matter systems, due to their ability to study large system sizes over long time scales. Common methods for parametrising CG models include iterative Boltzmann inversion (IBI) [1] and force matching [2]. While these usually give good structural accuracy, they often yield interaction potentials with poor transferability to different state points. This is mainly due to the fact that the pair potentials only include multi-body effects in an averaged out way, which is only correct at the state point at which the potential was parametrised. The thermodynamic accuracy of these CG models is often poor, particularly in reproducing free energies of mixing, which we have shown for a range of octane/benzene mixtures.

We show that parametrising CG models from multiple state points, using multistate IBI [3], can help with the problem of poor transferability in some circumstances. However, there are still issues with this approach. The resulting models do not necessarily improve upon the accuracy of calculated thermodynamic quantities relative to models derived from a single reference point. It has been proposed that including a correction to the pair potential, which depends on the local environment of the CG bead, could lead to improved accuracy and transferability. Here, we propose a method to parametrise such a potential, which aims to keep the structural accuracy of a CG model parametrised at a single state point, but provides more accurate thermodynamic quantities and is transferable over a range of concentrations and temperatures.

[1] D. Reith, M. Putz, F. Muller-Plathe, *J. Comput. Chem.* **24**, 1624 (2003).

[2] S. Izvekov, G. A. Voth, *J. Phys. Chem. B* **109**, 2469 (2005).

[3] T. C. Moore, C. R. Iacovella, C. McCabe, *J. Chem. Phys.* **140**, 224104 (2014).

## Exploring Multistep Intersystem Crossing Pathways of Cinnamate-Based Sunscreens by Automated Reaction Path Search Methods

Kaoru Yamazaki<sup>1,2</sup>, Yasunori Miyazaki<sup>3</sup>, Yu Harabuchi<sup>2</sup>, Tetsuya Taketsugu<sup>2</sup>,  
Satoshi Maeda<sup>2</sup>, Yuuki Onitsuka<sup>3</sup>, Hiroshi Kohguchi<sup>3</sup>, Masahiro Ehara<sup>4</sup>,  
Takayuki Ebata<sup>3</sup>

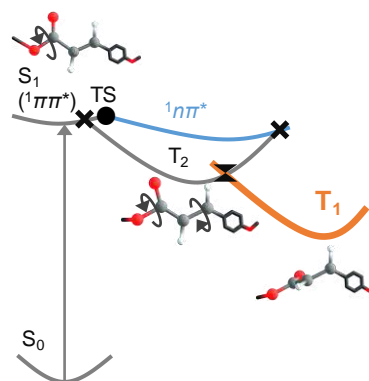
<sup>1</sup> Institute for Materials Research, Tohoku University,  
2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

<sup>2</sup> Department of Chemistry, Faculty of Science,  
Hokkaido University, Sapporo 060-0810, Japan

<sup>3</sup> Department of Chemistry, Graduate School of Science,  
Hiroshima University, Higashi-Hiroshima 739-8526, Japan

<sup>4</sup> Institute for Molecular Science, 38 Myodaiji, Okazaki 444-8585, Japan

Cinnamate derivatives are widely used molecules in the nature as the chromophore of photo-active yellow protein, sunscreens of many plants to protect their DNA *etc.* Understanding the nonradiative decay (NRD) mechanisms should realize new effective sunscreens and other photofunctional materials. In this study, we investigated the NRD pathways of jet-cooled *para*-methoxy methylcinnamate (*p*-MMC) and *para*-methoxy ethylcinnamate (*p*-MEC) by picosecond and nanosecond pump-probe spectroscopy. The possible NRD pathways were calculated by the single component artificial force induced method [1] combined with the (time-dependent) density functional theory.



**Figure 1.** Schematic of the multi-step ISC pathway of *p*-MMC

We found that *p*-MMC and *p*-MEC at low excess energy undergo multistep intersystem crossing (ISC) from the bright  $S_1$  ( $^1\pi\pi^*$ ) state to the  $T_1$  ( $^3\pi\pi^*$ ) state mostly via stepwise ISC through  $T_2$  state followed by the internal conversion from  $S_1$  to the dark  $^1n\pi^*$  state in  $\sim 100$  ps as shown in Figure 1 [2]. This multistep ISC results in the torsion of  $C=C$  double bond by  $\sim 95^\circ$  in the  $T_1$  state [2]. This result suggests that the ISC processes play an indispensable role in the photo-protecting sunscreens in natural plants.

[1] A recent review: S. Maeda *et al.*, *Chem. Rec.* **16**, 2232 (2016)

[2] K. Yamazaki *et al.*, *J. Phys. Chem. Lett.* **7**, 4001 (2016)

## Trajectory Surface Hopping Study of the Photodissociation Dynamics of Phenol

Weiwei Xie and Wolfgang Domcke

*Department of Chemistry, Technical University of Munich, Lichtenbergstr. 4, 85747  
Garching, Germany*

Nonadiabatic transitions between adiabatic potential-energy surfaces, especially at conical intersections, are ubiquitously involved in the photophysics and photochemistry of polyatomic molecules. Because a full quantum treatment of the coupled dynamics of electrons and nuclei is computationally highly demanding for polyatomic molecules, the quasi-classical trajectory surface-hopping (TSH) model, in which the electrons are described quantum mechanically and the nuclear motion classically, is an attractive alternative to full quantum dynamics for the simulation of nonadiabatic photochemical processes. Two well-established approximations for the modeling of non-classical electronic transitions are the time-honored Landau-Zener (LZ) formula [1] and Tully's fewest switching (TFS) algorithm [2]. In the present study, the accuracy of these two TSH algorithms has been critically evaluated in comparison with exact nonadiabatic quantum dynamics calculations for a model of the photoinduced hydrogen-atom elimination reaction in phenol. The model comprises three electronic states ( $S_0$ ,  $^1\pi\pi^*$ ,  $^1\pi\sigma^*$ ), two nuclear degrees of freedom (the OH stretching coordinate and the CCOH torsional angle) and exhibits two conical intersections ( $^1\pi\pi^*/^1\pi\sigma^*$  and  $^1\pi\sigma^*/S_0$ ) [3]. Considering photoexcitation from different vibrational levels of the  $S_0$  state to the  $^1\pi\pi^*$  state, we examined the time-dependent electronic population dynamics as well as the branching ratio of the two dissociation channels. The results of fully converged TSH calculations (up to  $10^5$  trajectories) are compared with the results of exact quantum wave-packet calculations. When an even number of quanta is initially populated in the torsional mode (which is the coupling mode at both conical intersections), both TSH methods qualitatively reproduce the time-dependent electronic population dynamics, but are inaccurate in the prediction of the electronic branching ratio. When an odd number of quanta is initially prepared in the torsional mode, the population dynamics of the  $^1\pi\pi^*$  state is reproduced with reasonable accuracy, but both TSH algorithms fail to reproduce the time evolution of the populations of the  $^1\pi\sigma^*$  and  $S_0$  states and the electronic branching ratio. The failures of the TSH methods can be attributed to the importance of nonadiabatic tunneling effects in the photodissociation of phenol.

### References

- [1] L. D. Landau, *Phys. Zeitschr. Sov.* **2**, 46 (1932); C. Zener, *Proc. Roy. Soc. A* **137**, 696 (1932).
- [2] J. C. Tully, *J. Chem. Phys.* **93**, 1061 (1990).
- [3] Z. Lan, W. Domcke, V. Vallet, A. L. Sobolewski, S. Mahapatra, *J. Chem. Phys.* **122**, 224315 (2005).



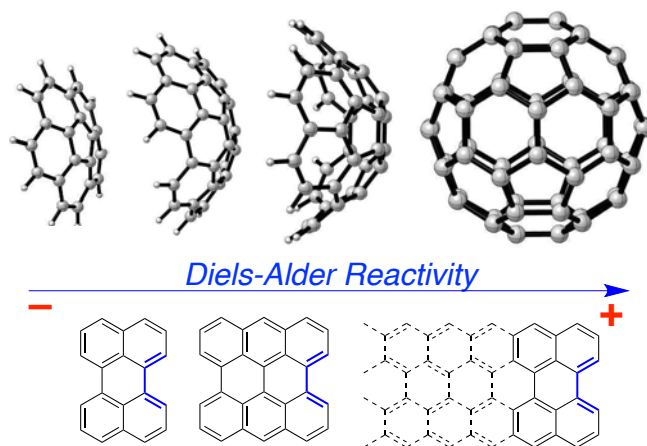
## Reactivity and Selectivity of Polycyclic Aromatic Hydrocarbons: Shape and Size Dependence

Yago García-Rodeja<sup>1</sup>, Israel Fernández<sup>1,\*</sup>

<sup>1</sup>*Departamento de Química Orgánica I, Facultad de CC. Químicas, Universidad Complutense de Madrid, 28040-Madrid, Spain, e-mail: israel@quim.ucm.es*

The Diels-Alder reactivity and selectivity of Polycyclic Aromatic Hydrocarbons (PAHs) have been explored computationally within the DFT framework. To this end, the [4+2]-cycloaddition reactions between maleic anhydride and both planar PAHs<sup>[1]</sup> and buckybowl<sup>[2]</sup> have been considered.

For bowl-shaped PAHs, it was found that there is a smooth convergence to the C<sub>60</sub> barrier energy if the size of the buckybowl is increased.<sup>[3]</sup> Similarly, the process involving the bay regions of planar PHAs becomes more and more exothermic and the associated activation barriers become lower and lower when the size of the system increases.<sup>[4]</sup> This enhanced reactivity follows an exponential behavior that reaches its maximum for systems having 18–20 benzenoid rings in their structures, a value which can be extrapolated for the analogous process involving graphene. The origins of these reactivity trends have been quantitatively analyzed by means of the Activation Strain Model<sup>[5]</sup> (ASM) of reactivity in combination with the Energy Decomposition Analysis (EDA) method.



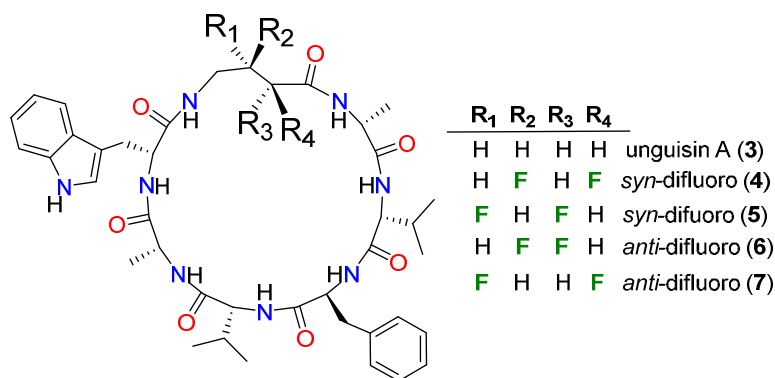
- [1] E. H. Fort, P. M. Donovan, L. T. Scott, *J. Am. Chem. Soc.* **131**, 16006 (2009).
- [2] L.T. Scott, *Chem. Soc. Rev.* **44**, 6464 (2015).
- [3] Y. García-Rodeja, M. Solà, F. M. Bickelhaupt, I. Fernández, *Chem. Eur. J.* **22**, 1368 (2016).
- [4] Y. García-Rodeja, M. Solà, I. Fernández, *Chem. Eur. J.* **22**, 10572 (2016).
- [5] I. Fernández, F. M. Bickelhaupt, *Chem. Soc. Rev.* **43**, 4953 (2014).

## Conformational Changes Induced by Fluorination: Extended Molecular Dynamics of Unguisin Peptides

Natalia Díaz<sup>1</sup>, Dimas Suárez<sup>1</sup>

<sup>1</sup>*Departamento de Química Física y Analítica, Universidad de Oviedo,  
Avda. Julián Clavería 8, Oviedo (Asturias), Spain*

Stereoselective fluorination constitutes a valuable strategy to fine-tuning the conformation of functional molecules [1]. Potential applications in medicinal chemistry and biotechnology arise from the introduction of fluorine atoms in peptides because these are flexible systems where conformation determines function. Unguisin A is a natural macrocyclic heptapeptide that incorporates  $\gamma$ -aminobutyric acid (GABA) as one of the amino acid residues. Besides natural unguisin A, four stereoisomers of the GABA analog 2,3-difluoro-4-aminobutyric acid have been synthesized and their structures analyzed by nuclear magnetic resonance and molecular modeling [2]. To complement the previous results, we perform extensive molecular dynamics simulations in DMSO solution in order to explore the conformational space accessible to natural unguisin A and the four fluorinated variants. To parametrize the non-standard GABA residue in **3-7**, atomic charges are adjusted to reproduce the electrostatic potential computed for different conformers of the molecule and selected torsional angles along the GABA main chain are refined. For each trajectory, structural analysis of polar and hydrophobic contacts, conformational clustering, and quantum mechanical energy calculations are carried out to provide an accurate description of the fluorine-substitution effects.



[1] L. Hunter, *Beilstein J. Org. Chem.* **6**, No. 38 (2010).

[2] X.-G. Hu, D. S. Thomas, R. Griffith, L. Hunter, *Angew. Chem. Int. Ed.* **53**, 6176 (2014).

## Development of the Quantitative Structure-Property Relationships (QSPR) for Predicting Char Yield of Polybenzoxazines

M. Sairi<sup>1</sup>, B. J. Howlin<sup>1</sup>, I. Hamerton<sup>2</sup>

<sup>1</sup>Department of Chemistry, University of Surrey, Guildford, GU2 7XH, United Kingdom.

<sup>2</sup> Bristol Composites Institute (ACCIS), Department of Aerospace Engineering, University of Bristol, Queen's Building, University Walk, Bristol, BS8 1TR, United Kingdom.

Polybenzoxazines (pBox) are a relatively new addition to the family of thermoset polymers and offer great potential in fire resistant applications. Depending on the monomer structure employed, pBox can form char yields of up to 81 %. The char acts as a surface barrier which insulates and slows the escape of volatile decomposition gases into the fire front, thus protecting the remaining virgin materials from further degradation and resulting a slower fire spread across the area. Benzoxazines polymerise through a ring opening polymerisation reaction to form a highly crosslinked network and the presence of an additional polymerisable functional group in some of the benzoxazines, *e.g.* acetylenic, provides further crosslinks in the polymer system (Figure 1).

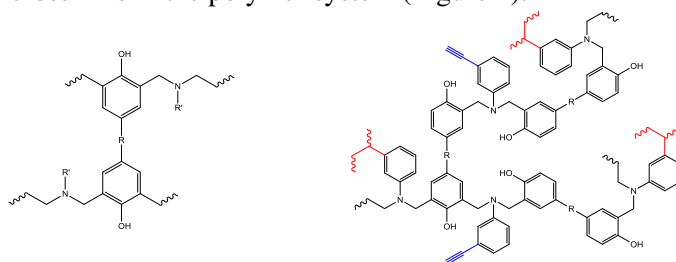


Figure 1. Possible crosslinked system in (left) polybenzoxazines and (right) polybenzoxazines with polymerisable functional group (R and R' = alkyl or phenyl).

In this work, a prediction model based on Quantitative Structure-Property Relationships (QSPR) was successfully generated to provide a tool for predicting the percentage char yield formed by pBox. This provides a picture of which structure will lead to a pBox with higher char yield and better flame resistance prior to synthesis. A data set containing thirty-three pBox structures with their experimental percentage char yields were collected from various sources. These were then compiled and used in the model development. This data set is considered small when compared to the analogous, Quantitative Structure-Activity Relationships (QSAR) method which normally works with thousands of data for the same purpose. The small data is due to the limited data available in the polymer literature. We have adapted the QSAR method, which has been widely used in medicinal and pharmaceutical industries to polymers and the unique idea in this method is, to use monomer structures of the polymers of interest, rather than simulating the complex network structure of polymer system to develop the model. Despite the small data set used, the model has proven to be successful in providing prediction data with outstanding agreement to the experimental values, with an average error of less than 5% [1]. The generated model also shows impressive statistics for its predictive power over a series of internal and external validation tests as well as better predictions than the Van Krevelen group contribution prediction method. The model has performed well despite the limitations and we believe that this method has a great potential in years to come.

[1] M. Sairi, B. Howlin, and I. Hamerton, *Polymers*, **8**, 166 (2016).

## Embedding metal atoms in icosahedral structures: biicosahedral metallaboranes as three-dimensional analogues of naphthalene

**Alexandru Lupan<sup>1</sup>, Amr A.A. Attia<sup>1</sup>, R. Bruce King<sup>2</sup>**

<sup>1</sup>*Department of Chemistry, Faculty of Chemistry and Chemical Engineering,  
Babeş-Bolyai University, Cluj-Napoca, Romania*

<sup>2</sup>*Department of Chemistry and Center for Computational Quantum Chemistry,  
The University of Georgia, Athens, GA, United States*

Boron chemistry allows the concept of aromaticity to be extended from the two-dimensional planar hydrocarbon systems constructed with hexagonal benzene rings to three-dimensional borane deltahedra. The structures based on icosahedra (Fig. 1) such as the  $B_{12}H_{12}^{2-}$  dianion and the isoelectronic carboranes exhibit special stability. Very stable metallaboranes and metallacarboranes are obtained by substituting BH vertices with transition metal units such as cyclopentadienylmetal vertices [1].

Consideration of the well-known very stable icosahedral  $B_{12}H_{12}^{2-}$  as a three-dimensional analogue of benzene was extended by the recent synthesis of the biicosahedral  $B_{21}H_{18}^-$  as a three-dimensional analogue of naphthalene. The preferred structures of metallaboranes derived from  $B_{21}H_{18}^-$  have been examined by density functional theory [2]. The isoelectronic species  $CpNiB_{20}H_{17}$  and  $CpCoCB_{19}H_{17}$  have the 46 skeletal electrons expected by the Wade-Mingos and Jemmis rules for a structure consisting of two face-sharing icosahedra. The CpM units in these structures energetically prefer to be located at a meta vertex of the biicosahedron. The analogous ferraboranes  $CpFeB_{20}H_{17}$  with only 44 skeletal electrons also have related biicosahedral structures. The presence of an agostic hydrogen atom bridging an Fe–B edge compensates for the two-electron deficiency in  $CpFeB_{20}H_{17}$  relative to  $CpNiB_{20}H_{17}$ . The nucleus-independent chemical shift (NICS) values of these systems indicate them to be strongly aromatic.

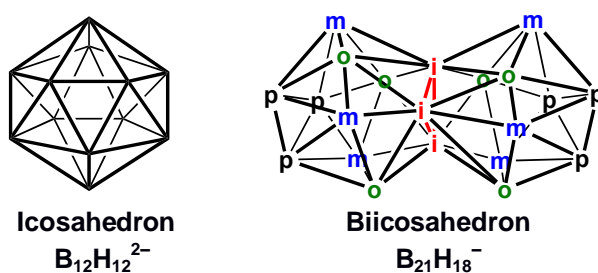


Figure 1. Comparison of the icosahedral structure of  $B_{12}H_{12}^{2-}$  and the biicosahedral structure of  $B_{21}H_{18}^-$ . The ipso (i), ortho (o), meta (m) and para (p) vertices are labeled.

[1] A. A. Attia, A. Lupan, R. B. King, *J. Comput. Chem.* **37**, 64 (2016).

[2] A. A. Attia, A. Lupan, R. B. King, *Phys. Chem. Chem. Phys.* **18**, 11707 (2016).

## **Towards Rationalizing the Trends in the Electronic Structure of MX<sub>2</sub> 3d Transition Metal Dihalide Monolayers**

**Cheng-chau Chiu<sup>1</sup>, Chung-Yu Wang<sup>1</sup>, Bo-Jie Huang<sup>1</sup>, Jer-Lai Kuo<sup>1</sup>**

*<sup>1</sup>Institute of Atomic and Molecular Sciences, Academia Sinica,  
No. 1, Roosevelt Rd., Sec. 4, Taipei, 10617, Taiwan*

Due to their wide possibilities of applications, monolayers formed by transition metal dichalcogenides, like MoS<sub>2</sub> have been in the focus of recent research. At variance, the interest in the isostructural transition metal dihalide monolayers is yet comparatively low. Only a few studies have been conducted to explore such species in a systematic way. [1,2]

In this study, we use periodic DFT methods at both LDA and GGA level to investigate, which combinations of 3d-transition metal and halide anion can form stable structures that may eventually be synthesized, and try to predict their electronic properties.

A somewhat surprising finding is that the valence isoelectronicity principle seems to only hold partially here: MX<sub>2</sub> monolayers formed by the same metal but different halide anions seem to have different ground state electronic structures with differing magnetic moments. In addition, we see that there are some differences between the electronic structures predicted by LDA and GGA calculations. Both findings are associated with differences in the relative stability between high spin and low spin states. We will try to illustrate that, despite the differences between the LDA and GGA data, the results obtained with the two types of functionals follow the same trend.

[1]S.-H. Lin, J.-L. Kuo, *Chem. Phys. Phys. Chem.* **16**, 20763 (2014)

[2]P. Miró, M. Audiffred, T. Heine, *Chem. Soc. Rev.* **43**, 6537 (2014)

## Rapid, accurate, precise and reliable relative free energy prediction using ensemble based thermodynamic integration

**Agastya P. Bhati, Shunzhou Wan, David W. Wright, and Peter V. Coveney**

*Centre for Computational Science, Department of Chemistry, University College London,  
20 Gordon Street, London WC1H 0AJ, United Kingdom*

The accurate prediction of the binding affinities of ligands to proteins is a major goal in drug discovery and personalised medicine. The use of *in silico* methods to predict binding affinities has been largely confined to academic research until recently, primarily due to the lack of their reproducibility, as well as lack of accuracy and time to solution. In the last few years, an ensemble based molecular dynamics approach, called ESMACS, has been proposed that provides a route to reliable predictions of free energies meeting the requirements of speed, accuracy, precision and reliability.[1-3] Here, we describe our approach to thermodynamic integration, known as TIES, which substantially improves the speed, accuracy, precision and reliability of calculated relative binding free energies.[4] We report the performance of TIES when applied to a diverse set of protein targets and ligands. The results are in very good agreement with experimental data (90% of the predictions agree to within 1 kcal/mol) while the method is reproducible by construction. Statistical uncertainties of the order of 0.5 kcal/mol or less are achieved. Work is ongoing to extend the application of TIES to calculate the relative binding affinities of protein mutations (TIES\_PM). This methodology, which is being pursued in the CompBioMed Centre of Excellence (<http://www.compbiomed.eu/>), has the potential to positively impact the drug design process in the pharmaceutical domain as well as in personalised medicine, with concomitant major industrial and societal impact. TIES is an automated workflow that can be completely run in 8 hours or less, depending on the architecture and hardware available. To exhibit this feature as well as the excellent scalability of TIES, in an unprecedented study we harnessed the combined power of Phases 1 and 2 of PRACE's Tier-0 SuperMUC at the Leibniz Rechenzentrum in Garching, resulting in accurate relative binding affinity predictions of more than 50 biomolecular systems[5] at a sustained performance in excess of 1 petasflop throughout.

[1.] Sadiq S. K.; Wright D. W.; Kenway O. A.; Coveney P. V. *J. Chem. Inf. Model.* **2010**, 50, 890, DOI: 10.1021/ci100007w

[2.] Wright D. W.; Hall B. A.; Kenway O. A.; Jha S.; Coveney P. V. *J. Chem. Theory Comput.* **2014**, 10, 1228, DOI: 10.1021/ct4007037

[3.] Wan S.; Knapp B.; Wright D. W.; Deane C. M.; Coveney P. V. *J. Chem. Theory Comput.* **2015**, 11, 3346, DOI: 10.1021/acs.jctc.5b00179

[4.] Bhati A. P.; Wan S.; Wright D. W.; Coveney P. V. *J. of Chem. Theory Comput.* **2017**, 13(1), 210-222, DOI: 10.1021/acs.jctc.6b00979

[5.] Highfield R. Science Museum Blog. <https://blog.sciencemuseum.org.uk/supercomputer-bid-to-create-the-first-truly-personalised-medicine/>

---

**Molecular Modeling, Docking, NBO, and Vibrational Studies of New  $\alpha$ -aminophosphonates as Antitumor Agents Targeting MCF7**

**Mohamed K. Awad, Faten M. Atlam, Hend A. Hekal**

*Theoretical Applied Chemistry Unit (TACU), Chemistry Department, Faculty of Science,  
Tanta University, 31527, Egypt*

The quantum chemical calculations are performed using density functional theory (DFT) to study the effect of the molecular and electronic structures on the biological activity of the investigated compounds. A novel series of Diphenyl (aryl) (4-oxo-quinazolin-4(3H)-ylamino) methyl phosphonates 3a-3d is obtained from the reactions of 3-amino-4(3H)-quinazolinone with different aromatic aldehydes and triphenylphosphite in the presence of copper triflate as a Lewis acid catalyst. The calculations show that the electron-withdrawing substituent increases the biological activity of the  $\alpha$ -aminophosphonates more than the electron donating group which was in a good agreement with the experimental results. Also, a good agreement between the experimental FT-IR and the calculated one was found. From NBO study, the sum of the total values of stabilization energies  $E(2)$  for compound 3b are much greater than those of compound 3c which leads to increase the conjugated interaction in compound 3b and reduced the gap energy which shifts the absorption wave length near IR region and thus enhances the efficiency of compound 3b as photocurrent compound. The molecular docking simulation is done to show the mode of interaction between the studied molecules and MCF7-cell line.

## **The Master Factors Influencing the Potency of BACE-1 Alzheimer Inhibitors: Computational & Molecular Docking Studies**

**Faten M. Atlam, Mohamed K. Awad, Rehab S. Khalil**

*Chemistry Department, Theoretical Applied Chemistry Unit (TACU), Faculty of Science,  
Tanta University, Tanta, Egypt*

Density functional theory (B3LYP/6-31G (d)) is performed to study the effect of molecular and electronic structures of the investigated BACE-1 Alzheimer inhibitors on their biological activities and discuss the correlation between their inhibition efficiencies and quantum chemical descriptors.  $IC_{50}$  values of the investigated compounds are mostly affected by the substituted  $R_2$  Phenyl ( $S_2$ ) moiety. The calculations show that the presence of electron withdrawing group increases the biological activity. SAR studies show that the electronic descriptors,  $E_{HOMO}$ ,  $\Delta E$ , lipophilicity, hardness and ionization potential index, are the most significant descriptors for the correlation with the biological activity. Molecular docking simulation is performed to explain the mode of interaction between the most potent drug and the binding sites of BACE-1 target. A good correlation between the experimental and theoretical data confirms that the quantum chemical methods are successful tools for the discovery of novel BACE-1 drugs.



## Maximum Probability Domains: Theoretical Foundations and Computational Algorithms

Guillaume Acke<sup>1</sup>, Stijn De Baerdemacker<sup>1, 2</sup>, Benoît Braïda<sup>3</sup>, Ángel Martín Pendás<sup>4</sup>, Dimitri Van Neck<sup>2</sup>, Patrick Bultinck<sup>1</sup>

<sup>1</sup>*Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 S3, 9000 Ghent, Belgium*

<sup>2</sup>*Center for Molecular Modeling, Ghent University, 9052 Zwijnaarde, Belgium*

<sup>3</sup>*Laboratoire de Chimie Théorique, CNRS and UPMC Univ Paris 6, 4 place Jussieu, 75252 Paris, France*

<sup>4</sup>*Departamento de Química Física y Analítica, Universidad de Oviedo, 33006 Oviedo, Spain*

The Lewis model of the chemical bond treats electrons as discrete pairs, localized in a certain region of space. On the other hand, the molecular orbital approach to quantum chemistry considers electrons as delocalized over the entire space. Many new ways to extract Lewis-structural information from the wave function have been suggested, providing links between quantum and traditional chemistry.

One of these novel approaches is the use of maximum probability domains (MPDs) [1, 2]. This method statistically localizes electrons in domains, by determining those regions of spin-position space for which the probability of finding a given number of electrons is maximal. This method has successfully been applied to interpret covalent and ionic bonding [3, 4]. However, MPDs have not yet been characterized by other chemical descriptors, which leaves their links with other conceptual quantities ill described. Furthermore, MPDs obtained from current implementations suffer from numerical inaccuracy, which clouds their properties [5].

In this poster, I will introduce the theory of MPDs, extend it with novel concepts and novel algorithms [6]. I will show how this theory can be applied to a range of chemical phenomena, and how this interpretation can lead to increased chemical understanding.

- [1] A. Savin, K.D. Sen (ed) In: Reviews of modern quantum chemistry. World Scientific, Singapore, 43 (2002).
- [2] E. Cancès, R. Keriven, F. Lodier, A. Savin, *Theor. Chem. Acc.*, **111**, 373-380 (2004).
- [3] M. Causà et al., *Struct. Bond*, **150**, 119-142 (2013).
- [4] M. Menéndez et al., *Comp. Theor. Chem*, **1053**, 142-149 (2015).
- [5] M. Menéndez, A. M. Pendás, *Theor. Chem. Acc.*, **133**, 1539 (2014).
- [6] G. Acke et al., *Mol. Phys.*, **114**, 7-8, 1392-1405 (2016).

**DFT studies on Catalytic CO<sub>2</sub> fixation by Monoethanolamine****Maneeporn Puripat<sup>1</sup>, Waraporn Parasuk<sup>2</sup>, Vudhichai Parasuk<sup>1,3,\*</sup>**<sup>1</sup> *Computational Chemistry Unit Cell, Department of Chemistry, Faculty of Science,  
Chulalongkorn University, Bangkok 10330, Thailand*<sup>2</sup> *Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok 10900,  
Thailand*<sup>3</sup> *Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330,  
Thailand.*

The theoretical investigation of catalytic carbon dioxide (CO<sub>2</sub>) fixation by monoethanolamine (MEA) was performed at the M06-2X/6-31+g(d,p) level to explore its reaction mechanism. The calculation results demonstrated that the most favorable pathway initially started with the nucleophilic addition of MEA on CO<sub>2</sub>, followed by proton transfer aided by the extra MEA to form carbamate ion and then carbamic acid. The carbamate ion could absorb another CO<sub>2</sub> and render MEA back for further CO<sub>2</sub> capture. However, this process could be harmed by the formation of 2-oxazolidone. Thus, the kinetic of 2-oxazolidone formation was also studied. Noticeably, thermodynamic control plays a major role to precede the reaction, which proves that 2-oxazolidone cannot take place. The degradation of MEA must proceed through another mechanism.

## Tunneling of hydrogen transfer reactions on and in interstellar ices

Thanja Lamberts<sup>1</sup>, Johannes Kästner<sup>1</sup>

<sup>1</sup>*Inst. for Theoretical Chemistry, University Stuttgart, Pfaffenwaldring 55, Stuttgart, Germany*

The darkness readily observed between the stars on a clear nightsky is far from empty. The low temperatures ( $T = 10 - 20$  K) in so-called dark molecular clouds in combination with the typical low particle densities ( $n = 10^4 \text{ cm}^{-3}$ ) make it seem unlikely for chemistry to take place efficiently. The chemistry that occurs can be partly explained by the presence of small ice-coated dust grains on which molecules freeze out. These grains thus act as a molecule reservoir, while also being an energy sink for exothermic reactions. Barriers at cryogenic temperatures can only be overcome, however, when tunneling is invoked as a crucial component of the reaction mechanism. Hydrogen is the most abundant element in the interstellar medium and many surface reactions involve hydrogen transfers, ultimately leading to the formation of saturated species such as  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_6$  [1]. Therefore, tunneling can also affect the deuterium fractionation, *i.e.*, the D/H ratio, of the products [2].

Rate constants for tunneled reactions are calculated through instanton theory, while the ice surface is taken into account via, *e.g.*, small clusters or multiscale modeling approaches (QM/MM). We elaborate on the influence of an ice environment on reaction rate constants, how and when an ice can be approximated without taking into account all degrees of freedom, and how the rate constants are to be interpreted in the light of astrochemical mean-field models and observations.

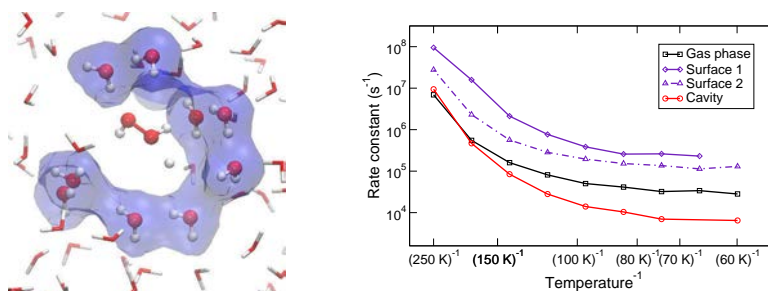


Figure 1: Left: QM/MM setup of the reaction between H and  $\text{H}_2\text{O}_2$  inside a cavity in an amorphous ice; solid spheres indicate the QM atoms. Right: Unimolecular rate constants of the same reaction in the gas phase, on a surface, and in the cavity.

- [1] T. Lamberts *et al.*, *Phys. Chem. Chem. Phys.* **18**, 33021 (2016), H. Kobayashi *et al.*, *Astrophys. J.* **837**, 155 (2017)
- [2] J. Meisner *et al.* *J. Chem. Phys.* **144**, 174303 (2016), T. Lamberts *et al.* *Astron. Astrophys.* **599**, A132 (2017)

## Proton collisions on prebiotic candidates: HCN oligomers

Marie-Christine Bacchus-Montabonel<sup>1</sup>

<sup>1</sup>*Institut Lumière Matière, Université Lyon 1, CNRS, Campus Lyon Tech la Doua, 10 rue Ada Byron, 69622 Villeurbanne cedex, France*

Among the complex organic molecules detected in space, in the interstellar medium, on meteorites or comets, special interest is devoted to the potentially exobiologic-relevant species. In the hypothesis, widely discussed, of a possible exogen origin of life, the transport of such compounds and their survival, particularly their resistance to the solar UV radiation or cosmic rays is indeed a fundamental question. Hydrogen cyanide has been detected for a long time in the interstellar medium, planetary atmospheres and even comets and appears as a feedstock molecule at the origin of life. Its easy oligomerization drives strong interest on its first polymers, cyanomethanimine and aminomalononitrile, furthermore that the E-cyanomethanimine has been detected recently in the star-forming region Sgr B2(N). We have thus undertaken a detailed theoretical study of the charge transfer collision dynamics induced by impact of HCN dimers and trimers with protons, which could be an important process in particular in proton-rich environments [1]. The present results are compared to previous studies on proton-induced damage on different prebiotic compounds, 2-aminooxazole and hydantoin, as well as DNA and RNA building blocks, nucleobases and sugar 2-deoxy-D-ribose moiety [2,3], in order to analyse the behaviour of these different possible precursors and extract some qualitative trends on damage of prebiotic species under spatial radiation.

The theoretical treatment has been developed through *ab-initio* quantum chemistry molecular calculations followed by a semiclassical collision dynamics. With regard to the various temperatures of astrophysical environments, the calculations have been carried out in a wide collision energy range. The conformational effect could be also evidenced. The charge transfer appears more efficient for these non-cyclic species than previously observed for species with a planar ring. This might induce a highest resistance in proton-induced collisions for HCN oligomers, or even for the 2-deoxy-D-ribose in its furanose form (non-planar 5-membered ring) compared to nucleobases or prebiotic compounds as 2-aminooxazole or hydantoin constructed on a planar ring. This might point out a possible sensitivity relied to the geometry of the ring. Such conclusions have however to be handled with care as they consider only reactions in the gas phase as shown by calculations considering solute-solvent interactions with a controlled analysis of water clusters [4]. Further developments are in progress.

[1]M.C. Bacchus-Montabonel, *PCCP* (2017) DOI: 10.1039/C7CP00826K.

[2]M.C. Bacchus-Montabonel, *J. Phys. Chem A* **118**, 6326 (2014); **119**, 728 (2015).

[3]M.C. Bacchus-Montabonel, *Chem. Phys. Lett* **664**, 173 (2016).

[4]M.C. Bacchus-Montabonel, F. Calvo, *Phys. Chem. Chem. Phys.* **17**, 9629 (2015).

## Active Site Protonation and the Reactivation of Acetylcholine Esterase

Etienne Derat<sup>1</sup>, Thomas Driant<sup>1,2</sup>, Paul Bauer<sup>2</sup>, Shina Caroline Lynn Kamerlin<sup>2</sup>

<sup>1</sup>*Institut Parisien de Chimie Moléculaire, UMR 8232, Université Pierre et Marie Curie, 4 place Jussieu, Paris, France*

<sup>2</sup>*Department of Cell and Molecular Biology, Uppsala University, BMC Box 596, S-751 24 Uppsala, Sweden*

Organophosphorus compounds such as Tabun, VX or sarin, are highly potent neurotoxins that target the enzyme acetylcholine esterase (AChE). This enzyme is a member of the serine protease family, with a major role in neurotransmission. When AChE is inhibited, cholinergic synapses are overactivated, leading to either death by respiratory system failure, or permanent and severe neurological conditions. Since AChE inhibitors are covalently linked to one of the key residues of the active site, reversibility is not spontaneous. Current strategies for reactivation are therefore based on strong nucleophiles [1] but show limited applicability despite decades of research in this area.

A few years ago, our group demonstrated that the inhibition mechanism could be more complex than previously envisaged [2], due to hydrophobic interactions and a network of hydrogen bonds. Thus, when the reactivation simulation project was started, careful attention was devoted to the protonation of key active site residues. By using highly correlated QM/MM calculations (Figure 1), it was shown that the key parameter for reactivation is not nucleophilicity of the reactivator but its acid/base properties in the active site [3]. On this basis, as well as new work using free energy reactive molecular dynamics, a novel mechanism of reactivation that maintains the protonation state of key active site residues that does not rely on the main entrance channel will be shown.

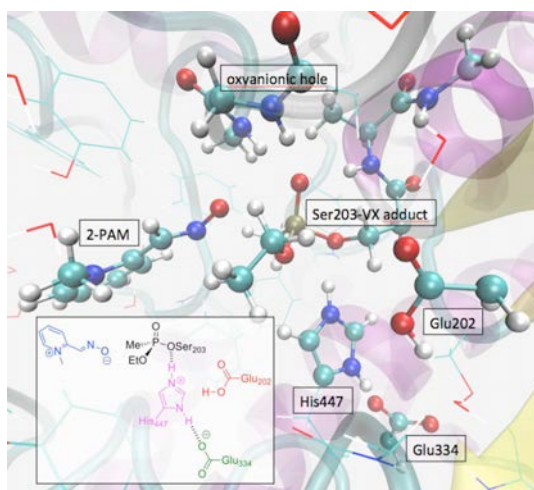


Figure 1: View of the active site of AChE, inhibited by an organophosphorous and in presence of a common reactivator (2-PAM).

Acknowledgments: French DoD (Ph.D. Thesis to T.D.) and EMBO for a visiting fellowship

[1] G. Mercey, T. Verdelet, J. Renou, M. Kliachyna, R. Baati, F. Nachon, L. Jean, P.-Y. Renard, *Acc. Chem. Res.* **45**, 756 (2012).

[2] O. Kwasnieski, L. Verdier, M. Malacria, E. Derat, *J. Phys. Chem. B* **113**, 10001 (2009).

[3] T. Driant, F. Nachon, C. Ollivier, P.-Y. Renard, E. Derat, *ChemBioChem* (2017), DOI 10.1002/cbic.201600646.

## Splitting the Coulomb Hole into its Dynamic and Nondynamic parts

**M. Via-Nadal<sup>1</sup>, M. Rodriguez-Mayorga<sup>1,2</sup>, E. Ramos-Cordoba<sup>1,3</sup>, E. Matito<sup>1,4</sup>**

<sup>1</sup>*Donostia International Physics Center (DIPC) & Kimika Fakultatea, Euskal Herriko Unibertsitatea (EHU), Donostia-San Sebastián (Spain)*

<sup>2</sup>*Institut de Química Computacional i Catàlisi (IQCC) & Departament de Química, Universitat de Girona (UdG), Girona (Spain)*

<sup>3</sup>*Department of Chemistry, University of California Berkeley, California (USA)*

<sup>4</sup>*IKERBASQUE, Basque Foundation for Science, Bilbao (Spain)*

The account of electron correlation in quantum calculations is a most important challenge in current computational chemistry. Whereas the dynamic part of electron correlation accounts for the interactions due to the movement of the electrons, the nondynamic correlation is important in systems where the ground state cannot be described by a single determinant.

The wavefunction includes information regarding electron-electron interactions. However, it becomes more intuitive to use the pair probability (or reduced two-electron density matrix). The intracule density [1], a contraction of the pair probability, is the probability function for the interelectronic vector that retains the information of electron correlation, but with the advantage of working with functions of lower dimensionality.

The introduction of electron correlation decreases the probability of finding two electrons close to each other, and in turn the probability of finding them in longer interelectronic distances increases. This consequence of electron repulsion can be easily assessed by means of the Coulomb hole, defined as the difference between the exact or FCI (correlated reference) intracule and the HF (uncorrelated reference) intracule densities [2]. In our approach, we use the Hartree-Fock-like (HFL) density matrix functional as a qualitative separator between the dynamic and nondynamic correlation parts [3].

In this context, a systematic study over a group of diverse diatomic molecules has been performed with the aim to assess the magnitude of the electron correlation, and to reveal the nature of the type of correlation present in the molecule.

- [1] A. K. Thakkar, *Density Matrices and Density Functionals*, 553, Reidel Publishing Company (1987).
- [2] C. A. Coulson and A. H. Neilson, *Proc. Phys. Soc. London* **78**, 831 (1961).
- [3] E. Ramos-Cordoba, P. Salvador and E. Matito. *Phys. Chem. Chem. Phys.* **18**, 24015 (2016).

## Protein Oxidation mechanisms via OH radical

**Jon Uranga<sup>1</sup>, Jon I. Mujika<sup>1</sup>, Rafael Grande<sup>1</sup>, Eloy Ramos-Cordoba<sup>1,2</sup>, Oier Lakuntza<sup>3</sup>, Jon M. Matxain<sup>1</sup>**

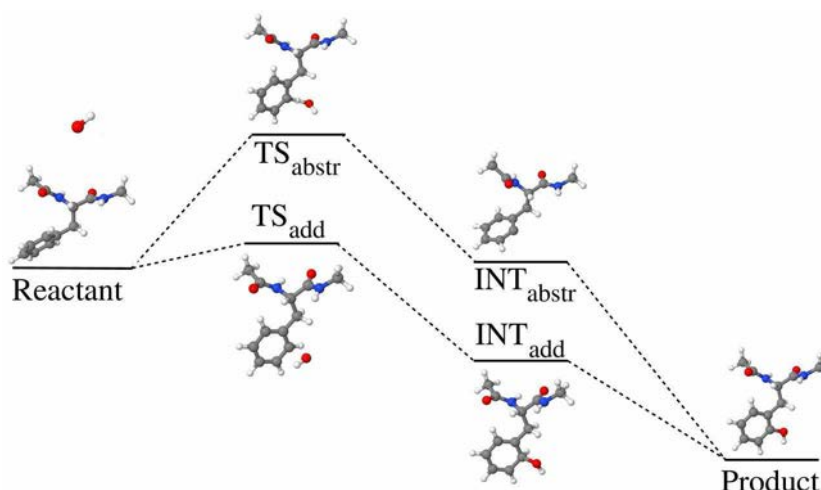
<sup>1</sup>*Euskal Herriko Unibertsitatea (UPV/EHU) and Donostia International Physics Center (DIPC), PK 1072, 20080 Donostia, Spain*

<sup>2</sup>*Department of Chemistry, University of California Berkeley, 94720 Berkeley, CA, USA*

<sup>3</sup>*Institut Català d'Investigació Química (ICIQ), Av. Països Catalans, 16, 43007, Tarragona, Spain*

Proteins perform a wide variety of essential tasks in an organism. However, their oxidation is an unavoidable process which could render structural changes or even enzyme inactivation. In this sense, the main responsible for such oxidation event are reactive species, chemically unstable species which promote oxidation. Those species are accidentally formed from time to time and have been related to aging [1]. Carbonyl groups are common oxidized products, usually employed as markers to reveal the oxidation level. On the other hand, protein oxidation yield selective backbone cleavage which is applied in sequencing.

Overall, protein oxidation is of great interest, due to the consequences that brings to the macromolecule and its possible applications. In essence, this work is devoted to the understanding of the oxidation reaction involving the hydroxyl radical ( $\cdot\text{OH}$ ) and proteins. Different reaction mechanisms were systematically analyzed with the purpose of ranking the most vulnerable locations at the side chains. Moreover, possible oxidized products are considered and discussed as well as their relevance.



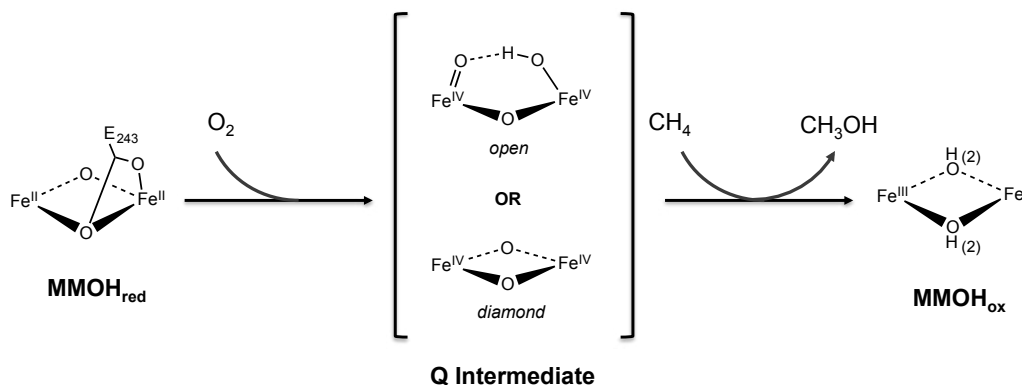
[1] D. Harman, *J. Gerontol.* **11**, 298 (1956).

## QM/MM Investigation of Structure–Spectroscopy Correlations in the Intermediate Q of Soluble Methane Monooxygenase

Christine Schulz, Serena DeBeer, Frank Neese, Dimitrios A. Pantazis

Max Planck Institute for Chemical Energy Conversion, Stiftstr. 34-36,  
45470 Mülheim an der Ruhr, Germany

In nature methanol is produced by methane monooxygenase, a metalloenzyme expressed with a dicopper core as a membrane protein or, in case of copper deficiency, with a diiron core as soluble methane monooxygenase (sMMO). Although several catalytic intermediates have been identified spectroscopically, the electronic structure of the reactive intermediate Q formed in the final step before binding and activation of methane remains under debate. There is contradictory support for either a diamond (bis- $\mu$ -oxo) or an open ( $\mu$ -oxo) core<sup>[1]</sup> from different spectroscopic techniques and computational studies, with the diamond core being favored so far. However, new spectroscopic studies<sup>[2]</sup> furnish evidence in favor of an open core structure, which would be more consistent with the fact that biomimetic model complexes with an open core motif show higher activity in methanol production.<sup>[3]</sup> Here we revisit the active site of sMMO with an updated set of models and spectroscopy-oriented quantum chemical calculations to provide an experimentally consistent interpretation of the electronic and geometric structure of intermediate Q.



- [1] M. O. Ross, A. C. Rosenzweig, *J Biol Inorg Chem.* **22**, 307 (2017)
- [2] R. G. Castillo, R. Banerjee, C. Alpres, G. Rhode, E. Bill, L. Que, J. Lipscomb, S. DeBeer, *manuscript in preparation*.
- [3] G. Xue, R. De Hont, E. Münck, L. Que, *Nat. Chem.* **2**, 400 (2010).



# Reaction Mechanism of Hydrogermylation/Hydrostannylation of Unactivated Alkenes with Two-Coordinate $E^{\text{II}}$ Hydrides ( $E = \text{Ge}, \text{Sn}$ )

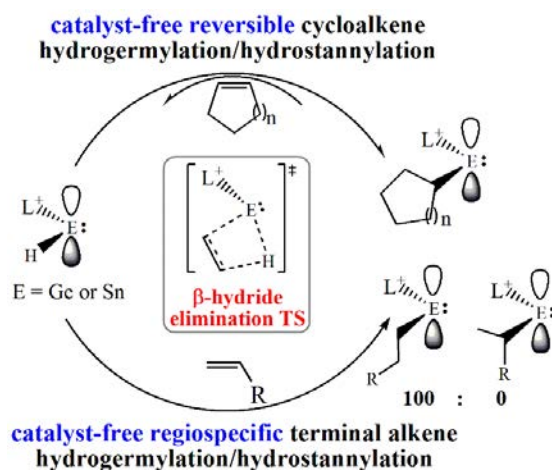
Lili Zhao,<sup>1,2</sup> Markus Hermann,<sup>1</sup> Cameron Jones,<sup>3</sup> Gernot Frenking<sup>1,2</sup>

<sup>1</sup>*Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, 35032, Marburg, Germany*

<sup>2</sup>*Institute of Advanced Synthesis(IAS), Nanjing Tech University, Nanjing, 211816, China*

<sup>3</sup>*School of Chemistry, Monash University, P.O. Box 23, Melbourne, Victoria, 3800, Australia*

**Abstract:** Quantum chemical studies have been performed to elucidate the mechanism of the catalyst-free hydrometallation reactions between two-coordinate hydrido-tetraylenes  $:E(H)(L^+)$  ( $E = \text{Ge}, \text{Sn}$ ) and a range of unactivated terminal and cyclic alkenes. The calculations suggest that the addition reactions of the germylene and stannylene to the cyclic and acyclic alkenes occur as one-step processes via formal [2+2] addition of the E-H fragment across the C-C  $\pi$  bond. The reactions have moderate barriers and are weakly exergonic. The steric bulk of the tetraylene amido groups has little influence on the activation barriers and on the reaction energies of the anti-Markovnikov pathway, but the Markovnikov addition is clearly disfavored by the size of the substituents. The addition of the tetraylenes to the cyclic alkenes is less exergonic than the addition to the terminal alkenes, which agrees with the experimentally observed reversibility of the former reactions. EDA-NOCV analysis of the transition state for the hydrogermylation of cyclohexene shows that the reaction takes place with simultaneous formation of the Ge-C and (Ge)H-C' bonds. The dominant orbitals of the germylene are the  $\sigma$ -type lone-pair MO of Ge which serves as donor orbital and the vacant  $p(\pi)$  MO of Ge which acts as acceptor orbital for the  $\pi^*$  and  $\pi$  MOs of the olefin.



[1] L. Zhao, M. Hermann, C. Jones, G. Frenking, *Chem. -Eur. J.*, 22, 11728 (2016).

## Influence of Semiempirical Dispersion Correction on the DFT Description of Inorganic Layered Compounds: Alkaline-earth Fluorohalides (MFX)

Daniel Sethio<sup>1</sup>, Latévi Max Lawson Daku<sup>1</sup>, Hans Hagemann<sup>1</sup>

<sup>1</sup>Department of Physical Chemistry, University of Geneva, Quai Ernest Ansermet 30, 1211 Geneva, Switzerland

Alkaline-earth fluorohalides, MFX, have received a lot of attention in material and optical sciences owing to the remarkable photophysical and photochemical properties, which they can exhibit upon incorporation of photoactive rare-earth ions. The MFX host compounds crystallize in the tetragonal  $P4/nmm$  Matlockite structure: they exhibit a layered ionic structure which corresponds to a simple  $-F^- - M^{2+} - X^- - X^- - M^{2+} - F^-$  - stacking of the ion layers along the  $c$  axis (see Figure ). Due to their layered structure and especially the presence of the anionic double layer, the description of the structures and properties of the MFX compounds within density functional theory (DFT) may suffer from the inaccurate description of the dispersion interactions, which can be observed with local, semilocal, and hybrid density functionals. This deficiency of standard approximate functionals could indeed explain the overestimation of the  $c$  parameter reported for PbFI. To investigate this question, periodic DFT calculations have been performed to study the crystal structures, mechanical and spectroscopic properties of the MFX compounds ( $M = Ca, Sr, Ba, Pb$  and  $X = Cl, Br, I$ ). The PBE and B3LYP functionals and their DFT-D2 dispersion-corrected variants were employed. For these layered ionic compounds, it proved necessary to modify the semi-empirical D2 dispersion correction.

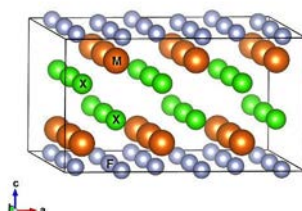


Figure 1: The tetragonal  $P4/nmm$  Matlockite structure of MFX alkaline-earth fluorohalides: 3 x 3 x 1 supercell showing the layer stacking.

- [1] A. Otero-de-la-Roza and E. R. Johnson, *J. Chem. Phys* **137**, 054103 (2016).
- [2] B. Civalleri, et al. *Cryst. Eng. Comm.* **10**, 405 (2008).
- [3] M. P. Andersson *J. Theor. Chem.* **2013**, 327839 (2013).

## Investigation of Catalytic Dehydrocoupling of Dimethylamine-borane by Titanocene: A DFT and Topologic Study

Jingwen ZHU, Emilie-Laure ZINS, M. Esmail ALIKHANI

MONARIS, UMR 8233, Université Pierre et Marie Curie, Sorbonne Universités, 4 Place Jussieu, 75005 Paris, France

With the increasing demand of clean energy carriers, ammonia borane and its related amine borane (AB) compounds [1] have emerged as attractive candidates for potential hydrogen storage vectors. In this context, mechanistic studies for the catalyzed dehydrogenation/dehydrocoupling of amine-boranes and phosphine-boranes have seen a quick development over the last decade. [2] Inexpensive, environmentally friendly, easily synthesized and stable organometallic compounds that efficiently catalyze the reaction are worth studying.

The dehydrocoupling of  $\text{HMe}_2\text{N}\cdot\text{BH}_3$  to form  $[\text{Me}_2\text{N}\cdot\text{BH}_2]_2$  catalyzed by titanocene was investigated both experimentally [3, 4] and theoretically. [5] However, the exact mechanism of this reaction still remains uncertain. Theoretical studies based on DFT calculation and topological tools were used to characterize precisely the reaction pathway and 3-centre 2-electron (3C/2e) intermediates. The following aspects will be developed:

- The 3C/2e interactions between metallic centre and B-H  $\sigma$  bond are characterized in both intermolecular intermediates ( $\sigma$  complexes) and intramolecular ones (agostic complexes).
- The empirical dispersion correction (GD3BJ) is shown to yield structures and relative energies for the different reaction pathways, in better agreement with experimental observations.
- The solvation effect associated with different basis sets may be a remarkable parameter that influences the energetic properties of this kind of reaction. Further investigations should help in finding an inexpensive and highly-efficient catalyst.

- [1] F. H. Stephens, V. Pons and R. T. Baker, *Dalton Trans.* **25**, 2613 (2007).  
[2] H. C. Johnson, T. N. Hooper and A. S. Weller, *Springer International Publishing* 153 (2015).  
[3] T. J. Clark, C. A. Russell and I. Manners, *J. Am. Chem. Soc.* **128**, 9582 (2006).  
[4] M. E. Sloan, A. Staubitz, T. J. Clark, C. A. Russell, G. C. Lloyd-Jones and I. Manners, *J. Am. Chem. Soc.* **132**, 3831 (2010).  
[5] Y. Luo and K. Ohno, *Organometallics* **26**, 3597 (2007).

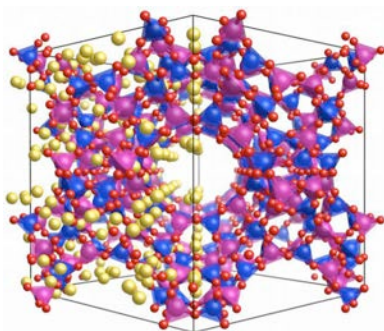
## Optimal Faujasite structures for post combustion CO<sub>2</sub> capture in swing adsorption processes

**Hector Prats<sup>1</sup>, Daniel Bahamon<sup>1</sup>, Gerard Alonso<sup>1</sup>, Xavier Giménez<sup>1</sup>, Pablo Gamallo<sup>1</sup>, Ramón Sayós<sup>1</sup>**

<sup>1</sup>*Departament de Ciència de Materials i Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, C. Martí i Franquès, 1 08028, Barcelona, Spain*

Carbon dioxide is the primary greenhouse gas generated by human activities, mainly from the combustion of fossil fuels for energy and transportation. Despite the development of alternative renewable energy sources, fossil fuels still dominate in almost all near future projections [1]. Therefore, many efforts have been addressed to the development of cost-efficient technologies for separation and capture of carbon dioxide. Solid adsorbents like zeolites or metal-organic frameworks are promising candidates [2].

In the present work, Grand Canonical Monte-Carlo (GCMC) simulations are used to assess optimum faujasite structures, the well-known family of zeolites, in CO<sub>2</sub> capture processes. Pressure Swing Adsorption (PSA), Vacuum Swing Adsorption (VSA) and Temperature Swing Adsorption (TSA) procedures have been considered to evaluate purity, selectivity, working capacity and isosteric heat in ten faujasite structures with different Al content. Results indicate that faujasites with high Al content are the most effective for TSA whereas intermediate Al content structures perform better at VSA conditions and ultimately, low Al content faujasites are more suitable for PSA process [3].



- [1] B. P. Spigarelli, S. K. Kawatra, *J. CO<sub>2</sub> Util.* **1**, 69 (2013).
- [2] J. M. Huck, L. Lin, A. H. Berger, M. N. Shahrak, R. L. Martin, A. S. Bhowan, M. Haranczyk, K. Reuter, B. Smit, *Energy Environ. Sci.* **7**, 4132 (2014).
- [3] H. Prats, D. Bahamon, G. Alonso, X. Giménez, P. Gamallo, R. Sayós, *J. CO<sub>2</sub> Util.* **19**, 100 (2017).

## Ni-Phosphine Bond Strengthening Through Coordination of the Strong $\sigma$ -Donors ECp\* (E= Al, Ga)

J. Hornung<sup>1</sup>, J. Weßing<sup>1</sup>, P. Jerabek<sup>2</sup>, G. Frenking<sup>3</sup>, C. Gemel<sup>1</sup>, R. A. Fischer<sup>1</sup>

<sup>1</sup>*Chair of Inorganic and Metal Organic Chemistry, Technical University Munich, Lichtenbergstr. 4, 85748 Garching, Germany*

<sup>2</sup>*Centre of Theoretical Chemistry and Physics, The New Zealand Institute for Advanced Study, Massey University Auckland, 0745 Auckland, New Zealand*

<sup>3</sup>*Fachbereich Chemie der Philipps-Universität Hans-Meerwein-Str. 4, 35032 Marburg, Germany*

The coordination chemistry of low valent group 13 ligands ECp\* (E=Al, Ga, In Cp\* = Pentamethylcyclopentadienyl) has been investigated intensively in the past 20 years, both theoretically and experimentally.<sup>[1]</sup> A large variety of heteroleptic complexes and clusters [TM<sub>a</sub>(ECp\*)<sub>b</sub>(L)<sub>c</sub>] (TM = transition metal; L=2 electron donor ligand, e.g.: PR<sub>3</sub>, CO, hydride...) have been investigated.<sup>[2]</sup> Most of these heterobimetallic compounds exhibit an 18VE count on the transition metal. However, in the chemistry of these molecules, low-coordinated TM(ECp\*)<sub>n</sub>-fragments play a crucial role, especially in the activation of strong bonds (C-H, C-C, Si-H), but also in the formation of higher nuclear clusters.<sup>[2]</sup>

We present the first systematic investigation about the in-situ formation of unsaturated bimetallic transition metal/group 13 metal complexes through experimental and computational methods. For this investigation, the series [Ni(ECp\*)<sub>a</sub>(PR<sub>3</sub>)<sub>4-a</sub>] (a=0-3) has been chosen as a model system. Complexes of this type are synthetically easily accessible by simple substitution reactions from Ni(cod)<sub>2</sub> (cod = 1,5-cyclooctadiene) and are thermally very robust and stable. Phosphine dissociation has been investigated experimentally by variable temperature UV-Vis-spectroscopy as well as computationally by energy decomposition analysis (EDA) with the natural orbital for chemical valence extension (NOCV). In accordance with the experimental results, the Ni-phosphine interaction energy increases with increasing number of ECp\* ligands. Closer investigations show that this can be related to an increase in electrostatic interactions introduced by Ni-P bond polarization by ECp\* ligands.

- [1] W. Uhl, M. Benter, S. Melle, W. Saak, G. Frenking, J. Uddin, *Organometallics* **1999**, *18*, 3778-3780.
- [2] C. Ganesamoorthy, J. Wessing, C. Kroll, R. W. Seidel, C. Gemel, R. A. Fischer, *Angew. Chem. Int. Ed.* **2014**, *53*, 7943-7947.

## Effects of Interphase Region on Glass Transition Temperature of Grafted Carbon Nanotubes Reinforced Epoxy Composites

Cai Jiang, Chaoyi Peng, Jingcheng Zeng, Jianwei Zhang\*

*Department of Materials Science and Engineering, National University of Defense Technology, Changsha, Hunan 410073, People's Republic of China*  
Corresponding E-mail: jwzhang.nudt@gmail.com

**Abstract:** Carbon nanotubes (CNTs) have been widely used to modify glass transition temperatures ( $T_g$ s) of polymers, due to their outstanding mechanical properties, as well as long aspect ratios and high surface areas [1-3]. Researchers have found that  $T_g$ s of the composites were affected dramatically by the interphase, while there still appeared to be lack of an agreement on how the interphase works.

In this work, in order to verify roles of interphase played in  $T_g$ s of CNT/epoxy composites, three types of interphase were produced between the carbon nanotubes (CNTs) and the cured epoxy resin matrix. It was achieved by selection of pristine CNTs (p-CNTs), amino groups grafted CNTs (NH<sub>2</sub>-CNTs) and hydroxyl groups grafted CNTs (OH-CNTs) as the reinforcement, respectively. Molecular dynamics (MD) simulations were conducted to study  $T_g$ s of the CNT/epoxy composites. For the simulation, p-CNTs and OH-CNTs reinforced epoxy composites were constructed separately, where the CNTs were not covalent bonded to the epoxy resin matrix. In the NH<sub>2</sub>-CNT/epoxy composites, two kinds of interphases between the amino groups in CNTs and the epoxy resin matrix were constructed, namely, with or without covalent bonds. The MD simulation results showed that  $T_g$ s of NH<sub>2</sub>-CNT/epoxy composites with covalent bonds increased, while  $T_g$ s of OH-CNT/epoxy composites and NH<sub>2</sub>-CNT/epoxy composites without covalent bonds decreased, compared with p-CNT/epoxy composites. The simulation results were also consistent with the dynamic mechanical analysis (DMA) results, which were also conducted in this work. Effects of interphases on  $T_g$ s of the CNT/epoxy composites were further explained by the MD simulations through investigating the microstructures of the CNT/epoxy composites.  $T_g$ s of the NH<sub>2</sub>-CNT/epoxy composites increased with the formation of covalent bonds, while the interfacial interactions between the NH<sub>2</sub>-CNTs and the epoxy resin matrix were enhanced. It could be indicated from the highest total interaction energy between the CNTs and the cured epoxy matrix, the lowest mean square displacement values of atoms in the matrix. While  $T_g$ s of the OH-CNT/epoxy composites decreased due to the weak interfacial interactions, where no such covalent bonds were formed. It can be inferred that the covalent bonds between the CNTs and the polymer matrix are beneficial and critical to increase  $T_g$ s of the CNT/polymer composites.

## DLPNO-CCSD(T) Scaled Methods for the Accurate Treatment of Large Supramolecular Complexes

**Joaquín Calbo<sup>1</sup>, Juan Carlos García-Sancho<sup>2</sup>, Enrique Ortí<sup>1</sup>, Juan Aragó<sup>1</sup>**

<sup>1</sup> *Instituto de Ciencia Molecular, Universidad de Valencia, E-46980 Paterna, Spain*

<sup>2</sup> *Departamento de Química Física, Universidad de Alicante, E-03080 Alicante, Spain*

The theoretical description of supramolecular complexes requires the use of accurate and cost-effective quantum-chemical methods to account for noncovalent interactions (NCI) in a balanced way. Over the last years, the development of novel theoretical approaches has led to methodologies showing an unprecedented degree of accuracy in the context of NCIs. The efficient domain-based local pair-natural orbital (DLPNO) approach developed by Neese *et al.*[1] has recently been coupled to the CCSD(T) method, offering a quantum-chemical method, dubbed as DLPNO-CCSD(T), that exhibits the high accuracy of the semicanonical CCSD(T) but with a significantly reduced computational cost. However, stringent thresholds such as in the TightPNO setup are required for the accurate treatment of NCIs.

Herein, we present scaled variants of the DLPNO-CCSD(T) method, dubbed as (LS)DLPNO-CCSD(T) and (NS)DLPNO-CCSD(T), to obtain accurate interaction energies in supramolecular complexes governed by noncovalent interactions.[3] The scaled DLPNO-CCSD(T) variants provide nearly TightPNO accuracy, which is essential for the quantification of weak noncovalent interactions, with a noticeable saving in computational cost. The new protocols have been used to study the role of CH- $\pi$  *versus*  $\pi$ - $\pi$  interactions in the supramolecular complex formed by the electron-donor truxene-tetrathiafulvalene (truxTTF) and the electron-acceptor hemifullerene (C<sub>30</sub>H<sub>12</sub>). (NS)DLPNO-CCSD(T)/CBS calculations reveal the higher stability of staggered (dominated by CH- $\pi$  interactions) *versus* bowl-in-bowl (dominated by  $\pi$ - $\pi$  interactions) arrangements in the truxTTF•C<sub>30</sub>H<sub>12</sub> heterodimer. Hemifullerene and similar carbon-based buckybowls are therefore expected to self-assemble with donor compounds in a richer way other than the typical concave-convex  $\pi$ - $\pi$  arrangement found in fullerene-based aggregates.

[1] a) C. Riplinger and F. Neese, *J. Chem. Phys.* **2013**, *138*, 034106. b) C. Riplinger, B. Sandhoefer, A. Hansen and F. Neese, *J. Chem. Phys.* **2013**, *139*, 134101.

[2] D. G. Liakos, M. Sparta, M. K. Kesharwani, J. M. L. Martin and F. Neese, *J. Chem. Theory Comput.* **2015**, *11*, 1525-1539.

[3] J. Calbo, J. C. Sancho-García, E. Ortí and J. Aragó, *submitted*.



## The molecular mechanism of ligand unbinding from the human telomeric G-quadruplex

Jia-Kai Zhou,<sup>a</sup> Dah-Yen Yang<sup>b</sup> and Sheh-Yi Sheu<sup>\*a</sup>

<sup>a</sup>*Department of Life Sciences and Institute of Genome Sciences  
National Yang-Ming University, Taipei 112, Taiwan  
E-mail: [sysheu@ym.edu.tw](mailto:sysheu@ym.edu.tw)*

<sup>b</sup>*Institute of Atomic and Molecular Sciences  
Academia Sinica, Taipei 106, Taiwan  
E-mail: [dyyang@po.iam.s.sinica.edu.tw](mailto:dyyang@po.iam.s.sinica.edu.tw)*

### Abstract:

G-quadruplexes become attractive drug targets in cancer therapy recently. The proposition of new drugs for the G-quadruplexes is essential to understanding the specific interactions between the ligand and receptor and to the underlying mechanisms of the binding–unbinding processes involving biomolecules and molecular recognition. In this study, we have investigated the mechanical properties and kinetic pathways of the ligands (BMVC and BMVC0) unbinding from the G-quadruplex by using steered molecular dynamics and umbrella sampling simulations. Based on the structural analyses and the PMF calculations, we have shown detailed atomistic insights and relevant free energies involved in the unbinding processes, which have not been determined in ensemble assays. These results could help to identify accessible binding sites and transient interactions. The simulations for both these ligands clearly reflect their distinct rupture force and PMF profiles, which can be correlated with G-quadruplex–ligand binding affinities, suggesting that this protocol could be applied to other G-quadruplex ligands to assess their robustness and rank a series of derivatives with similar potencies. On the other hand, the dynamics of the hydration shell water molecules around the G-quadruplex exhibits an abnormal Brownian motion, and the thickness and free energy of the hydration shell were estimated. A two-step relaxation scheme was theoretically developed to describe the kinetic reaction of BMVC and G-quadruplex interactions. Our findings confirm the seminal experimental data, highlighting the importance of using computer-based simulations to predict and complement experiments. This demonstration of simulations combined with theoretical analyses is valuable for further investigations on various G-quadruplex systems and could be helpful in structure-based drug design.

- [1] Jia-Kai Zhou, Dah-Yen Yang and Sheh-Yi Sheu, *Phys. Chem. Chem. Phys.*, **17**, 12857-12869(2015).



## Mechanically Controlled Electron Transfer in a Single-Polypeptide Transistor

Sheh-Yi Sheu<sup>a</sup> and Dah-Yen Yang<sup>b</sup>

<sup>a</sup>*Department of Life Sciences and Institute of Genome Sciences  
National Yang-Ming University, Taipei 112, Taiwan*

*E-mail: [sysheu@ym.edu.tw](mailto:sysheu@ym.edu.tw)*

<sup>b</sup>*Institute of Atomic and Molecular Sciences  
Academia Sinica, Taipei 106, Taiwan*

*E-mail: [dyyang@po.iam.s.sinica.edu.tw](mailto:dyyang@po.iam.s.sinica.edu.tw)*

### Abstract:

Proteins are of interest in nano-bio electronic devices due to their versatile structures, exquisite functionality and specificity. However, quantum transport measurements produce conflicting results due to technical limitations whereby it is difficult to precisely determine molecular orientation, the nature of the moieties, the presence of the surroundings and the temperature; in such circumstances a better understanding of the protein electron transfer (ET) pathway and the mechanism remains a considerable challenge. Here, we report an approach to mechanically drive polypeptide flip-flop motion to achieve a logic gate with ON and OFF states during protein ET. We have calculated the transmission spectra of the peptide-based molecular junctions and observed the hallmarks of electrical current and conductance. The results indicate that peptide ET follows an NC asymmetric process and depends on the amino acid chirality and  $\alpha$ -helical handedness. Electron transmission decreases as the number of water molecules increases, and the ET efficiency and its pathway depend on the type of water-bridged H-bonds. Our results provide a rational mechanism for peptide ET and new perspectives on polypeptides as potential candidates in logic nano devices.

- [1] Sheh-Yi Sheu and Dah-Yen Yang, *Scientific Reports*, **7**, 39792(2017).

## **DFT Study of the Selectivity of DOPA-decarboxylase**

**Emily C. Harrison, Abby Ritter, Larryn W. Peterson, and Mauricio Cafiero**

*Rhodes College, Department of Chemistry, 2000 N. Parkway, Memphis, TN 38112*

Abstract: L-DOPA is commonly used as a xenobiotic for patients with conditions such as Parkinson's disease. Clinically administered L-DOPA is transformed into dopamine by DOPA-decarboxylase. In order to be pharmacologically effective, L-DOPA must not be metabolized before it crosses the blood brain barrier. In order to prevent premature metabolism, DOPA-decarboxylase may be inhibited in the periphery. By selectively designing an inhibitor for the DOPA-decarboxylase enzyme, the effectiveness of the L-DOPA can be extended. A suite of dopaminergic derivatives have been developed as potential inhibitors of the DOPA-decarboxylase enzyme. The inhibitory effectiveness of these dopaminergic derivatives has been measured via in silico models in which the strength of interaction between each substrate and the enzymatic active site was analyzed. A crystal-structure of the DOPA-decarboxylase active site, docked with a known DOPA-decarboxylase inhibitor, Carbidopa, was isolated from the Protein Data Bank (PDB ID: 1JS3). The positions of novel dopaminergic derivatives were optimized in the active site using M062X/6-31G with implicit solvation and with flexible amino acid side-chains. Interaction energies between the ligands and the protein were calculated using M062X and MP2 with the 6-311+G\* basis set. At present, 6-nitrodopamine appears to be an effective competitive inhibitor of the DOPA-decarboxylase enzyme.

**DFT Study of the Selectivity of Monoamine Oxidase B (MAOB)**

**Samantha Jelinek, Audrey Woody, Mallory Morris, Larry W. Peterson, and  
Mauricio Cafiero**

*Rhodes College, Department of Chemistry, 2000 N. Parkway, Memphis, TN 38112*

Abstract: MAOB is an enzyme located on the outer mitochondria that is responsible for degrading penylethylamine, benzylamine, and dopamine. MAOB inhibitors are generally used as a treatment for Parkinson's disease because they stop the breakdown of dopamine. By selectively designing an inhibitor for the MAOB enzyme, the breakdown of dopamine can be reduced leading to an increase of the neurotransmitter. A suite of dopaminergic derivatives have been developed as potential inhibitors of the MAOB enzyme. The inhibitory effectiveness of these dopaminergic derivatives has been measured via in silico models in which the strength of interaction between each substrate and the enzymatic active site was analyzed. A crystal-structure of the MAOB active site, docked with the widely employed diabetes drug pioglitazone, was isolated from the Protein Data Bank (PDB ID: 4A79). The positions of novel dopaminergic derivatives were optimized in the active site using M062X/6-31G with implicit solvation and with relaxed amino acid side-chains. Interaction energies between the ligands and the protein were calculated using M062X and MP2 with the 6-311+G\* basis set. At present, we have designed novel inhibitors that bind much stronger than dopamine.

**Design of novel inhibitors for the aldehyde dehydrogenases I: Left Orientation****Caroline Magee, Emma Selner, Larryn Peterson, Mauricio Cafiero***Rhodes College, Department of Chemistry, 2000 N. Parkway*

Abstract: L-DOPA is commonly used as a xenobiotic for patients with conditions such as Parkinson's disease. L-DOPA is transformed into dopamine by DOPA-decarboxylase. Dopamine derived from L-DOPA is deactivated via metabolism by a series of enzymes including Aldehyde dehydrogenases (ALDH). The targeted inhibition of the ALDH enzyme may help to prolong the effectiveness of L-DOPA, resulting in a net increase in pharmacological efficiency. By selectively designing an inhibitor for ALDH, the effectiveness of the L-DOPA can be extended by regulating the metabolism of dopamine derived from L-DOPA. The effectiveness of a series of potential inhibitors has been measured via *in silico* models in which the strength of interaction between each substrate and the enzymatic active site was analyzed. A crystal-structure of the ALDH enzyme with an inhibitor bound in its active site (PDB ID: 4WP7) was used to create a model of the active site. Novel dopaminergic derivatives were optimized in the active site using M062X/6-31G with implicit solvation and with relaxed amino acid side-chains. Ligands can fit into the active site in a number of ways; in this work we examine the left orientation of the molecules. Interaction energies between the ligands and the protein were calculated using M062X with the 6-311+G\* basis set. Some potential inhibitors show promising results. Mutant enzymes were also studied for their affinity for the ligands.

## DFT analysis of the selectivity of Phenylalanine Hydroxylase

**Madison Perchik, Rachel Giampapa, Larryn Peterson, Mauricio Cafiero**

*Rhodes College, Department of Chemistry, 2000 North Parkway Memphis, TN 38112*

Abstract: There are many molecules that act on dopamine and dopamine-like binding sites in enzymes and transport proteins. Some effects of these proteins are beneficial while others are detrimental. We are designing inhibitors for this group of proteins. Phenylalanine hydroxylase (PheOH) is a tetrahydrobiopterin-dependent monooxygenase that influences the rate determining step of converting phenylalanine into tyrosine by hydroxylating phenylalanine. Both phenylalanine and tyrosine are important components in the anabolism of dopamine. A deficiency of PheOH can cause hyperphenylalaninemia, which gives rise to phenylketonuria (PKU), a severe disease that can cause mental retardation if one's diet isn't strictly monitored. A suite of dopaminergic derivatives has been developed as potential inhibitors of the PheOH enzyme. The inhibitory effectiveness of these dopaminergic derivatives has been measured via in silico models in which the strength of interaction between each substrate and the enzymatic active site was analyzed. A crystal-structure of the PheOH active site, with bound thienylalanine, was isolated from the Protein Data Bank (PDB ID: 1KW0). The positions of novel dopaminergic derivatives were optimized in the active site using M062X/6-31G with implicit solvation and with flexible amino acid side-chains. Interaction energies between the ligands and the protein were calculated using M062X and MP2 with the 6-311+G\* basis set. At present, none of the potential inhibitors examined interact as strongly as the natural substrate phenylalanine.

## Electron Transfer in Organic and Biological Materials

**Antoine Carof<sup>1</sup> and Jochen Blumberger<sup>1</sup>**

<sup>1</sup>*University College London, Department of Physics and Astronomy  
London, WC1E 6BT, UK  
antoine.carof@gmail.com*

Charge transfer processes are ubiquitous taking a prominent role in biology and material science. While experiments give valuable information on certain kinetic and thermodynamic properties of charge transfer events, they usually do not offer a molecular-level insight into these phenomena. Adequate simulations can bridge the gap between microscopic processes and macroscopic charge transports. For instance, a combination of Marcus theory, classical molecular simulation and master equation formalism can estimate complex charge transfer processes involving multiple redox sites in large systems [1]. But such rate-based approaches usually only work for localized charge carriers and in situations where the charge transfer is slow compared to the molecular motions that couple to the charge transfer. To surpass these limitations, we have recently implemented a fast non-adiabatic molecular dynamics approach (based on Tully's surface hopping) where the wavefunction of the charge carrier is explicitly propagated in the time-dependent potential created by (classical) nuclear motion [2,3]. First applications to hole transfer in the ethylene dimer successfully reproduced exact results from the theory [3] and applications to a chain of ethylene molecules successfully predicted a crossover from activated to band-like transport [2]. Here we present a new implementation of the method into the CP2K software that enables us to model fast charge transfer in larger, application relevant organic crystals consisting of thousands of atoms. We will present applications as well as a detailed analysis of the charge transfer mechanism predicted by our surface hopping approach.

[1] J. Blumberger, *Chem. Rev.*, **115**, 11191 (2015)

[2] J. Spencer J., F. Gajdos, J. Blumberger, *J. Chem. Phys.*, **145**, 64102 (2016)

[3] J. Spencer J., L. Scalfi, A. Carof, J. Blumberger, *Faraday Discuss.*, **195**, 215 (2016)

## HYDROGEN ATOM ABSTRACTION FROM ETHANOL BY ATOMIC HYDROGEN IN AQUEOUS SOLUTION

Suraj Kannath,<sup>1</sup> Paweł Adamczyk,<sup>1</sup> Antonio Fernandez-Ramos,<sup>2</sup>  
and Agnieszka Dybala-Defratyka<sup>1</sup>

*Institute of Applied Radiation Chemistry, Faculty of Chemistry, Lodz University of Technology, Zeromskiego 116,  
90-924, Lodz, Poland*

*Department of Physical Chemistry and Center for Research in Biological Chemistry and Molecular Materials  
(CIQUS), University of Santiago de Compostela, 15782 Santiago de Compostela, Spain*

Hydrogen abstraction from ethanol by atomic hydrogen is a well-known reaction which is one of the most important steps in ethanol decomposition.[1] Depending on temperature this reaction can proceed via three different channels resulting in three different products. It has been shown that at room temperature this reaction goes through only one pathway, however, the reaction can proceed via two transition states (gauche (g) and trans (t)) which interconvert in each other by internal rotation.[2,3] Recent computational research over this reaction is based on continuum model of solvation. In this work we expand solvation model to test the effect of specific explicit solvation on predicted kinetic isotope effects (KIEs).

Different models of aqueous solution including continuum and explicit solvation have been applied. Pure quantum mechanical calculations were used for smaller models whereas hybrid QMMM calculations were used for larger models. Kinetic isotope effects (KIEs) have been calculated for all hydrogen atoms using various theoretical approaches such as multipath variational transition state theory (MP-VTST) and path integrals methods.[3,4,5] These methods allow incorporating quantum effects such as tunneling and recrossing for multiple reaction paths with thermal rate constants determination which are further used for kinetic isotope effects calculation. The influence of environment on the obtained isotopic fractionation has been also analyzed and discussed.

**Acknowledgements:** This work is supported by NCN (National Science Centre) Poland, Sonata-BIS grant (2015-2020). Computing time at the PLGrid infrastructure (Poland) is gratefully acknowledged.

[1] Meana-Pañeda, R.; Fernández-Ramos, A. *J. Chem. Phys.* **2014**, *140*, 174303.

[2] Lossack, A. M.; Roduner, E.; Bartels, D. M. *J. Phys. Chem. A* **1998**, *102*, 7462.

[3] Simón-Carballido, L.; Alves, T.V.; Dybala-Defratyka, A.; Fernández-Ramos, A. *J. Phys. Chem. B* **2016**, *120*, 1911.

[4] Yu, T.; Zheng, J.; Truhlar, D.G. *J. Phys. Chem. A* **2012**, *116*, 297–308.

[5] Major, D. T.; Gao, J. *J. Chem. Theory Comput.* **2007**, *3*, 949-960

## Getting ion-protein interactions right in Molecular Dynamics simulations

**Elise Duboué-Dijon<sup>1</sup>, Philip E. Mason<sup>1</sup>, Pavel Jungwirth<sup>1</sup>**

*<sup>1</sup>Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences,  
Flemingovo nam. 2, Prague 16000, Czech Republic*

Ion-biomolecules interactions are ubiquitous and play a central role in a number of fundamental biological processes, from calcium signaling to insulin storage. However, assessing the interaction of ions with biomolecules is not easy, neither experimentally nor computationally, because of the complexity of the systems involved. Indeed, quantum descriptions are too expensive to allow the study of large systems, while solvation and pairing properties of divalent cations are poorly reproduced by standard classical force fields because of polarization and charge transfer effects.

Our goal is to improve the description of divalent cations in simulations and use it to tackle biologically relevant problems. Since there is surprisingly little data available about the interaction of non transition metal divalent cations (zinc, calcium, magnesium) with typical protein groups (acetate, histidine), our strategy is first to obtain reference data on small model systems. These simple systems are studied both with *ab initio* Molecular Dynamics simulations and neutron-scattering experiments and the results are used to develop a scaled charge description of the ions, which takes into account electronic polarization in a mean field way [1-2]. This strategy allows us to design an accurate and computationally cheap description for the studied divalent cations.

The obtained force field is applied to biologically relevant systems, such as the interaction of ions with the insulin molecule, and how this changes with the multimerization state of insulin (monomer, dimer, hexamer). This question is fundamental to better understand the role of ions in insulin storage in the ion-rich secretory granules, and critically depends on a proper description of ion-protein interactions.

[1] I. Leontyev, A. Stuchebrukhov, *Phys. Chem. Chem. Phys.*, **13**, 2613 (2011).

[2] M. Kohagen, P.E. Mason, P. Jungwirth, *J. Phys. Chem B*, **118**, 7902 (2014).



## Design and synthesis of novel inhibitors for the Tyrosine Hydroxylase enzyme

**Rebecca Evans, Larryn Peterson, Mauricio Cafiero**

<sup>1</sup>*Department of Chemistry, Rhodes College, 2000 North Parkway Memphis, TN 38112*

Catecholamines are responsible for the fight or flight response and can be attributed to many functions within the sympathetic nervous system. Tyrosine Hydroxylase is the rate determining enzyme in the synthesis of the catecholamine, dopamine. Tyrosine Hydroxylase converts tyrosine to L-DOPA, which is administered in the treatment of Parkinson's patients. The inhibition of Tyrosine Hydroxylase allows for less feedback inhibition from catecholamines, aiding dopamine production. A crystal structure of the active site of Tyrosine Hydroxylase with a known inhibitor bound was obtained from the protein data bank (PDB ID: 2TOH) [1]. In this work, dopaminergic derivatives were inserted into the enzymatic active site *in silico* in order to test the strength of the interactions between the substrate and active site, to determine if any of these derivatives could be effective inhibitors. These derivatives were optimized with implicit solvent with M062X/6-31G and relaxed amino acid side-chains. Interaction energies between the ligands and protein were determined using M06L and MP2 with the 6-311+G\* basis set. Results shows that some of our dopaminergic derivatives show promise as inhibitors for Tyrosine Hydroxylase.

[1] Goodwill, K. E.; Sabatier, C.; Stevens, R. C. *Biochemistry* 1998, 37 (39), 13437–13445.

## Tricoordinate boron as donor ligand: bonding and reactivity patterns in iron pincer complexes

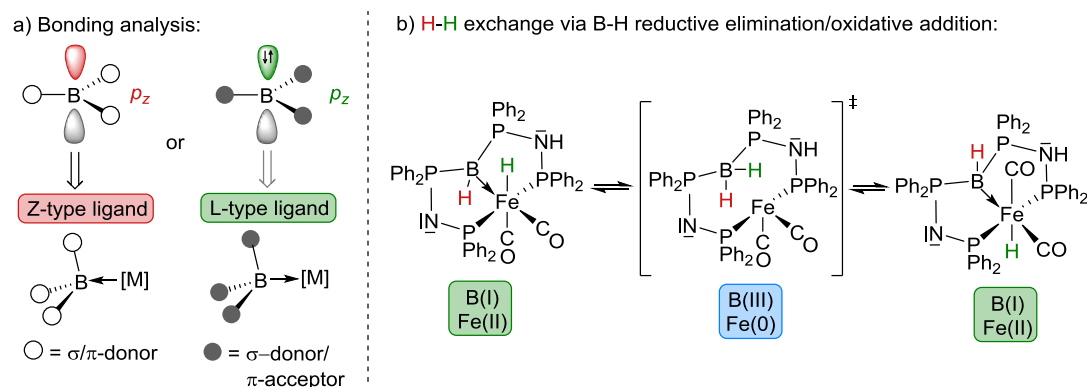
**Lisa Vondung and Robert Langer\***

*Department of Chemistry, Philipps-Universität Marburg, Hans-Meerwein-Straße 4,  
35032 Marburg, Germany*

Tricoordinate boron compounds usually behave as Lewis acids, owing to their vacant  $p_z$ -orbital. If employed in transition metal complexes, they then function as electron-accepting (Z-type) ligands. Nonetheless, effort has been made recently to synthesize nucleophilic boron compounds.[1-3] This becomes possible with strong  $\pi$ -accepting substituents on boron, which stabilize the filled  $p_z$ -orbital. If used as ligands, these boron-compounds serve as electron-donating (L-type) ligands.

In this work we investigated an iron-PBP-pincer complex with a tricoordinate boron atom as a ligand.[4] Different methods of bonding analysis revealed that the boron atom acts as an electron-donating ligand, although it is only stabilized by phosphines. Experimental X-ray and NMR data supports this result.

The complex also shows an intramolecular H-H exchange. Possible exchange pathways were investigated with a combination of kinetic measurements and DFT calculations. A reversible reductive B-H elimination was identified as the present mechanism. (De)protonation of the ligand backbone strongly influences the exchange process, which is explained by the different stabilities of the involved species.



- [1] J. Cid, H. Gulyás, J. J. Carbó, E. Fernández, *Chem. Soc. Rev.* **41**, 3558 (2012).
- [2] R. Kinjo, B. Donnadieu, M. A. Celik, G. Frenking, G. Bertrand, *Science* **333**, 610–3 (2011).
- [3] W. Lu, H. Hu, Y. Li, R. Ganguly, R. Kinjo, *J. Am. Chem. Soc.* **138**, 6650–61 (2016).
- [4] L. Vondung, N. Frank, M. Fritz, L. Alig, R. Langer, *Angew. Chemie Int. Ed.* **55**, 14450–14454 (2016), *Angew. Chem.* **128**, 14665–14670 (2016).

**Design of novel inhibitors for the aldehyde dehydrogenases I: Left Orientation****Caroline Magee, Emma Selner, Larryn Peterson, Mauricio Cafiero***Rhodes College, Department of Chemistry, 2000 N. Parkway*

Abstract: L-DOPA is commonly used as a xenobiotic for patients with conditions such as Parkinson's disease. L-DOPA is transformed into dopamine by DOPA-decarboxylase. Dopamine derived from L-DOPA is deactivated via metabolism by a series of enzymes including Aldehyde dehydrogenases (ALDH). The targeted inhibition of the ALDH enzyme may help to prolong the effectiveness of L-DOPA, resulting in a net increase in pharmacological efficiency. By selectively designing an inhibitor for ALDH, the effectiveness of the L-DOPA can be extended by regulating the metabolism of dopamine derived from L-DOPA. The effectiveness of a series of potential inhibitors has been measured via *in silico* models in which the strength of interaction between each substrate and the enzymatic active site was analyzed. A crystal-structure of the ALDH enzyme with an inhibitor bound in its active site (PDB ID: 4WP7) was used to create a model of the active site. Novel dopaminergic derivatives were optimized in the active site using M062X/6-31G with implicit solvation and with relaxed amino acid side-chains. Ligands can fit into the active site in a number of ways; in this work we examine the left orientation of the molecules. Interaction energies between the ligands and the protein were calculated using M062X with the 6-311+G\* basis set. Some potential inhibitors show promising results. Mutant enzymes were also studied for their affinity for the ligands.

## How many water molecules does it take to dissociate the hydrogen halides?

Alba Vargas-Caamal,<sup>1</sup> José Luis Cabellos,<sup>1</sup> Filiberto Ortiz-Chi,<sup>2</sup> Albeiro Restrepo,<sup>3</sup> Gabriel Merino.<sup>1</sup>

<sup>1</sup>*Departamento de Física Aplicada, Cinvestav-IPN Unidad Mérida. Km. 6 Antigua carretera a Progreso, Cordemex, C.P. 97310, Mérida, Yuc., México.*

<sup>2</sup>*Cátedra CONACYT, División Académica de Ciencias Básicas, Universidad Juárez Autónoma de Tabasco, C.P. 86690, Cunduacán, Tabasco, México.*

<sup>3</sup>*Instituto de Química, Universidad de Antioquia UdeA. Medellín, Colombia.  
e-mail: alba.vargas@cinvestav.mx*

How many water molecules does it take to dissociate an acid? To answer this question, we systematically explored the potential energy surfaces of the hydrogen halides (HX, X= F, Cl, Br, and I) with up to seven water molecules using a modified kick algorithm called *Bilatu* [1] and Density Functional Theory (DFT) computations. The discussions are based on the B2PLYPD3/def2-TZVP results. Our conclusions indicate that hydrogen fluoride is partially dissociated with up to seven water molecules. Whereas, on the basis of ZPE-corrected electronic energies, the number of water molecules needed for HCl dissociation is four, in agreement with other reports. [2,3] However, on the basis of Gibbs free energies computed at room temperature, this number is five due to the inclusion of entropic factors. [4]. Finally, HBr and HI dissociate in the presence of four and three water molecules, respectively. Such decrease in the number of water molecules is related to the electronegativity of the halogen, and to their acidic strengths in aqueous solutions. The interactions which stabilize the clusters are: water–water and HX–water hydrogen bonds, ionic and long range X $\cdots$ H interactions, as well as microsolvation of H<sub>3</sub>O<sup>+</sup> in the form of Eigen, quasi-Eigen cations and intermediate Zundel-Eigen-type structures. We carried out an analysis of bonding based on Wiberg Index, average dipole moments, [5] and O $\cdots$ HX and H-X distances collected in Stern-Limbach plots. [6] The results provide a classification of clusters according to their non-, partially- and fully-dissociated character of the H–X bond which periodic trends are observed.

[1] J. L. Cabellos, F. Ortiz-Chi, A. Ramírez, G. Merino, *Bilatu 1.0*. Cinvestav, Mérida, (2013).

[2] C. Amirand, D. Maillard, *J. Mol. Struct.* **176**, 181 (1988).

[3] M. Farnik, M. Weimann, M. A. Suhm, *J. Chem. Phys.* **118**, 10120 (2003).

[4] A. Vargas-Caamal, J. L. Cabellos, F. Ortiz-Chi, H. S. Rzepa, A. Restrepo, G. Merino, *Chem. Eur. J.* **22**, 2812-2818 (2016).

[5] N. Guggemos, P. Slavicek, V. V. Kresin, *Phys. Rev. Lett.* **114**, 043401 (2015).

[6] H. H. Limbach, P. M. Tolstoy, N. Perez-Hernandez, J. Guo, I. G. Shenderovich, G. S. Denisov, *Isr. J. Chem.* **49**, 199-216 (2009).

## The Reactivity of the $\alpha$ -O in Fe-Zeolites: a Multireference Approach.

Simon Hallaert<sup>1</sup>, Max Bols<sup>2</sup>, Pieter Vanelderen<sup>2</sup>, Robert Schoonheydt<sup>2</sup>, Bert Sels<sup>2</sup>, Kristine Pierloot<sup>1</sup>

<sup>1</sup>Department of Chemistry, KU Leuven, Celestijnenlaan 200F, Leuven, Belgium

<sup>2</sup>Centre for Surface Chemistry and Catalysis, KU Leuven, Celestijnenlaan 200F, Leuven, Belgium

The current commercial method to produce methanol involves a two steps procedure using syn gas and is rather energy intensive[1, 2]. Finding a direct way to oxidize methane to methanol would make this process more economical and environmentally friendly. In this respect, Fe-containing zeolites have drawn the attention of many scientists as they are able to oxidize methane to methanol under ambient conditions[3]. Only recently, the structure of the reactive intermediates in these zeolites has been elucidated using VTVH-MCD spectroscopy and quantum chemical calculations [4]. The reactive species, called  $\alpha$ -O, is a high spin square pyramidal Fe(IV)=O moiety. This Fe(IV) core is a common motif in nonheme iron enzymes (NHE) and in man-made model complexes[5], however not all Fe(IV)=O are as reactive as the others. In this work the reactivity of the  $\alpha$ -O core is investigated using multireference ab initio calculations (CASSCF/CASPT2 and DMRG-SCF/DMRG-CASPT2). The calculations identified two low lying, thermally accessible  $^5E$  excited states. Analysis of the CASSCF wavefunction shows that the oxyl character in the  $^5E$  states is much higher than in the  $^5A$  ground state. Oxyl character of Fe(IV)=O is related to its reactivity in hydrogen atom transfer (HAT) [6], this therefore indicates that the  $^5E$  states are more reactive than the ground state. Evaluation of the reaction path with DMRG-CASPT2 shows the involvement of the  $^5E$  and therefore proves that this reactive state is involved in HAT. The remarkable reactivity of  $\alpha$ -O in methane hydroxylation can thus be explained by the involvement of low lying excited states. These findings may guide scientist in the synthesis of new reactive catalyst for C-H bond activation.

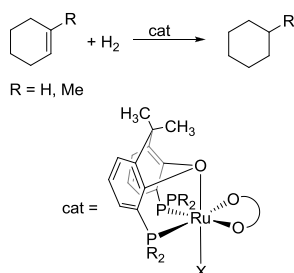
- [1] A. Riaz, G. Zahedi, J. J. Klemesš, *J. Cleaner Prod.* **2013**, 57, 19–37.
- [2] A. Galadima, O. Muraza, *J. Nat. Gas Sci. Eng.* **2015**, 25, 303–316.
- [3] V. Sobolev, K. Dubkov, O. Panna, G. Panov, *Catal. today* **1995**, 24, 251–252.
- [4] B. E. Snyder, P. Vanelderen, M. L. Bols, S. D. Hallaert, L. H. Böttger, L. Ungur, K. Pierloot, R. A. Schoonheydt, B. F. Sels, E. I. Solomon, *Nature* **2016**, 536, 317–321.
- [5] A. R. McDonald, L. Que, *Coord. Chem. Rev.* **2013**, 257, 414–428.
- [6] S. Ye, F. Neese, *Current opinion in chemical biology* **2009**, 13, 89–98.

## Ruthenium-Xantphos catalyzed olefin hydrogenation - How well does contemporary DFT predict experimentally observed energy spans?

Kai Rohmann<sup>1</sup>, Markus Hölscher<sup>1</sup>, Walter Leitner<sup>1</sup>

<sup>1</sup>*Institute of Technical and Macromolecular Chemistry, RWTH Aachen University,  
Worringer Weg 2, 52074 Aachen, Germany*

There is general consensus that DFT is the method of choice for the fast and reliable prediction of the structures of organometallic compounds. However, the use of predictive DFT computations prior to experimental work for the in-silico-design of catalyst structures has been hampered for many years by the fact that quantitative prediction of accurate overall activation barriers for typical organometallic reactions was not reliably possible. In this context the past decade has witnessed an impressive improvement with regard to the quantitative accuracy of contemporary DFT computations.[1-4] Accordingly, the question arises if DFT computations can be used for predictive catalyst design prior to experimental art. In this work we contribute to an answer by presenting accurate experimentally derived overall activation barriers (energy spans[5]) for the hydrogenation of cyclic olefins using molecularly defined ruthenium xantphos complexes (see Figure 1 below). We also show the DFT-derived underlying reaction mechanisms for these hydrogenations and also present a thorough comparison of computed energy spans obtained by state-of-the-art DFT computations. The work presented illustrates that by considering a few remaining experimental and computational boundaries DFT has reached a state which makes computational catalyst design prior to experimental work to be possible.[6]



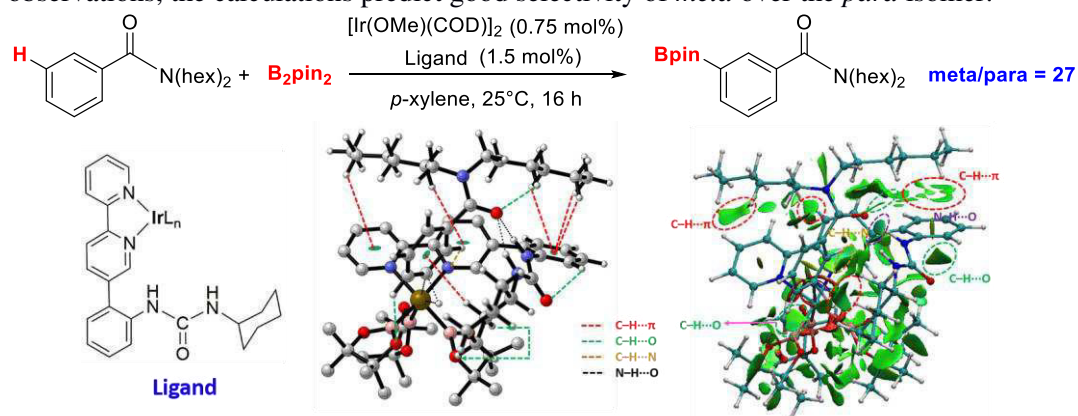
- [1] D. G. Gusev, *Organometallics* **2013**, 32, 4239-4243
- [2] M. Steinmetz, S. Grimme, *ChemistryOpen* **2013**, 2, 115-124.
- [3] W. Lai, J. Yao, S. Shaik, H. Chen, *J. Chem. Theory Comput.* **2012**, 8, 2991-2996.
- [4] R. Peverati, D. G. Truhlar, *Phys. Chem. Chem. Phys.* **2012**, 14, 13171-13174.
- [5] S. Kozuch, S. Shaik, *Acc. Chem. Res.* **2011**, 44, 101-110.
- [6] K. Rohmann, M. Hölscher, W. Leitner, *J. Am. Chem. Soc.* **2016**, 138, 433-443.

## Theoretical Investigation on the Role of Non-Covalent Interactions in a Regioselective Aryl C(sp<sup>2</sup>)-H Borylation Reaction

Anju Unnikrishnan<sup>1</sup>, Raghavan B. Sunoj<sup>2</sup>

<sup>1,2</sup>Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400076, India

The efficient and selective activation of C-H bonds has been an important domain of development in organic chemistry. The task of achieving high activity and control in selectivity (both regio- and stereo-) in C-H activation reactions has been accomplished with the use of transition metals under homogeneous catalytic conditions. The present computational study delineates interesting mechanistic features of the first catalyst-controlled regioselective C-H borylation of aromatic compounds.<sup>1</sup> The important aim of this study is to examine how the *meta* selectivity is accomplished through a secondary interaction between the ligand (tethered to the catalyst framework) and the substrate (an N,N-disubstituted aryl amide). The idea of H-bond directed regioselectivity is a newer concept making use of non-covalent interactions in C-H activation reactions. DFT studies have been undertaken to address two vital issues; the mechanism and the origin of selectivity. The mechanism primarily consist of oxidative addition of Ir(III)(bpy)tris(boryl) complex (active catalyst) to the C-H bond of the substrate, reductive elimination leading to the bond formation between the aryl carbon and the boron atom of the Bpin ligand, followed by the catalyst regeneration. The oxidative addition transition state involving a C-H activation exhibits a multi-centre interaction between H, C, Ir and B atoms. Apart from the interaction between the H bonding donor (ligand) and the acceptor (substrate), several non-covalent interactions like C-H... $\pi$  are also found to play a vital role in deciding the overall outcome of the reaction (Scheme 1). In line with the experimental observations, the calculations predict good selectivity of *meta* over the *para* isomer.



**Scheme 1.** Ir(III)-catalyzed *meta*  $\text{sp}^2$  C-H borylation transition state with all the favorable interactions responsible for selectivity.

- [1] Y. Kunitobu, H. Ida, M. Nishi, M. Kanai, *Nat. Chem.* **7**, 712 (2015).
- [2] A. Unnikrishnan, R. B. Sunoj, (manuscript in preparation).

**DFT study of CH bond activation of Os<sup>+</sup>, Ir<sup>+</sup>, and Pt<sup>+</sup> reacting with acetylene****Zikri Altun<sup>1</sup>, Erdi A. Bleda<sup>1</sup>, and Carl Trindle<sup>2</sup>**<sup>1</sup>*Department of Physics, Marmara University, Ziverbey, Istanbul, Turkey*<sup>2</sup>*Department of Chemistry, University of Virginia, Charlottesville, USA*

Metal cations form complexes with acetylene, and can in some cases catalyze the transformation of three acetylenes into benzene[1]. Our study[2] of the complexes of Fe(+) with acetylenes revealed a number of FeC<sub>n</sub>H<sub>n</sub> (n=6) structures some of which have distinct acetylenic fragments while others contain C<sub>k</sub>H<sub>k</sub> rings including those with k=4 and 6. Fe(+)C<sub>4</sub>H<sub>4</sub> is an intermediate in the process, while the most stable of the complexes is Fe(benzene) cation. When Fe is detached and benzene is produced the Fe(+) catalyzed process is complete. Although many states of the system are multiconfigurational, we found that DFT provides a reasonable depiction of the reaction profile.

For metals Os and Ir, M(+)C<sub>4</sub>H<sub>4</sub> is observed[3], but further reaction with acetylene produces M(+)C<sub>6</sub>H<sub>4</sub> and free diatomic hydrogen. Our purpose here is to explore the relative stability of M(+)benzene for M = Os, Ir, and perhaps Pt compared with the Fe(+)benzene complex. We will also establish the relative stability of the M(+)C<sub>6</sub>H<sub>4</sub> series with Fe(+)C<sub>6</sub>H<sub>4</sub>, and explore the reaction paths producing either benzene or hydrogen from M(+)C<sub>4</sub>H<sub>4</sub> + C<sub>2</sub>H<sub>2</sub>.

**Acknowledgement:**

The authors are grateful to the Body Foundation and BAPKO of Marmara University for travel and computational support.

[1] K.Bohme and H. Schwarz, *Angew. Chem. Int. Ed.* 44, 2336 – 2354 (2005)

[2] Z. Altun, E.Bleda, and C. Trindle, *Molecular Physics*,

DOI:10.1080/00268976.2016.1274440 (2016)

[3] R. Wessendrup and H. Schwarz, *Organometallics*, 16,461-466 (1997)

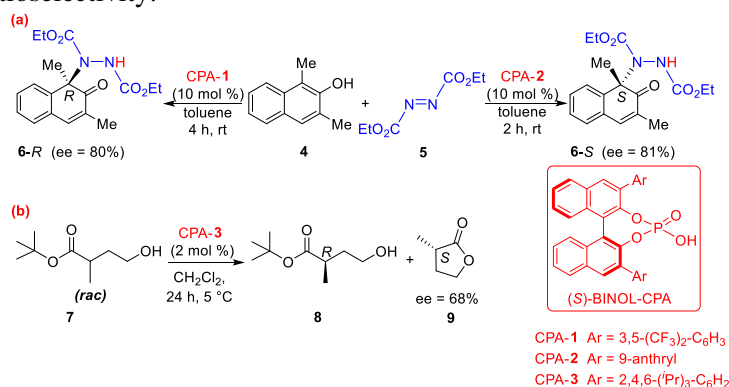


## Insights on Chiral Induction using (*S*)-BINOL-Phosphoric Acids in Enantioselective Reactions through Transition State Modeling

Avtar Changotra, Raghavan B. Sunoj

Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400076, India

Noncovalent interactions play a ubiquitous role in asymmetric organocatalytic reactions.<sup>1</sup> The overall stereoselectivity of such reactions often depends on the cumulative effect of such weak noncovalent interactions. Transition state models for the stereocontrolling step developed by using DFT computations helped us to gain valuable molecular insights in the chiral BINOL-phosphoric acid (CPA) catalyzed (a) asymmetric dearomatization of  $\beta$ -naphthols through an amination reaction<sup>2</sup> and (b) enantioselective lactonization of  $\alpha$ -substituted  $\gamma$ -hydroxy esters (Scheme 1).<sup>3</sup> Interesting mechanistic insights gained through the identification of various intermediates and transition states will be discussed in the poster. The differences in the preferred orientation of the substrates with respect to the 3,3' substituents in the chiral cavity of the catalyst and the associated changes in the set of weak noncovalent interactions between CPA-1 (predominantly C-H $\cdots$ F interactions between the substrates **4** and **5** and the 3,5-(CF<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub> groups of CPA-1) and CPA-2 (C-H $\cdots$  $\pi$  interactions between the substrates and 9-anthryl groups of CPA-2) are responsible for the inversion in the sense of enantioselectivity from *R* (**6-R**) to *S* (**6-S**) (Scheme 1(a)).<sup>4</sup> The 3,3'-aryl groups on the BINOL framework (CPA-3) plays an important role in placing the substrate **7** in the chiral cavity such that lactonization occurs preferentially through one of the prochiral faces (*si*) of the ester leading to the formation of *S* lactone **9** (Scheme 1(b)). A network of favorable noncovalent interactions such as C-H $\cdots$  $\pi$ , C-H $\cdots$ O, and lone pair $\cdots$  $\pi$  between the ester and CPA-3 is found to be the origin of enantioselectivity.<sup>5</sup>



**Scheme 1.** (*S*)-BINOL-phosphoric acid catalyzed (a) asymmetric dearomatization of  $\beta$ -naphthol through amination reaction and (b) kinetic resolution of hydroxy esters.

[1] A. J. Neel, M. J. Hilton, M. S. Sigman, F. D. Toste *Nature* **543**, 637 (2017).

[2] S.-G. Wang, Q. Yin, C.-X. Zhuo, S.-L. You *Angew. Chem., Int. Ed.* **54**, 647 (2015).

[3] G. Qabaja, J. E. Wilent, A. R. Benavides, G. E. Bullard, K. S. Petersen *Org. Lett.* **15**, 1266 (2013).

[4] A. Changotra, S. Das, R. B. Sunoj *Org. Lett.* (2017). DOI: 10.1021/acs.orglett.

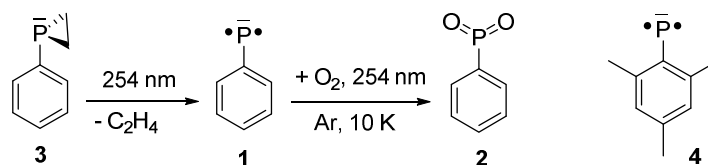
[5] A. Changotra, R. B. Sunoj *Org. Lett.* **18**, 3730 (2016).

## Generation of Parent Phenylphosphinidene and its Oxidation to Phenyldioxophosphorane, the Elusive Phosphorous Analogue of Nitrobenzene

Artur Mardyukov<sup>1</sup>, Dominik Niedek,<sup>1</sup> Peter R. Schreiner<sup>1</sup>

<sup>1</sup>Institute of Organic Chemistry, Justus-Liebig University, Heinrich-Buff-Ring 17, 35392 Giessen, Germany

Phosphinidenes ( $R-\bar{P}:$ ) are the phosphorus analogues of carbenes and nitrenes. While the chemistry of carbenes and nitrenes has been well established,<sup>1</sup> that of the phosphinides has just begun blossoming.<sup>2</sup> Due to their high reactivity, the chemical properties of phosphinidenes have been deduced almost exclusively from trapping or complexation experiments.<sup>3</sup> Several methods for their generation have been reported in the literature,<sup>4,5</sup> including attempts toward observation of triplet mesitylphosphinidene (**4**) via EPR spectroscopy.<sup>6</sup> Phenylphosphinidene **1** is the parent of **4** and has never been observed experimentally.



Although **1** is highly reactive, its reactions with small molecules has only scarcely been studied; this would lead to several interesting novel species that have never been observed before. A prime example is the reaction of **1** with molecular oxygen ( $^3P-O_2$ ) that may directly lead to phenyldioxophosphorane (PhPO<sub>2</sub>, **2**), a novel compound that constitutes the phosphorous analogue of ordinary nitrobenzene.

The talk reports the first synthesis, IR, and UV-Vis spectroscopic characterization of parent phenylphosphinide (**1**) and its oxidation product phenyldioxophosphorane (**2**). Triplet phenylphosphinidene **1** was characterized by IR and UV-vis spectroscopy for the first time and matching of its spectra with density functional theory (DFT) computations. Matrix isolation studies of **1** reveal an unprecedented high reactivity towards molecular oxygen, in contrast to its nitrene analogue, even at temperatures as low as 10 K.<sup>7</sup>

- (1) R. A. Moss, M. S. Platz, M. Jr. Jones, Editors *Reactive Intermediate Chemistry*, John Wiley & Sons, Inc., (2004).
- (2) H. Aktas, J. C. Sootweg, K. Lammertsma, *Angew. Chem., Int. Ed.* **49**, 2102 (2010).
- (3) Lammertsma, K.; Vlaar, Mark J. M. *Eur. J. Org. Chem.* **2002**, 1127 (2002).
- (4) S. Shah, M. C. Simpson, R. C. Smith, J. D. Protasiewicz, *J. Am. Chem. Soc.* **123**, 6925 (2011).
- (5) A. H. Cowley, F. Gabbai, R. Schluter, D. Atwood, *J. Am. Chem. Soc.* **114**, 3142 (1992).
- (6) X. Li, S. I. Weissman, T. -S. Lin, P. P. Gaspar, A. H. Cowley, A. I. Smirnov, *J. Am. Chem. Soc.* **116**, 7899 (1994).
- (7) A. Mardyukov, N. Niedek, P. R. Schreiner, *J. Am. Chem. Soc.* **139**, 5019 (2017).

## Effects of solvents and temperature on NMR chemical shifts in hydrogen-bonded complexes

Yukihiro Ota<sup>1</sup>, Motoyuki Shiga<sup>2</sup>

<sup>1</sup>Kobe Center, Research Organization for Information Science and Technology, Kobe, Japan

<sup>2</sup>CCSE, Japan Atomic Energy Agency, Kashiwa, Japan

Chemical shift in nuclear magnetic resonance (NMR) spectroscopy [1] is one of the important probes of determining the structures of chemical bonds. The shift of NMR frequency is sensitive to the variations of electronic structures around nuclei. Using NMR and UV-vis spectroscopy, Koeppe *et al.* [2] studied proton's position in a hydrogen bond of anionic complexes,  $[AHX]^-$ , with phenols/organic acids (AH) and carboxylic/inorganic acids (HX). They found extending (shrinking) behaviors of the distance between A (X) and H with a decrease of solvent polarity, even though the acidity of HX is stronger than that of AH in water solvents; solvent polarity allows the change of the proton donor in  $[AHX]^-$ .

In this paper, we theoretically study the chemical shift of H sandwiched between A and X, to understand the effect of solvent polarity and thermal vibrations on chemical shifts. Among different systems in the experiments [2], we focus on a complex composed of dichloroacetic ( $A^- = CHCl_2COO^-$ ) and hydrochloric acids ( $X^- = Cl^-$ ) since in this system the solvent polarity is controlled by temperature. The main calculations are performed by GAUSSIAN 09 [3]. The structural optimization is done at the MP2/6-31G\*\* level of theory, whereas the NMR shielding tensor is calculated at four different kinds of theoretical levels, MP2/6-31G\*\*, MP2/6-31++G\*\*, MP2/6-311++G\*\*, and B3LYP/aug-cc-pVTZ, with the gauge-independent atomic orbital method. First, we examine the solvent effects with the polarizable continuum model, changing the dielectric constants followed by the experimental settings. Our calculations qualitatively recover the dependence on solvents' dielectric constants in the experiments. Therefore, we claim that the behaviors of the proton chemical shifts in the experiments are attributed to the change of solvation structure. Next, we study the thermal effects, taking vibration corrections with respect to the normal modes of the complex into account. We find that the vibration corrections have impacts on a quantitative improvement of the theoretical evaluation on the chemical shifts, on three kinds of calculation levels (MP2/6-31G\*\*, MP2/6-31++G\*\*, and B3LYP/aug-cc-pVTZ). We will also argue the effects of anharmonic corrections from a stretching mode of the target proton, indicating a strong anharmonicity on the potential energy surface along this normal mode.

[1] F. A. F. Mulder, M. Filatov, *Chem. Soc. Rev.* **39**, 578 (2010).

[2] B. Koeppe *et al.*, *J. Am. Chem. Soc.* **135**, 7533 (2013).

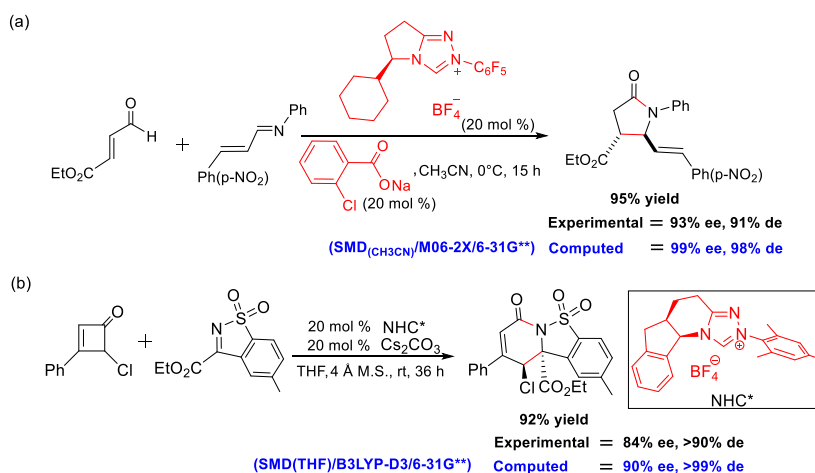
[3] M. J. Frisch *et al.*, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT (2013).

## Mechanistic Insights and Origin of Stereoinduction on NHC Catalysed Asymmetric Reactions using Transition State Modelling

Monika Pareek and Raghavan B. Sunoj

Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400076, India

In recent years, N-heterocyclic carbenes (NHCs) have emerged as powerful nucleophilic organocatalyst and as ligands in transition metal catalysts in a wide range of asymmetric reactions. NHCs renders umpolung reactivity on reaction with aldehydes and ketones by forming different type of reactive intermediate such as acyl anion equivalent, homoenolate, enolate, or  $\alpha$ -acylvinyl anion equivalent.<sup>1</sup> In this poster, we wish to present mechanistic insights and origin of stereoinduction on two such asymmetric reactions catalysed by chiral NHCs using transition state models. First asymmetric transformation involves dual cooperative catalytic reaction between enal and imine to form *trans*  $\gamma$ -lactam catalysed by chiral NHC and Brønsted acid (Scheme1(a)).<sup>2</sup> The mechanistic studies helps us to understand the role of *in situ* generated Brønsted acid, its explicit and cooperative participation with NHC lowers the energetic barrier for both the Breslow intermediate formation and in the stereocontrolling step.<sup>3</sup> The second reaction is C—C bond activation of cyclobutenone and subsequent reaction with sulfonyl imine to form  $\delta$ -lactam with high enantio- and diastereoselectivity in the presence of chiral NHC (Scheme1(b)).<sup>4</sup> In both the asymmetric reactions, the stereocontrol is found to be due to an effective number of C—H $\cdots\pi$ , N—H $\cdots$ O, and  $\pi\cdots\pi$  noncovalent interactions. The vital energy difference between the stereocontrolling transition states originates from the differential noncovalent interactions present in different stereochemically mode of additions.<sup>3,5</sup>



**Scheme 1.** (a) Cooperative asymmetric reaction catalysed by chiral NHC and Brønsted acid to form *trans*  $\gamma$ -lactam, and (b) chiral NHC catalysed C—C bond activation reaction to form  $\delta$ -lactam.

[1] M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **510**, 485 (2014).

[2] X. Zhao, D. A. DiRocco, T. Rovis, *J. Am. Chem. Soc.* **133**, 12466 (2011).

[3] M. Pareek, R. B. Sunoj, *ACS Catal.* **6**, 3118 (2016).

[4] B.-S. Li, Y. Wang, Z. Jin, P. Zheng, R. Ganguly, Y. R. Chi, *Nat. Commun.* **6**, 6207 (2015).

[5] M. Pareek, R. B. Sunoj, *Org. Lett.* **18**, 5932 (2016).

## Halogen Bonding involving Aromatic acceptors

**S. J. Ang<sup>2,3</sup>, Adrian M. Mak<sup>2</sup>, Michael B. Sullivan<sup>2</sup>, M. W. Wong<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore.*

<sup>2</sup>*Institute of High Performance Computing, 1 Fusionopolis Way, #16-16 Connexis North, Singapore 138632, Singapore.*

<sup>3</sup>*NUS Graduate School for Integrative Sciences and Engineering, Centre for Life Sciences (CeLS), #05-01, 28 Medical Drive, Singapore 117456, Singapore*

Interest in halogen bonding (XB) has received renewed interest recently, with many theoretical studies themed on lone-pair-type XB donors. XB is also manifested in various fields such as crystal engineering, organocatalysis, functional materials, and drug design. A survey of structures within the protein data bank (PDB) revealed 33% of XB interactions involve close contacts between  $\pi$ -systems and a halogen (X) group.<sup>1</sup> Our survey of crystal structures in the Cambridge Structural Database (CSD), shows 43% of the total XB close contacts involve  $\pi\cdots X$  interactions, of which 91% involve aromatic rings. Delocalization of  $\pi$ -electrons on the plane of the ring make the attribution of favorable XB sites on the conjugated system a difficult task, in contrast with the straightforward case in lone-pair type XBs. We report here, the locations of favorable XB binding sites involving Cl<sub>2</sub> as an XB donor, with different polycyclic aromatic hydrocarbons (PAHs) and heteroaromatic compounds as XB acceptors, deduced from PES scans using dispersion-corrected DFT, which in turn will provide useful insights into molecular assembly in functional material synthesis and applications.

[1] Y. Lu, Y. Wang, W. Zhu, *Phys. Chem. Chem. Phys.* **2010**, *12*, 4543–4551.

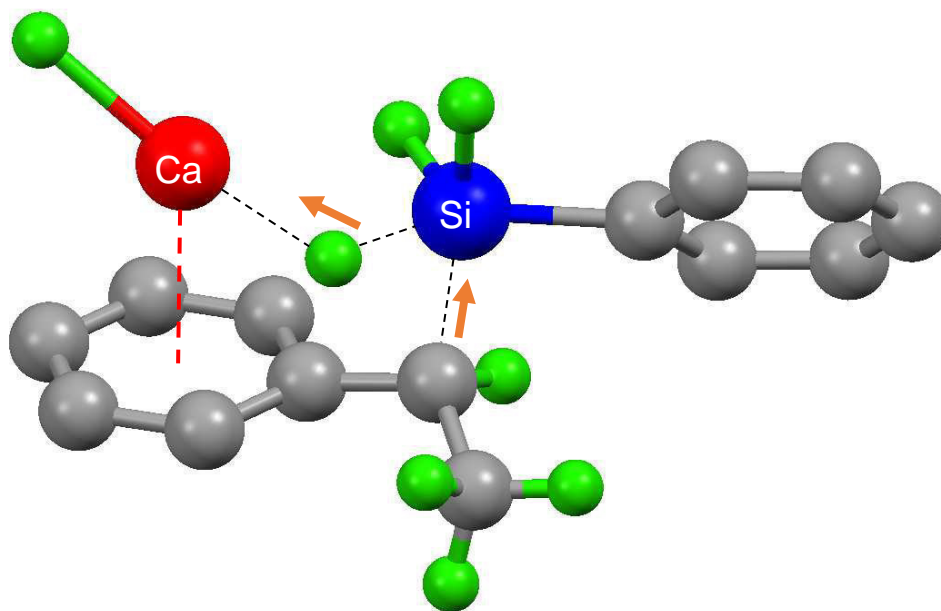
## Mechanistic Insight into the Hydrosilylation of Alkenes Using Early Main-Group Metal Catalysts

H. Elsen, N. van Eikema Hommes, A. Görling, S. Harder\*

*Friedrich-Alexander University Erlangen-Nuremberg*

*Egerlandstr. 1-3 91058 Erlangen*

The key to developing highly efficient catalysts is to fully comprehend the reaction mechanism. Computational chemistry allows us to model the reactions and possible alternatives. We here present density-functional calculations for the hydrosilylation of conjugated alkenes using Ca and K-based catalysts introduced by Harder *et al.* [1]. The Markovnikov or anti-Markovnikov regiochemistry strongly depends on the catalyst and on the reaction medium. We compare the results of gas-phase and PCM solvent model calculations for the full catalytic system and model systems thereof. Our mechanistic insights are discussed within the framework of the growing number of early main group metal catalysts for alkene hydrosilylation [2].



**Figure 1.** Transition state for the silicon-carbon bond formation with concerted hydride transfer (arrows representative of movement during the transition state)

[1] F. Buch, J. Brettar, S. Harder, *Angew. Chem. Int. Ed.* **2006**, 45, 2741.

[2] (a) V. Leich, T. Spaniol, L. Maron, J. Okuda, *Chem. Commun.*, **2014**, 50, 2311; (b) V. Leich, T. Spaniol, L. Maron, J. Okuda, *Organometallics* **2016**, 35, 1179.

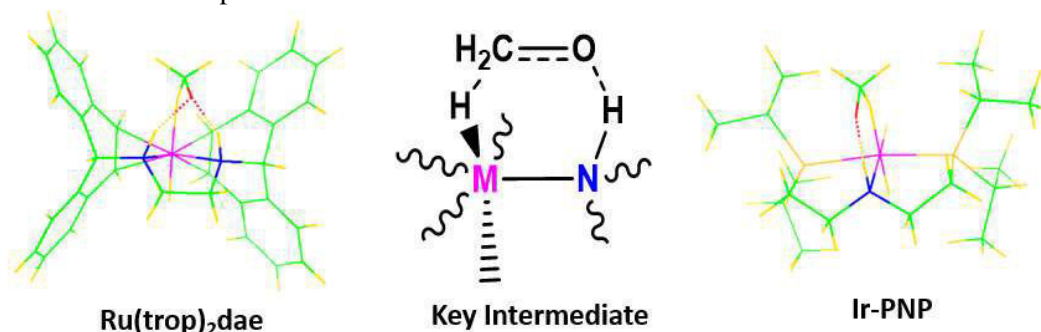
## Mechanistic insights into aqueous methanol dehydrogenation

Vivek Sinha<sup>1</sup>, Nitish Govindarajan<sup>1</sup>, Evert Jan Meijer<sup>1</sup>, Monica Trincado<sup>2</sup>,  
Hansjörg Grützmacher<sup>2</sup> and Bas de Bruin<sup>1</sup>

<sup>1</sup>HIMS, Universiteit van Amsterdam, Amsterdam, The Netherlands.

<sup>2</sup>Laboratorium für Anorganische Chemie, ETH, Zürich, Switzerland

Developing a Hydrogen economy can address the coupled problems of energy and environmental crises. Practical aspects like storage and production limit the use of molecular hydrogen directly as a fuel. Simple molecules like water, ammonia or methanol are carriers of hydrogen. Organometallic fuel cells [1] covered with arrays of inorganic catalysts which release the full hydrogen content of simple molecules are of particular interest. We have performed a molecular level mechanistic study of aqueous-methanol dehydrogenation over a ruthenium catalyst (Ru(trop)<sub>2</sub>dad) [2]. Detailed exploration of the redox, electronic and chemical non-innocence of the ligands present in the catalytic system has been performed using DFT and CASSCF calculations. We further explore the key transition steps in alcohol dehydrogenation pathways by several other homogeneous catalysts. Our studies provide hints towards a deeper understanding of the explicit role of substrate, solvent and base concentration and how such systems can be incorporated in an OMFC device set-up.



A H-bonded methoxide-like species coordinated to the metal via alkyl hydrogen is the key intermediate in several methanol-dehydrogenation systems.

[1] S.P. Annen, V. Bambagioni, M. Bevilacqua, J. Filippi, A. Marchionni, W. Oberhauser, H. Schönberg, F. Vizza, C. Bianchini, H. Grützmacher, *Angew. Chem.*, **72**, 7229 (2010).

[2] R.E. Rodriguez-Lugo, M. Trincado, M. Vogt, F. Tewes, G. Santiso-Quinones, H. Grützmacher, *Nat. Chem.*, **5**, 342 (2013).

## On the Mechanism of Silver-Catalyzed Isomerization of Cubane and Homocubane.

**Said Jalife,<sup>1</sup> Sudip Pan,<sup>1</sup> María A. Fernández-Herrera<sup>1</sup> and Gabriel Merino.<sup>1</sup>**

<sup>1</sup>*Applied Physics, Center for Research and Advanced Studies of the National Polytechnic Institute, Cinvestav-Mérida. Km 6 Antigua Carretera a Progreso, Mérida, México.*

The attraction for polycyclic cage molecules has continued since the synthesis of the cubane skeleton by Eaton and Cole more than five decades ago.<sup>1</sup> Although considerable strained energy is contained within these molecules, a highly thermal stability is expected. Such behavior has been rationalized according to the Woodward-Hoffmann rules of orbital symmetry conservation.<sup>2</sup> However, evidence has shown that symmetry-disallowed isomerizations of several strained cage molecules are catalyzed by transition metal ions. Such is the case of cubane and homocubane, which are readily isomerized to cuneane structures under the presence of silver (I) ions, similar pathways have been observed for the homocubyl cation.<sup>3</sup> Despite the arguments that support a non-concerted mechanism for the valence isomerization of these systems, the possibility of a intervening concerted mechanism remains to be fully elucidated.<sup>4</sup> In the present work, we studied the silver-catalyzed isomerization for cubane and homocubane systems by means of ab-initio computations. Our results indicate that a silver ion reduces significantly the activation energies (ca. 3.0 kcal/mol) and that a stepwise mechanism is involved.

[1] P. E. Eaton, T.W. Cole, *J. Am. Chem. Soc.* **86**, 3157 (1964).

[2] R. B. Woodward, R. Hoffmann, *Angew. Chem., Int. Ed. Engl.* **8**, 781 (1969).

[3] S. Jalife, J. I. C. Wu, G. Martínez-Guajardo, P. v. R. Schleyer, M. Fernández-Herrera, G. Merino, *Chem. Commun.* **51**, 5391 (2015).

[4] V.I. Labunskaya, Ad. Shebaldo, M. L. Khidekel, *Usp. Khim.* **43**, 3 (1974).



**Effect of an external electric field on the structure and dynamics of CaO films**

**Mikhail S. Kuklin<sup>1</sup>, Andrey S. Bazhenov<sup>2</sup>, Karoliina Honkala<sup>2</sup>, Sergio Tosoni<sup>3</sup>,  
Gianfranco Pacchioni<sup>3</sup>, Hannu Häkkinen<sup>1,2</sup>**

<sup>1</sup>*Department of Physics and* <sup>2</sup>*Department of Chemistry/Nanoscience Center, University of  
Jyväskylä, FI-40014, Jyväskylä, Finland*

<sup>3</sup>*Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, via Cozzi 55, 20125  
Milano, Italy*

Oxide films play a key role in a broad range of economically relevant fields due to the thickness-dependent properties. The recent scanning tunneling microscopy (STM) study suggested that carrier transport in CaO films deposited on Mo support proceeds via strong phonon excitations with a signal depending on the film thickness [1]. To check the assumption about phonon-assisted transport, we present a density functional theory (DFT) study of a detailed investigation of the phonons together with structural and electronic properties of freestanding and Mo(100)-supported CaO films as functions of the film thickness and intensity of the external electric field [2]. Calculations were carried out by using CRYSTAL14 code within the framework of the PWGGA functional with 10% of the exact part. Phonon eigenvalues and eigenvectors were subsequently calculated for optimized freestanding and Mo-supported CaO films. The external electric field was applied along a non-periodic direction to reproduce experimental sample bias in the STM setup. Our study demonstrates that phonon frequencies negligibly depend on the applied electric field; a small increase in the energy of CaO phonons was detected upon increase of the film thickness that is in line with experimental findings. Effect of Mo support was found to be in the systematic decrease of the energy of phonons that is known as the phonon softening. Even though structural properties were negligibly affected by the electric field, significant effect on the electronic structure of CaO films was observed. Particularly, reduction of the band gap of CaO films was found under the applied electric field with more pronounced effect on thicker films. It is explained by the band dispersion that comes from the loss of the symmetry of oxide films in the presence of electric field.

[1] Y. Cui, S. Tosoni, W.-D. Schneider, G. Pacchioni, N. Nilius, H.-J. Freund, *Phys. Rev. Lett.* **114**, 016804 (2015).

[2] M.S. Kuklin, A.S. Bazhenov, K. Honkala, S. Tosoni, G. Pacchioni, H. Häkkinen, *Phys. Rev. B* **95**, 165423 (2017).

## Coordination chemistry of Zn<sup>2+</sup>: Tetrahedral coordination or penta-coordination? A DFT analysis and review.

Walid Lamine,<sup>a,b</sup> Salima Boughdiri,<sup>b</sup> Christophe Morell,<sup>a</sup> Lorraine Christ,<sup>c</sup>  
Henry Chermette<sup>a</sup>

*a* Université de Lyon, Institut des Sciences Analytiques, UMR CNRS 5280, Université Claude Bernard Lyon 1, ENS-Lyon,  
69622 Villeurbanne Cedex, France

*b* Université de Tunis El Manar, Faculté des Sciences de Tunis, UR11ES19 Unité de recherche Physico-Chimie des Matériaux condensés,  
El-Manar II, 2092, Tunis, Tunisie

*c* Université de Lyon, Institut de Recherches sur la Catalyse et l'Environnement de Lyon, IRCELYON, UMR CNRS 5256, Université Lyon 1,  
69626 Villeurbanne Cedex, France

The coordination chemistry of the Zn<sup>2+</sup> cation is mainly dominated by a tetrahedral geometry which agrees well with the 18 electrons rule. However, several compounds exhibit a penta-coordination which would lead to a 20 electrons environment in which an axial ligand is added to a quasi-square planar geometry, but no octahedral geometry exists. The purpose of this work is to rationalize this situation, using conceptual density descriptors and to see how all the known Zn<sup>2+</sup> complexes fit into these two optional geometries, and predict the geometries of any Zn<sup>2+</sup> complexes.

In a first approach the properties of the [ZnCl<sub>4</sub>]<sup>2-</sup> cluster will be studied, and some general rules will be extracted. These results prompted us to extend these studies also to other known Zn(II)- complexes based on sal(ph)en ligand recognized by their self-assembled behavior and in which the Zinc metal center can adopt either tetrahedral [1], or penta-coordination [2], hence depending on the nature of the bridging diamine. The properties and structures of these moieties are analyzed and rationalized.

### References:

- [1] - G. Zhang, Q. Li, G. Proni, *Inorg. Chem. Comm.* 2014, **40**, 47–50.
- [2] - M. M. Belmonte, S. J. Wezenberg, R. M. Haak, D. Anselmo, E. C. Escudero-Adan, J. Benet-Buchholz and A. W. Kleij, *Dalton Trans.*, 2010, **39**, 4541–4550

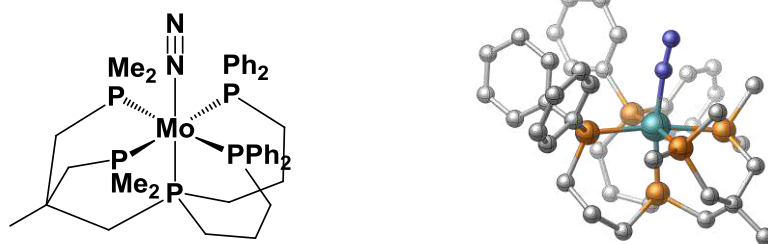
## Synthetic nitrogen fixation with mononuclear molybdenum complexes: Electronic-structural and mechanistic insights from DFT

Benedikt Flöser<sup>1</sup>, Felix Tuczek<sup>1</sup>

<sup>1</sup>*Department of Inorganic Chemistry, University of Kiel, Max-Eyth-Straße 2, Kiel, Germany*

The fixation of molecular dinitrogen from the atmosphere performed by the enzyme nitrogenase has drawn considerable interest, and although large advancements have been made towards understanding the involved processes, many questions yet remain.[1]

So far various model systems for synthetic nitrogen fixation have been presented some of which exhibit catalytic ammonia formation. Recently our group identified and synthesized a promising model complex featuring a new pentadentate ligand systems that was designed to envelop the metal center completely and thus minimize spurious side reactions (cf. Fig. 1).[2]



**Fig. 1:** Schematic and optimized structure of the Mo(0)-N<sub>2</sub> pentaPod complex. Hydrogen atoms are omitted for clarity.

An in-depth study of this [Mo(N<sub>2</sub>)(pentaPod)] complex was conducted including spectroscopic characterization, evaluation of the activation towards protonation and an extensive DFT study of the reactive pathway leading from N<sub>2</sub> to NH<sub>3</sub>. The latter provided a useful comparison to previously synthesized complexes and demonstrated the potential of this complex for a catalytic nitrogen fixation cycle.[3]

- [1] S. Hinrichsen, H. Broda, C. Gradert, L. Söncksen, F. Tuczek, *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.* **2012**, 108, 17.
- [2] S. Hinrichsen, A. Kindjajev, S. Adomeit, J. Krahmer, C. Nather, F. Tuczek, *Inorg. Chem.* **2016**, 55, 8712.
- [3] B. M. Flöser, F. Tuczek, *Coord. Chem. Rev.* **2016**.  
<http://dx.doi.org/10.1016/j.ccr.2016.11.003>

## Effects of External Electric Field and Anisotropic Long-Range Reactivity on Charge Separation Probability

Sangyoub Lee and Kyusup Lee

*Department of Chemistry, Seoul National University, Seoul 08826, South Korea*

The recombination of geminate charge pairs generated by radiation has been investigated intensively, especially in an effort to design more efficient solar cells. In this work, we employ the recently proposed solution method for Fredholm integral equations of the second kind to treat the effects of external electric field and anisotropic long-range reactivity on the recombination dynamics of a geminate charge pair. A closed-form analytic expression for the ultimate separation probability of the pair is presented. In previous theories, analytic expressions for the separation probability were obtained only for the case where the recombination reaction can be assumed to occur at a contact separation. For this case, Noolandi and Hong obtained an exact expression for the separation probability. However, the solution was expressed as an infinite series of two complicated functions, each of which is also expressed as an infinite series, and involved expansion coefficients that need to be determined by solving a set of linear equations containing infinite sums. As such, an approximate analytic expression proposed by Braun has been widely used. However, Braun's expression overestimates the separation probability when the electric field is large. Very recently, Seki and Wojcik obtained an approximate expression for separation probability that is very accurate when the Onsager distance is large, so that the expression is useful for low permittivity materials. However, when the Onsager distance is small, their expression fails. In this work, we have derived an approximate analytic expression that is accurate enough for all parameter values. In addition the expression is applicable also when the interaction between the geminate charge pair is described by screened Coulombic potential, and the recombination reaction has an anisotropic and long-range reactivity. We also provide the expression for the separation probability when the initial separation between the geminate charge pair is larger than the contact distance.

- [1] J. Noolandi and K. M. Hong, *J. Chem. Phys.* **70**, 3230 (1979).
- [2] C. L. Braun, *J. Chem. Phys.* **80**, 4157 (1984).
- [3] K. Seki and M. Wojcik, *J. Phys. Chem. C* **121**, 3632 (2017).

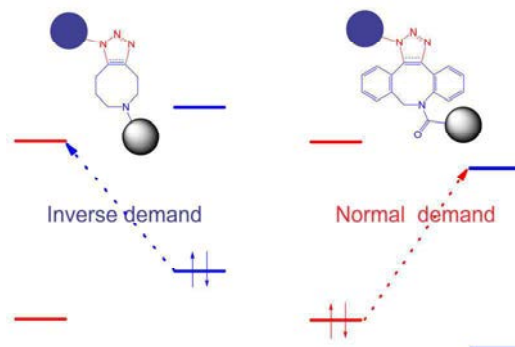
## Activation Strain Analyses for copper-free click reactions of alkyl azides with cyclooctynes and dibenzocyclooctynes

Felipe S. Vilhena<sup>1</sup>, F. Matthias Bickelhaupt<sup>2</sup>, José W. M. Carneiro<sup>1</sup>

<sup>1</sup>Department of Inorganic Chemistry, Universidade Federal Fluminense (UFF), Niterói, Rio de Janeiro

<sup>2</sup>Department of Theoretical Chemistry and Amsterdam Center for Multiscale Modeling (ACMM), Vrije Universiteit Amsterdam, Amsterdam, Netherlands

The copper-free click chemistry reactions known as strain-promoted azide-alkyne cycloaddition (SPAAC) [1] have gained a wide range of applications for coupling reactants *in vivo*. In this work we explored through DFT at B3LYP/6-311++G(d,p) level 1,3-dipolar cycloaddition reactions of alkyl azides with cyclooctynes and dibenzocyclooctynes. We used activation strain model (ASM) [2] and the molecular orbital (MO) [3] to investigate the steric and electronic factors that govern the reactivity and regioselectivity in these reactions.



**Figure 1.** Frontier molecular interactions in 1,3-dipolar cycloaddition.

Three concepts arise for the 1,3-dipolar cycloadditions of alkyl azides: (i) cyclooctynes leads to an inverse electron-demand; (ii) dibenzocyclooctynes favor the normal electron-demand; (iii) the *anti* regiochemistry preference is observed. The higher reactivity of dibenzocyclooctynes than corresponding cyclooctynes is the result of a more stabilizing interaction energy and not so much a low strain energy. The *anti* regiochemistry preference is favoured by a normal electron-demand interaction which also goes with less distortion of the dipole.

### References

- [1] J. C. Jewett, C. R. Bertozzi, *Chem. Soc. Rev.* **39**, 1272 (2010).
- [2] W.-J. van Zeist, F. M. Bickelhaupt, *Org. Biomol. Chem.* **8**, 3118 (2010).
- [3] F. M. Bickelhaupt, E. J. Baerends, In: *Reviews in Computational Chemistry*; K. B. Lipkowitz, D. B. Boyd, Eds.; Wiley-VCH: New York, 2000, Vol. 15, pp. 1-86.

## Computational study of the electrochemical reduction of [(dpp-bian)Re(CO)<sub>3</sub>Br]<sup>0</sup>: mechanism and EPR spectroscopy of intermediates.

Alexey Dmitriev<sup>1,2</sup>, Pavel Abramov<sup>1,3</sup>, Nina Gritsan<sup>1,2</sup>

<sup>1</sup>Novosibirsk State University, 2 Pirogova Street, Novosibirsk, Russia

<sup>2</sup>Institute of Chemical Kinetics and Combustion, 3 Institutskaya Street, Novosibirsk, Russia

<sup>3</sup>Institute of Inorganic Chemistry, 3 Akad. Lavrentiev Avenue, Novosibirsk, Russia

The [(dpp-bian)Re(CO)<sub>3</sub>Br]<sup>0</sup> complex belongs to well-known family of rhenium(I) tricarbonyl diimine complexes. Usually, this type of complexes exhibit phosphorescence characterized by high quantum yields and very large Stokes shifts and is prone to catalyze the CO<sub>2</sub> photo- and electrochemical reduction to produce energy-rich compounds. This makes these complexes promising candidates for a variety of applications.

Recently [1], a mechanistic study of the CO<sub>2</sub> reduction in the presence of 2,2'-bipyridyl-based Re(I) and Mn(I) *fac*-tricarbonyl electrocatalysts has been performed using IR spectroscopy and a series of intermediates has been proposed. For electrochemical reduction of complex **1**, our collaborators were able to register the EPR spectra of two intermediates. However, the electronic structure of proposed intermediates in the reduction of Re(I) tricarbonyl diimine complexes has never been verified using quantum chemistry. It should be noted that the calculation of both the electronic structure and spin-Hamiltonian parameters (HFC constants, g-factors etc.) for complexes of 5d elements especially with open-shell ligands is a non-trivial task, and at least, full-electron calculations with scalar relativistic Hamiltonian are required [2].

The report will present results of our theoretical study on the mechanism of complex **1** electrochemical reduction. To calculate Gibbs free energy of the elementary reactions, the structures of proposed intermediates were optimized at the B97-D3/def2-TZVP level in DMF solution using the COSMO solvation model. The optimized geometries of primary reduced complex **1**<sup>•</sup> and other reduced paramagnetic complexes were used for the calculations of their g-tensors and hyperfine coupling (HFC) constants on Re, Br and N atoms of the ligand. All-electron DFT with scalar relativistic Hamiltonian (DKH2 or ZORA) and a number of functionals have been used in these calculations. It was found that application of BHandHLYP hybrid functional and WTBS basis set for Re leads to most reliable values of HFC constants.

[1] C. W. Machan, M. D. Sampson et. al., *Organometallics* **33**, 4550 (2014).

[2] P. Abramov, N. Gritsan, E. Suturina et al., *Inorg. Chem.* **54**, 6727 (2015).

Acknowledgements: This work was supported by the Russian Science Foundation (project 16-13-10155).

**Non-analytical functionals – A new strategy in density functional theory****Kati Finzel<sup>1</sup>, Patrick Bultinck<sup>1</sup>**<sup>1</sup>*Ghent University, Ghent Quantum Chemistry Group, Krijgslaan 281 (S3), 9000 Gent, Belgium*

Non-analytical functionals provide the functional values at a given point of interest rather than an analytical correspondence between the functional values and all possible input functions. In contrast to conventional functional design, where a certain ansatz for the energy of the system has to be chosen, non-analytical functionals are constructed with the help of exact functional properties, and as such yield the exact energy provided the corresponding input potential is exact. This offers a new strategy for a systematic development of potential-functionals applicable in the computation of molecular complexes and material design.

## Numerical Nuclear Second Derivatives on a Grid: A Faster and Enabling Method for Hessian Calculations

Tzuhsiung Yang and John F. Berry\*

*Department of Chemistry, University of Wisconsin—Madison, 1101 University Avenue,  
Madison, WI USA*

The computation of nuclear second derivatives (NSD) is an essential routine in quantum chemical investigations. Previous work has contributed to the analytical evaluation of NSD (aNSD)<sup>[1]</sup> and to the improvement of integral evaluation<sup>[2]</sup> and storage to enable NSD evaluations for larger systems within a manageable wall clock time in a less demanding hardware framework. Another facet of NSD computations focuses on hardware-enabled faster and more capable integral evaluations based on specialized processors such as graphic processing units (GPUs).<sup>[3]</sup> This facet of NSD computation is complimentary to the continuing development of theory and mathematical approximations.

Herein, we describe another facet of improving NSD computations focusing on the utilization of grid computing to enable numerical differentiations of analytical first derivatives (aNFD) to calculate NSD (nNSD). The advantage of nNSD over aNSD is that it circumvents the costly evaluation of the coupled-perturbed Hartree-Fock or Kohn-Sham equations. Hence, the scaling of nNSD is on the same order as aNFD. The unfavorable pre-scaling factor, which is twice of the degrees of freedom in central differences, of the nNSD is reduced to unity by distributing each differentiation to a remote computer. In our case, C<sub>22</sub>H<sub>14</sub> with 626 basis functions (BFs) and 1764 density fitting functions (DFFs) using RIJCOSX-B3LYP-D3 took 22±5 min using the nNSD-on-grid method vs 52 min using aNSD on 16 processors (total CPU time = 848 min). In addition, the nNSD-on-grid method allows NSD readily tractable for macromolecules. NSD can be evaluated for an insulin molecule (C<sub>253</sub>H<sub>374</sub>N<sub>76</sub>O<sub>76</sub>S<sub>6</sub>; 12266 BFs and 33956 DFFs) using nNSD-on-grid while I/O bottleneck forbids aNSD. Lastly, nNSD-on-grid enables NSD using correlated wavefunctions on larger molecules (> 50 atoms). NSD of a molecular dichromium complex with 62 atoms, 1138 BFs, and 3012 DFFs can be evaluated using NEVPT2:CAS(2,2).

Grid computing on numerical methods can outperform analytical methods in terms of wall clock time and the size of systems treatable. The nNSD-on-grid method presented in this abstract is one example of this concept and a pioneer for future implementations.

[1] a) *International Reviews in Physical Chemistry* **19**, 61-95 (2000); b) A. Komornicki and G. Fitzgerald, *The Journal of Chemical Physics* **98**, 1398-1421 (1993)

[2] P. Deglmann, F. Furche and R. Ahlrichs, *Chemical Physics Letters* **362**, 511-518 (2002)

[3] I. S. Ufimtsev and T. J. Martinez, *Journal of Chemical Theory and Computation* **5**, 2619-2628 (2009)



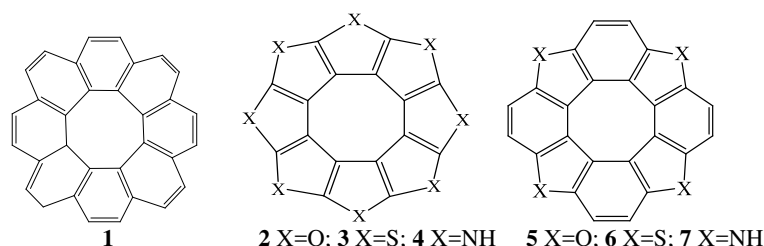
## A Study of the Global and Local Aromaticity of Hetero[8]circulenes

Abulikemu Keremu<sup>1</sup>

<sup>1</sup> School of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, China

### Abstract

The global aromaticity of the hetero[8]circulenes and their double charged ions was investigated using the topological resonance energy (TRE) method<sup>[1]</sup>. The bond resonance energy (BRE) and circuit resonance energy (CRE) methods were used to evaluate local aromaticity<sup>[1-3]</sup>. Analysis was made of the effects of the types and the arrangement of heteroatoms on the global and local aromaticity of the molecules under consideration. The local aromaticity results obtained here using the CRE and BRE methods were compared with the nucleus independent chemical shift values (NICS (0) and NICS (1)) as reported in the literature<sup>[4-5]</sup>. With respect to local aromaticity, discrepancies arose between results we obtained using the CRE and BRE methods and those predicted by the NICS (0) and NICS (1) methods. We found that increases in the local aromaticity of the cyclooctatetraene rings have a significant effect in increasing the global aromaticity of the molecule as a whole. Both in the neutral and double charged states, the benzene, thiophene, furan, and pyrrole rings, which are fused to the cyclooctatetraene ring, retain their local aromaticity. Finally, the ring current results were analyzed.



**Fig.1.** The structure of the compounds in this study

### References:

- [1] J. Aihara, *J. Am. Chem. Soc.*, **128**, 2873 (2006).
- [2] J. Aihara, *J. Am. Chem. Soc.*, **117**, 4130 (1995).
- [3] R. Mattohti and A. Kerim, *RSC Adv.*, **6**, 108538 (2016).
- [4] C. B. Nielsen, T. Brock-Nannestad, P. Hammersh, T. K. Reenberg, M. Schau-Magnussen, D. Trpcevski, T. Hensel, R. Salcedo, G. V. Baryshnikov, B. F. Minaev, and M. Pittelkow, *Chem. Eur. J.*, **19**, 3898 (2013).
- [5] G. V. Baryshnikov, N. N. Karaush, R. R. Valiev, and B. F. Minaev, *J. Mol. Model.*, **21**, 136 (2015).

## A Study of the Global and Local Antiaromaticity of 1,4-Diazapentalene Derivatives

Muhetaer Yimieraishan<sup>1</sup>

<sup>1</sup>*School of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, China*

### Abstract

The global antiaromaticity of several types of heteroacenes bearing the 1,4-diazapentalene core was investigated using the topological resonance energy and magnetic resonance energy methods<sup>[1]</sup>. The bond resonance energy (BRE) and circuit resonance energy (CRE) methods were used to evaluate local antiaromaticity<sup>[1,2]</sup>. Analysis was made of the effects of the number and the arrangement of heteroatoms on the global and local antiaromaticity of the molecules under consideration. The local antiaromaticity results obtained here using the CRE and BRE methods were compared with the nucleus independent chemical shift values (NICS(1)zz) as reported in the literature<sup>[3]</sup>. Regarding local aromaticity, discrepancies arose between results we obtained using the CRE and BRE methods and those predicted by the (NICS(1)zz) method. We found that the fusion of aromatic rings to the 1,4-diazapentalene core may dilute its antiaromatic character. Ring current results show that when aromatic rings are fused to the 1,4-diazapentalene cores, the cores maintain strong paratropic ring currents; the aromatic ring sections however, maintain diamagnetic currents flows around their molecular perimeter.

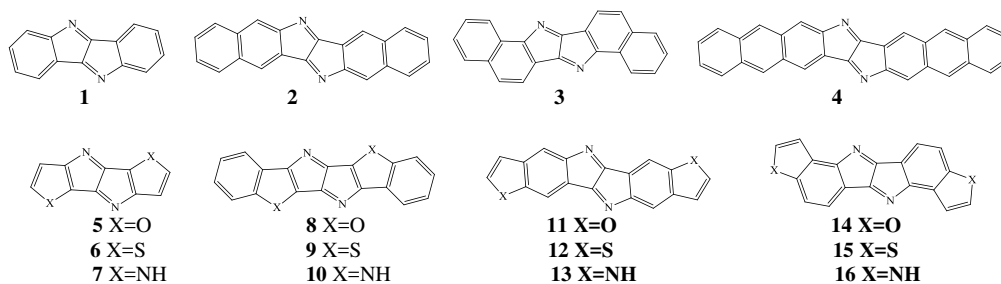


Fig.1. The structure of the compounds in this study

### References:

- [1] J. Aihara, *J. Am. Chem. Soc.*, **128**, 2873 (2006).
- [2] J. Aihara, *J. Am. Chem. Soc.*, **117**, 4130 (1995).
- [3] J. Zheng, X.H. Zhuang, L. Qiu, Y. Xie, X.B. Wan, Z.G. Lan, *J. Phys. Chem. A*, **119**, 3762 (2015).

## Time-dependent coupled-cluster method for laser-driven multielectron dynamics

Himadri Pathak<sup>1</sup>, Takeshi Sato<sup>1, 2</sup>, Kenichi L. Ishikawa<sup>1, 2</sup>

<sup>1</sup>*Department of Nuclear Engineering and Management, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

<sup>2</sup>*Photon Science Center, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

*Ab initio* description of light-matter interaction is a long-standing challenge for theoreticians, and recently gathering practical attention in the context of rapidly developing high-field physics and ultrafast science[1]. The time-dependent Schrödinger equation (TDSE) rigorously describes such electron dynamics. However, the exact solution of TDSE for an interesting chemical system is far beyond the reach, therefore, as an approximate but reasonably accurate solution to the TDSE, multiconfiguration time-dependent Hartree-Fock (MCTDHF) method has been developed for intense-laser driven multielectron dynamics[2]. Though powerful, the MCTDHF method suffers from exponential scaling of the computational cost with respect to the number of electrons. Attempts have been made by partitioning the orbital subspace to reduce the computational cost [3, 4, 5]. However, a problem with these approaches, except for the full configuration-interaction based MCTDHF and time-dependent complete-active-space self-consistent-field (TD-CASSCF) methods [3], is the lack of size-extensivity. An alternative method allowing size-extensive description of intense-laser driven multielectron dynamics with a moderate computational cost is strongly desired. The coupled-cluster (CC) method is an attractive candidate to fulfill this purpose, in viewing spectacular success of the method in the stationary theory[6]. Recently, Kvaal [7] has proposed a time-dependent version of the CC (TD-CC) method using adaptive bi-orthogonal orbitals and applied to a collision problem, which clearly requires further theoretical refinement. In the present contribution, we survey the theoretical background of the TD-CC method and present our recent development of real-time/real-space version of the TD-CC with numerical applications.

- [1] F. Krausz and M. Ivanov, *Rev. Mod. Phys.* **81**, 163 (2009).
- [2] J. Caillat, J. Zanghellini, M. Kitzler, O. Koch, W. Kreuzer, and A. Scrinzi, *Phys. Rev. A* **71**, 012712 (2005).
- [3] T. Sato and K. L. Ishikawa, *Phys. Rev. A* **88**, 023402 (2013).
- [4] H. Miyagi and L. B. Madsen, *Phys. Rev. A* **89**, 063416 (2014).
- [5] T. Sato and K. L. Ishikawa, *Phys. Rev. A* **91**, 023417 (2015).
- [6] R. J. Bartlett and M. Musiał, *Rev. Mod. Phys.* **79**, 291 (2007).
- [7] S. Kvaal, *J. Chem. Phys.* **136**, 194109 (2012).

## From G4(MP2)-6X to W3X-L: A Range of Efficient and Accurate Thermochemical Composite Protocols

**Bun Chan<sup>1</sup>, Leo Radom<sup>2</sup>**

<sup>1</sup>*Graduate School of Engineering, Nagasaki University, Bunkyo 1-14,  
Nagasaki 852-8521, Japan*

<sup>2</sup>*School of Chemistry, University of Sydney, NSW 2006, Australia*

The continuous development of quantum chemistry composite protocols has provided chemists with some powerful tools for quantitative computation of thermochemical quantities. Notably, the *Gn* and *Wn* series of composite methods are nowadays “household names” within the (computational) chemistry community. These two lines of methods have been designed with distinct philosophies, which result in their different capabilities that are often complementary with one another. The *Gn* procedures provide good and efficient approximations to CCSD(T) and are currently applicable to systems as large as C<sub>60</sub>, whereas *Wn* employ more rigorous formulations to produce even better accuracies but at the expense of computational efficiency. Over the last few years, we have constructed variants of *Gn* and *Wn* with the aim of combining their advantageous characteristics [1–6]. In this presentation, we will provide a synopsis on this collection of methodologies, with a focus on our more recent investigations.

- [1] B. Chan, J. Deng, L. Radom, *J. Chem. Theory Comput.* **7**, 112 (2011).
- [2] B. Chan, L. Radom, *J. Chem. Theory Comput.* **8**, 4259 (2012).
- [3] B. Chan, L. Radom, *J. Chem. Theory Comput.* **9**, 4796 (2013).
- [4] B. Chan, L. Radom, *J. Chem. Theory Comput.* **11**, 2109 (2015).
- [5] B. Chan, L. Radom, *J. Chem. Theory Comput.* **12**, 3774 (2016).
- [6] B. Chan, *J. Chem. Theory Comput.* DOI: 10.1021/acs.jctc.7b00219.

## Theoretical study of anatase (101) and rutile (110) TiO<sub>2</sub> nanotubes

Silva, G.O.<sup>1</sup>, Martins, J.B. L.<sup>1</sup>, Santos, J.D.<sup>2</sup>, Taft, C.A.<sup>3</sup>, Longo, E.<sup>4</sup>

<sup>1</sup>Laboratory of Computational Chemistry/ Chemistry Institute/ University of Brasilia/ CP 4478, Brasilia, Brazil

<sup>2</sup>Department of chemistry, University of Goias/ CP 75001970, Anapolis, Brazil

<sup>3</sup>Brazilian Center for Physical Research/ CP 22290180, Rio de Janeiro, Brazil

<sup>4</sup>Institute of Chemistry of Araraquara/ State University of São Paulo Júlio de Mesquita Filho/ CP 14800900, Araraquara, Brazil

<sup>1</sup>*gustavo\_olinto@hotmail.com*

Experimental and theoretical studies of nanotubes have increased over the last decades [1-2]. Simulations, molecular modeling and theoretical investigations were performed for different conformation of materials (nanotubes, surfaces, crystals) formed by various compounds (TiO<sub>2</sub>, ZnO, SnO<sub>2</sub>, GaAs), using quantum chemistry calculations in order to point out important structural and electronics properties of these materials.

Anatase and rutile nanotubes showed the same trend for the stability. It was noticed that a decrease in the value of the energy variation occurred dependent on the growth of the diameter, forming more stable structures. Increasing the length of the nanotubes did not influence the behavior change, that is, the smaller diameter structures remained more unstable than the larger diameter ones. Among the clusters obtained, we highlighted the nanotube anatase using large cluster that presented the lowest value of  $\Delta E$ , while rutile nanotubes showed smaller nanotubes for the lowest values of  $\Delta E$ .

The analysis of the energy variation of anatase and rutile nanotubes showed the stability is dependent on the growth of the diameter and consequently the decrease of the curvature. There were small variations in the results of *ab initio* calculations between the bases used in the study (6-31G and 6-311G).

**Acknowledgment:** CNPQ, CAPES, FAPEG, FAPDF

### References:

- [1] - E. Moraes, R. Gargano, J. R. S. Politi, E. A. Castro, J. D. Santos, E. Longo, J. B. L. Martins 1- Theoretical Investigation of ZnO Nanotubes: Size and Diameter. Current Physical Chemistry, v. 3, n. 4, p. 400-407, 2013.
- [2] – J. D. Santos, M. D. Ferreira, J. B. L. Martins, C. A. Taft, E. Longo, Computational Studies of [(SnO<sub>2</sub>)<sub>n</sub>]<sub>m</sub> Nanotubes. Current Physical Chemistry, v. 3, n. 4, p. 451-476, 2013.

## Ab initio construction of phase diagrams for molecular crystals.

Ctirad Červinka<sup>1</sup>, Gregory Beran<sup>2</sup>

<sup>1</sup>*Department of Physical Chemistry, University of Chemistry and Technology Prague,  
Technická 5, CZ 16628, Praha 6, Czech Republic*

<sup>2</sup>*Department of Chemistry, University of California Riverside, 501 Big Springs Rd, CA  
92521, Riverside, USA*

Due to the complex interplay of non-covalent interactions and an immense number of packing motives available, molecular crystals exhibit polymorphism. Considering its ubiquity, it seems there is no direct link between the complexity of a molecule and the number of its existing polymorphs. Polymorph screening and the determination of phase stability have long been experimentally challenging and expensive due to the difficulties of crystallization and the laborious calorimetric and spectroscopy experiments required to characterize polymorphs over broad ranges of pressures ( $p$ ) and temperatures ( $T$ ). However, the advent of reliable quantum chemistry calculations of cohesive energies and phonons creates new opportunities to predict phase stabilities *in silico*. Such a development should find many uses in pharmaceutical industry or modelling of processes in solid phase. [1]

Ab initio construction of a phase diagram consists in calculating the equilibrium curves of coexistence of the phases in the  $p - T$  coordinates. [2] In this work, many-body expansion [3, 4] and periodic quantum calculations [5] are used to obtain cohesive energies and phonon properties of the crystalline phases. Such data are processed by the quasi-harmonic approximation [6, 7] to yield the thermodynamic properties. The relevant criterion for assessing the phase stability at given  $p$  and  $T$  is the minimum molar Gibbs energy. Sublimation equilibrium is included in the phase diagrams in a relatively straightforward way since the vapor phases are assumed to be the ideal gas which can be treated by a combination of quantum calculations of molecular degrees of freedom and statistical-thermodynamics rules.

This work studies polymorphism on a test set of four simple molecules – methanol, ethane, benzene and imidazole, and seeks to determine how reliably phase stability and sublimation equilibrium can be predicted. Since the energy differences among various polymorphs usually range to a few  $\text{kJ mol}^{-1}$ , and the sublimation pressure depends exponentially on  $T$ , the highest accessible ab initio levels of theory need to be used for evaluation of cohesive energies. Vibration-based terms are calculated within the cheaper density functional theory framework. Several quantum chemistry methods are compared in this work and their effect on the resulting phase diagram is studied. Calculated data are confronted with their experimental counterparts so that the computational uncertainty can be estimated.

- [1] S. L. Price, S. M. Reutzel-Edens, *Drug Discovery Today* **21**, 912-923, (2016).
- [2] S. Hirata, K. Gilliard, et al. *Acc. Chem. Res.* **47**, 2721, (2014).
- [3] Y. N. Heit, K. D. Nanda et al. *Chemical Science* **7**, 246-255, (2016).
- [4] C. Červinka, M. Fulem et al. *J. Chem. Phys.* **144**, 064505, (2016).
- [5] C. Červinka, M. Fulem et al. *J. Phys. Chem. A* **120**, 2022-2034, (2016).
- [6] R. P. Stoffel, C. Wessel et al. *Angew. Chem. Int. Ed.* **49**, 5242-5266, (2010).

## Quantum Chemical Exploration of Transition Metal Mediated CO<sub>2</sub> Disproportionation and Hydrogenation

Lisa Roy<sup>1</sup>, Frank Neese<sup>1</sup>, Patrick L. Holland<sup>2</sup>, Shengfa Ye<sup>1</sup>

<sup>1</sup>*Department of Molecular Theory and Spectroscopy, Max Planck Institute for Chemical Energy Conversion, Stiftstrasse 34-36, Muelheim an der Ruhr, Germany*

<sup>2</sup>*Department of Chemistry, Yale University, New Haven, Connecticut 06520, United States*

Biological carbon fixation into organic matter occurs predominantly during the Calvin-Benson-Bassham Cycle (dark Photosynthetic cycle) that converts millions of tons of CO<sub>2</sub> into biomass with the intermediacy of the enzyme, RuBisCo. The key role here is played by the Mg<sup>+2</sup> centre at the active site of the metalloenzyme that promotes CO<sub>2</sub> fixation and feasible C-O bond cleavage to yield the desired product, phosphoglycerate. However chemical reduction of CO<sub>2</sub> is very challenging and involves high energetic requirement ( $E^{\circ} = -1.9$  V vs NHE) for the large structural rearrangement from linear CO<sub>2</sub> to bent CO<sub>2</sub><sup>-</sup>. Nevertheless, coupled multi-electron and multi-proton reactions occur at relatively modest potentials ( $E^{\circ} = -0.52$  V to  $-0.43$  V). This signifies that two-electron reduction of CO<sub>2</sub> requires efficient bi-functional catalyst.[1] Here, we have studied the mechanistic possibilities of two electron reduction of CO<sub>2</sub> primarily involving the following processes: (a) CO<sub>2</sub> Reductive Disproportionation ( $2\text{CO}_2 + 2\text{e}^- \rightarrow \text{CO} + \text{CO}_3^{2-}$ ) which is promoted by  $\kappa\text{N},\eta^6$ -arene-ligated  $\text{L}^{\text{tBu}}\text{Co}$ , where  $\text{L}^{\text{tBu}} = 2,2,6,6\text{-tetramethyl-3,5-bis(2,4,6-triisopropylphenylimido)hept-4-yl}$ . Our computational investigations reveal that a second metal-ligand complex is involved as a Lewis acid to polarize the target C-O bond and effectuate facile C-O bond cleavage involving a lower-barrier kinetic process than the monometallic pathway. (b) CO<sub>2</sub> hydrogenation by Hydride Transfer ( $\text{CO}_2 + \text{H}^+ + 2\text{e}^- \rightarrow \text{HCOO}^-$ ) studied with a series of phosphine-based metal-hydride complexes (from Group 8 and 9).[2] Our analysis shows that it is the stability of the Metal-Hydride complex derived from H<sub>2</sub>-Splitting that determines the rate determining step. This is an experimentally measured property called hydricity (or hydride affinity) which increases down a group and makes hydride transfer difficult for heavier metals (like Iridium).[3]

[1] B. Mondal, J. Song, F. Neese, S. Ye, *Curr. Op. Chem. Biol.* **25**, 130 (2015).

[2] B. Mondal, F. Neese, S. Ye, *Inorg. Chem.* **55**, 5438 (2016).

[3] J. T. Muckerman, P. Achord, C. Creutz, D. E. Polyansky, E. Fujita, *Proc. Nat Acad. Sc. USA* **109**, 15657 (2012).

## Molecular dynamics simulation reveals how phosphorylation of tyrosine 26 of PGAM1 upregulate glycolysis

Yan Wang<sup>1</sup>, Guanyu Wang<sup>1</sup>

<sup>1</sup>Department of Biology, Southern University of Science and Technology, No.1088 Xueyuan Blvd., Nanshan District, Shenzhen, P.R. China

Phosphoglycerate mutase 1 (PGAM1) catalyzes the eighth step of glycolysis and is often found upregulated in cancer cells. To test the hypothesis that the phosphorylation of tyrosine 26 residue of PGAM1 greatly enhances its activity, we performed both conventional and steered molecular dynamics simulations on the binding and unbinding of PGAM1 to its substrates, with tyrosine 26 either phosphorylated or not. We analyzed the simulated data in terms of structural stability, hydrogen bond formation, binding free energy, etc. We found that tyrosine 26 phosphorylation enhances the binding of PGAM1 to its substrates through generating electrostatic environment and structural features that are advantageous to the binding. Our studies have revealed considerable atomistic details of PGAM1, its substrates, and their interactions, which may provide valuable insights into computeraided design of drugs that specifically target cancer cells. Through virtual screening of chemical libraries, for example, small drug molecules may be found that can greatly weaken or even block the binding between PGAM1 phos and its substrates, while having little effects on PGAM1 wt. Our results may provide valuable insights into computer-aided design of drugs that specifically target cancer cells with PGAM1 tyrosine 26 phosphorylated.

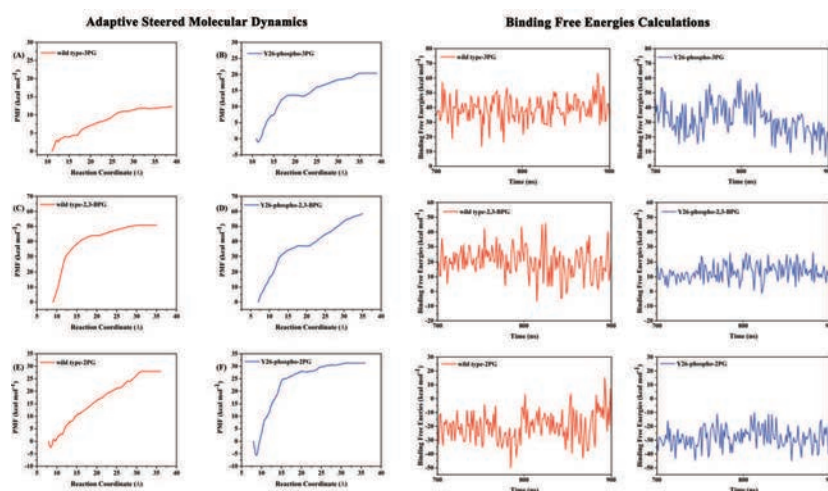


Figure 1: Left panel: The 3-Phosphoglyceric acid, 2-Phosphoglyceric acid and 2,3-Bisphosphoglyceric acid molecules were pulled out of the binding pocket of PGAM1, by using the Adaptive Steered Molecular Dynamics method. The results of PMF were shown in the left panel; Right panel: The results of calculations of binding free energies. All the energy unit is kcal/mol.



# Purely relativistic electric dipole moment interactions of the electron from quasi-relativistic calculations

Konstantin Gaul, Robert Berger

*Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, D-35032 Marburg, Germany*

A permanent electric dipole moment of the electron (eEDM) would violate parity  $\mathcal{P}$  and time-reversal  $\mathcal{T}$  symmetry simultaneously.[1, 2] By  $C\mathcal{PT}$ -theorem[3] this is directly connected to  $C\mathcal{P}$ -violation. Thus experiments that search for an eEDM provide sensitive tests of physics beyond the Standard Model of particle physics.[4] The best tests for the existence of an eEDM are provided from high-precision spectroscopy of molecules.[5] Due to enhancement effects of the electronic structure these measurements are sensitive to an energy regime of TeV.[1, 5] A theoretical prediction of interactions of the eEDM in molecules is indispensable for the interpretation and design of experiments. However, interactions of an eEDM in molecular systems are purely relativistic, i.e. they depend only on the lower component of the Dirac bi-spinor:[6]

$$\hat{H}_{\text{eEDM}} = -d_{\text{e}} \begin{pmatrix} \mathbf{0}_{2 \times 2} & \mathbf{0}_{2 \times 2} \\ \mathbf{0}_{2 \times 2} & \vec{\sigma} \cdot \vec{\mathcal{E}} \end{pmatrix}, \quad (1)$$

where  $\hat{H}_{\text{eEDM}}$  is the eEDM interaction Hamiltonian,  $d_{\text{e}}$  is the eEDM,  $\vec{\sigma}$  is the vector of the Pauli spin matrices and  $\vec{\mathcal{E}}$  is the internal electrical field of the molecule. Thus costly relativistic four-component electron correlation calculations are mostly employed for the description of eEDM interactions.

We present efficient quasi-relativistic methods in a zeroth order regular approximation (ZORA) framework for the calculation of purely relativistic eEDM interactions.[7] Thereby electron correlation is addressed via complex generalized Hartree-Fock (cGHF) or Kohn-Sham (cGKS) schemes. By comparisons of these numerical studies with analytical models a deeper understanding of  $\mathcal{P}$ ,  $\mathcal{T}$ -odd effects in molecules is provided.

- [1] W. Bernreuther, M. Suzuki, *Rev. Mod. Phys.* **1991**, 63, 313–340.
- [2] I. B. Khriplovich, S. K. Lamoreaux, *CP Violation without Strangeness*, Springer, Berlin, **1997**.
- [3] G. Lüders, *Dan. Mat. Fys. Medd.* **1954**, 28, 1–17.
- [4] D. J. Gross, *Proc. Natl. Acad. Sci. USA* **1996**, 93, 14256–14259.
- [5] N. Fortson, P. Sandars, S. Barr, *Phys. Today* **2003**, 56, 33.
- [6] E. Salpeter, *Phys. Rev.* **1958**, 112, 1642.
- [7] K. Gaul, R. Berger, *ArXiv e-prints* **Feb. 2017**, arXiv:1703.06838 [physics.chem-ph].

# STEEPLECHASE FOR 2-RDM APPROXIMATIONS

**M. Rodríguez-Mayorga<sup>1,2</sup>, E. Ramos-Cordoba<sup>1,4</sup>, M. Via-Nadal<sup>1</sup>, M. Piris<sup>1,3</sup>, E. Matito<sup>1,3</sup>**

<sup>1</sup>*Kimika Fakultatea, Euskal Herriko Unibertsitatea UPV/EHU, and Donostia International Physics Center (DIPC). P.K. 1072, 20080 Donostia, Euskadi, Spain.*

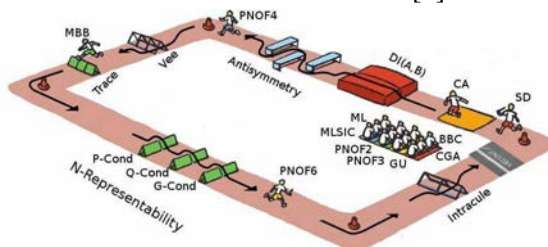
<sup>2</sup>*Institut de Química Computacional i Catàlisi (IQCC) and Departament de Química, Univ. Girona, Campus de Montilivi s/n, Girona, Spain.*

<sup>3</sup>*IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Spain.*

<sup>4</sup>*Department of Chemistry, Kenneth S. Pitzer Center for Theoretical Chemistry, University of California Berkeley, Berkeley, CA, USA.*

In this work, we will present some tests that we have performed to analyze the goodness of second-order reduced density matrices approximations (2-RDM) when the effects of correlation become important. The approximations studied are used to construct functionals in natural orbital functional theory (NOFT)[1]. The battery of tests presented here include: the delocalization index, the fulfillment of the sum rule, termwise error for the diagonal elements and for the whole matrix, the fulfillment of some  $N$ -representability[2, 3] conditions, the attainment of symmetry properties and some quantities related to the intracule density. The energy is usually the guiding star for the validation of NOFT functionals, therefore this battery of tests offers a wide variety of assessments that permit to check relevant features of the approximated 2-RDMs that are normally not put into test

To tune the correlation effects, we have chosen the Harmonium atom (HA) model[4] as our reference system. In HA, the effects of correlation are driven by one single parameter called the confinement strength. This model systems provides a realistic description of electron correlation effects and renders itself to analytic solutions for some values of the confinement strength. Harmonium has been used to calibrate DFT functionals[5] and third-order reduced density matrices[6].



- [1] J. Cioslowski, M. Piris and E. Matito, *J. Chem. Phys.* **143**, 214101(2015) (and references cited therein).
- [2] M. Piris, *Int. J. Quant. Chem.* **113**, 620(2013).
- [3] J. M. Herbert and J. E. Harriman, *J. Chem. Phys.* **118**, 10835(2003).
- [4] N. R. Kestner and O. Sinanoglu, *Phys. Rev.* **128**, 2687(1962).
- [5] J. Cioslowski and E. Matito, *J. Chem. Theory Comput.* **7**, 915(2011).
- [6] M. Rodríguez-Mayorga, E. Ramos-Cordoba, F. Feixas and E. Matito, *Phys. Chem. Chem. Phys.* **19**, 4522(2017).

## Excited States Insight to Assess Phototoxicity of Non-Steroidal Anti-Inflammatory Drugs.

Neus Aguilera-Porta<sup>1,2,3</sup>, Giovanni Granucci<sup>3</sup>, Jordi Muñoz-Muriedas<sup>2</sup>, Inés Corral<sup>1</sup>

<sup>1</sup>*Universidad Autónoma de Madrid, Departamento de Química, Madrid, Spain*

<sup>2</sup>*Università di Pisa, Dipartimento di Chimica e Chimica Industriale, Pisa, Italy.*

<sup>3</sup>*Computational Toxicology, GlaxoSmithKline, Ware, Hertfordshire, UK.*

The assessment of the photosensitivity of pharmaceuticals is essential to predict a loss of potency or production of toxic reactive species induced by an electronic excitation, as outlined in the International Council of Harmonization (ICH) S10 guidance. Our research aims of understanding the photophysical processes, including the deactivation mechanisms, initiated after light absorption of an UV-visible photon.

We have modelled the absorption spectra of non-steroidal anti-inflammatory drugs (NSAIDs), such as aspirin and ibuprofen in gas phase as well as in solvent. Multistate second order perturbation theory on state average complete active space self-consistent field wavefunctions MS-CASPT2//SA-CASSCF<sup>1,2,3</sup> and time dependent density functional theory (TD-DFT)<sup>4</sup> were the computational protocols for this purpose.

Starting from the spectroscopic state, we have mapped the topology of the potential energy surface relevant to the deactivation of these systems by performing minimum energy path calculations and locating the main stationary and crossing points along the singlet manifold. Some of these crossings involve a change of spin, allowing the transfer of populations to other manifolds with multiplicity different than that of the ground state (intersystem crossing, ISC).

These calculations provide an idea of the photophysical deactivation mechanisms that will next serve as a reference to obtain a time resolved picture of the evolution of the system upon its electronic excitation by means of non-adiabatic molecular dynamic simulations.

Our ultimate goal with these results is to design a model that would translate the main features of the deactivation mechanisms into a phototoxicity alert that can be introduced at early stages of the drug discovery process and help mitigate risks associated with photon absorption.

[1] B. O. Roos, in *Ab initio Methods in Quantum Chemistry II*, ed. K. P. Lawley, Wiley, Chichester, **1987**.

[2] K. Andersson, P. Å. Malmqvist and B. O. Roos, *J. Chem. Phys.*, **1992**, 96, 1218.

[3] J. Finley, P. Å. Malmqvist, B. O. Roos and L. Serrano-Andrés, *Chem. Phys. Lett.*, **1998**, 288, 299.

[4] Runge and E. K. U. Gross, *Phys. Rev. Lett.*, **1984**, 52, 997–1000.

## New porphyrin for application in Dye-Sensitized Solar Cells

Cassiano Minoru Aono<sup>1</sup>, Paula Homem-de-Mello<sup>1</sup>

<sup>1</sup>*Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Av. dos Estados - 5001, Santo André-SP, Brasil*

A possible renewable energy source are the Dye-Sensitized Solar Cells (DSSC) [1]. The choice of the dye plays an important role in the solar cell's efficiency and to employ D- $\pi$ -A dyes have shown promising results. This type of dye is formed by an electron donor group (D) and an acceptor group (A), both connected by a  $\pi$ -conjugated system, e.g. porphyrins, since they are formed by an extended conjugated system [2]. In this work, we propose new porphyrinic derivatives and performed density functional theory (DFT) calculations for geometry optimization, as well as to obtain the vibrational frequencies. To study the electronic properties, time dependent DFT (TD-DFT) calculations were performed. M06 functional and 6-311G(d,p) basis set were used in all calculations. Solvent effects (THF) were included with IEFPCM continuum model. All calculations were made using Gaussian09 package. Our studies [3] showed that porphyrin with secondary amines bonded in *meso* position presents promising absorption spectra and Kohn-Sham molecular orbitals with a significant push-pull effect. There is also a noticeable influence of linker's dihedral angle

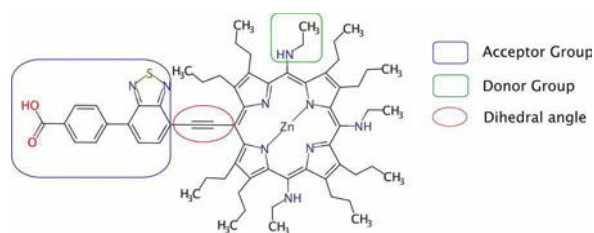


Figure 1: Porphyrin's structure

and propane groups in  $\beta$  position to create a steric hindrance in order to make dye loses its planar structure. In fact, the obtained compound has adequate absorption spectrum and Kohn-Sham orbitals what enable this molecule as a possible dye to be applied in more efficient DSSC.

angle (indicated in Figure 1) in the increase of push-pull effect. We have observed that when the set formed by porphyrin's ring and the acceptor group loses its planar structure this effect increase. In this sense, we have decided to propose a structure with secondary amines in *meso* position

[1] B. O'Regan & M. Grätzel, *Nature* **353**, 737 (1991)

[2] S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, B. F. E. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, Md. K. Nazeeruddin & M. Grätzel, *Nature Chemistry* **6**, 242 (2014)

[3] C. M. Aono, P. Homem-de-Mello. Manuscript in preparation.

## Systematic search for chemical reactions in gas-phase contributing to methanol formation in the interstellar medium.

V. Gámez<sup>1</sup>, A. Galano<sup>\*1</sup>

<sup>1</sup>*Departamento de Química. Universidad Autónoma Metropolitana-Iztapalapa. San Rafael Atlixco 186, Col. Vicentina. Iztapalapa. C.P. 09340. Ciudad de México. México*  
<sup>1</sup>*gamvick@gmail.com*

Methanol is among the molecules found in the Interstellar medium (ISM) considered as a potential precursor of more complex, prebiotic species, like sugars and aminoacids.<sup>1,2</sup> Observed mainly in very low density and extremely cold places, called molecular clouds, their chemistry is dominated by the following features to be viable: (i) the reactions must involve at most two reactants, (ii) they must be significantly exergonic, and (iii) they must be very fast (with very small or no activation energy).<sup>3-6</sup> There are numerous studies proposing possible chemical routes yielding methanol in the ISM, with or without involving interstellar grain mantles.<sup>7-10</sup> Unfortunately, the existent approaches fail to reproduce the observed fractional abundance of methanol in molecular clouds.<sup>5</sup>

The goal of this work is to perform a systematic search for reactions that yield methanol (exclusively on the gas-phase). The strategy included 82 molecules identified in the ISM, and 7 proposed intermediates. The search engine combines the molecules with the minimum number of atoms necessary to form methanol. The search led to 678 reactions involved in chemical routes toward molecular complexity. For each one, several selection criteria were applied: i) thermochemical viability ii) high exergonicity, iii) free radicals and/or ionic reactants, iv) maximum number of necessary elementary steps, v) lower energy isomers and vi) reaction barriers. After applying all of them, 15 reactions are proposed as potential candidates to contribute to methanol formation in the ISM. It is expected that including them into the models would improve the agreement with the observed methanol abundance in molecular clouds.

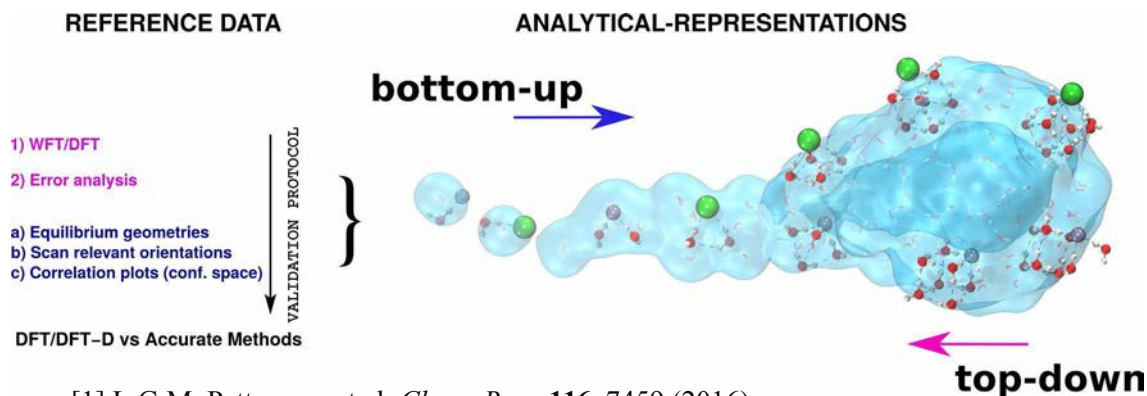
- [1] Y. J. Kuan, *et al.*, *Adv. Space Res.* **33**, 31 (2004).
- [2] N. Balucani, *Int J Mol Sci* **10**, 2304 (2009).
- [3] V. Wakelam, *et al.*, *Space Sci. Rev.* **156**, 13 (2010).
- [4] E. Bergin, *Chem. Ind. (London)*, 659 (2001).
- [5] W. D. Geppert, *et al.*, *Faraday Discuss* **133**, 177 (2006).
- [6] E. Herbst, *Phys. Chem. Chem. Phys.* **16**, 3344 (2014).
- [7] S.B. Charnley, *et al.*, *Astrophys. J.* **448**, 232 (1995).
- [8] R. L. Hudson, M. H. Moore, *Icarus* **140**, 451 (1999).
- [9] H. Hidaka, *et al.*, *Astrophys. J.* **614**, 1124 (2004).
- [10] D. E. Woon, *Phys. Chem. Chem. Phys.*, **17**, 28705 (2015).

## Modeling of ions in aqueous environments: from the gas to the condensed phase

D.J. Arismendi-Arrieta<sup>1</sup>, R. Rodríguez-Segundo<sup>1</sup>, R. Prosmiti<sup>1</sup>

<sup>1</sup>*Institute of Fundamental Physics IFF-CSIC, Serrano 123, 28006 Madrid, Spain.*

Much effort have been made to understand the influence of solutes on the HB network of aqueous environments [1,2], however there is still a lot of debate regarding its dynamic heterogeneity and a integral picture of the involved molecular mechanisms, as well as, the underlying interactions is still missing. In this contribution, we present a family of *ab-initio* polarizable interaction potentials [3,4] and we provide a systematic route for the development of transferable interactions able to describe properties in clusters, ionic solutions (in the infinite dilute or concentrated regimes) and in surfaces of aqueous electrolytes. By construction, these effective many-body potentials are compatible with any TTM-based model and could be parametrized for any general water potential. They include an explicit treatment of 2B short and long range interactions adjusted to electronic structure data coming from energies, forces, polarizabilities and dipoles (for both bottom-up and top-down approaches, see Fig 1), while many-body effects are taken into account through damped polarization schemes. Additionally, we further compare with currently available semiempirical and *ab initio*-based potential surfaces and we provide a systematic protocol to validate and assess the accuracy-performance of modern DFT approximations [5] (including the effect of semilocal approach, exact-exchange/correlation admixture, range-separation, as well as dispersion-correction terms) for alkali and halide water systems, with respect to reference CCSD(T)-F12/DF-MP2 calculations on a representative set of configurations [6]. Further investigations of static and dynamical response properties in gas and condensed-phase environments are currently in progress.



- [1] L.G.M. Pettersson et al. *Chem. Rev.* **116**, 7459 (2016)
- [2] Pengfei Li et al. *Chem. Rev.* **117**, 1564 (2017)
- [3] D. J. Arismendi-Arrieta et al. *J. Phys. Chem. B* **120**, 1822 (2016)
- [4] R. Rodríguez et al. in preparation (2017)
- [5] M.G. Medvedev et al. *Science* **355**, 49 (2017)
- [6] D. J. Arismendi-Arrieta et al. in preparation (2017)

# A Study of the Global and Local Aromaticity of Azaacepentalenes

Abulimiti Abudoukadeer

School of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, China

## Abstract

The global aromaticity of the azaacepentalenes was investigated using the topological resonance energy (TRE) and magnetic resonance energy (MRE) methods<sup>[1]</sup>. The bond resonance energy (BRE) and circuit resonance energy (CRE) methods were used to evaluate local aromaticity<sup>[1,2]</sup>. Analysis was made of the effects of the types, number, and arrangement of nitrogen atoms on the global and local aromaticity of the molecules under consideration. Our TRE results show that acepentalene (**1**) is antiaromatic with negative TRE energy. However, the azaacepentalenes (**2-16**) are aromatic with positive TREs. Peripheral nitrogen substitution causes a decrease in aromaticity. The local aromaticity results obtained here using the CRE and BRE methods were compared with the nucleus independent chemical shift values (NICS(1)) as reported in the literature<sup>[3]</sup>. Our CRE and BRE results show that azaacepentalenes (**2-16**) are stabilized primarily by the  $6\pi$  electronic system. Ring current results predict that a strong diamagnetic current flows around the whole molecular perimeter.

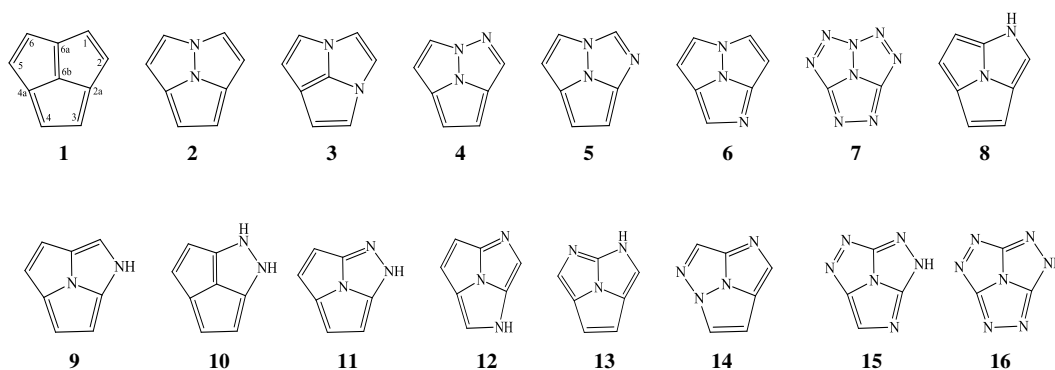


Fig.1. The structure of the compounds in this study

## References:

- [1] J. Aihara, *J. Am. Chem. Soc.*, **128**, 2873 (2006).
- [2] J. Aihara, *J. Am. Chem. Soc.*, **117**, 4130 (1995).
- [3] M. Mascal, *J. Org. Chem.*, **72**, 4323 (2007).



## Recent Advances in Approximate Excited State Calculations in the ADF Modeling Suite

Robert R ger<sup>1,2,3</sup>, Erik van Lenthe<sup>1</sup>, Lucas Visscher<sup>2</sup>, Thomas Heine<sup>3</sup>

<sup>1</sup>*Software for Chemistry and Materials, De Boelelaan 1083, Amsterdam*

<sup>2</sup>*Division of Theoretical Chemistry, VU University Amsterdam*

<sup>3</sup>*Wilhelm-Ostwald-Institute for Physical and Theoretical Chemistry, University of Leipzig*

We present recent advances in the approximate calculation of excited states that have recently been implemented in the ADF modeling suite:

1. Intensity selection as a technique for the accelerated calculation of UV/Vis absorption spectra for large systems.
2. The calculation of vibrationally resolved absorption and emission spectra with density functional based tight binding (DFTB) and its linear response extension (TD-DFTB).
3. A new method named TD-DFT+TB that combines ideas from TD-DFTB excited state calculations with a ground state from DFT. We show that the new method is an excellent approximation to full TD-DFT calculations while being computationally very efficient. Furthermore the new method does not require the availability of DFTB parameters for the studied system.

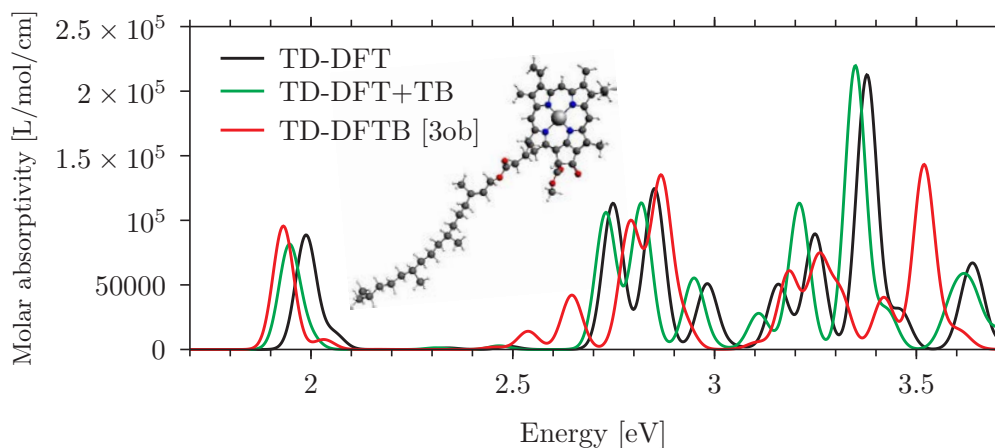


Figure 1: UV/Vis absorption spectrum of chlorophyll A calculated with different methods.

- [1] Robert R ger et al., *J. Chem. Theory Comput.* **11**, 157–167 (2014)  
[2] Robert R ger et al., *J. Chem. Phys.* **145**, 184102 (2016)  
[3] Robert R ger et al., *J. Chem. Phys.* **144**, 184103 (2016)



## Combined Theoretical and Experimental Studies on Polymer and Plasticizer Interactions

Avtar Singh<sup>1</sup>, S. Radhakrishnan<sup>1</sup>, M.B.Talawar<sup>1</sup>, Arvind Kumar<sup>1</sup>, Manoj Gupta<sup>1</sup>

<sup>1</sup> High Energy Material Research Laboratory, Pune, India

Assessment of interactions among polymer and plasticizer molecules is important criterion for design and development of composite propellant formulations. The objective of this study is to screen plasticizers for selected polymers viz, hydroxyl terminated polybutadiene (HTPB), nitrile butadiene rubber (NBR) and glycidylazide polymer (GAP) which are used in the advanced propellant formulations. The solubility parameter is a measure of non-bonded interactions and it can be a quantitative tool for assessing the interactions. It is evaluated by Gee's equilibrium swelling experiments for cross-linked polymers and intrinsic viscosity measurements for linear polymers. The solubility parameter determined from swelling studies for partially cross-linked HTPB and GAP is 17.97 and 23.62 J<sup>1/2</sup>cm<sup>-3/2</sup> respectively. Further, solubility parameter of HTPB achieved from intrinsic viscosity measurements is also comparable with swelling study data which reveals that there is no significant change in solubility parameter of linear and cross-linked HTPB. Classical mechanics based molecular dynamics simulations employing COMPASS force field are also used to evaluate solubility parameter of polymers viz, HTPB, NBR, GAP, and plasticizers, NG, DOA, DEGDN, BTTN, TEGDN, BuNENA, and TMETN. Experimental data of studied systems overall matched well with the simulation results. Flory-Huggins interaction parameter ( $\chi$ ) is also calculated for identifying the suitable pair of plasticizer and polymer based on the enthalpy contributions. It is inferred from predicted solubility parameter data that energetic plasticizers are not compatible with HTPB; while n-Butyl-nitrateoethylnitramine(Bu-NENA) is found to be the most suitable plasticizer for NBR and GAP. Overall, this study finds its importance in identifying an appropriate plasticizer for any specific polymer, which is the foremost critical step for achieving successful propellant formulations with desired characteristics.

**Keywords:** Modeling and Simulation, Molecular Dynamics, Solubility parameter, Miscibility, Energetic materials.

**Acknowledgement:** The authors thank Director HEMRL for his approval to publish this work.

### References

- [1] G. Stater and D. Mark Husband, *Molecular Structure of the Ideal Solid Propellant Binder, Propellants, Explos. Pyrotech.* 16, 167-176 (1991).
- [2] X. FU, X. fan, X. Ju, X. QI, J. LI and H. YU, *Molecular Dynamic Simulation on Interaction between HTPE Polymer and Energetic Plasticizer in solid propellant.* RSC Adv.,5, 52844-52851(2015).

## CO, NO, and NO<sub>2</sub> Adsorptions on Boron Antisite (B<sub>N</sub>) in Boron-Rich Boron Nitride Nanotube (BNNT)

Heechol Choi<sup>1</sup> and Hyeonhu Bae<sup>1,2</sup>

<sup>1</sup>*Plasma Technology Research Center, National Fusion Research Institute (NFRI), 37 Dongjangan-ro, Gunsan, Jeollabuk-do 54004, Republic of Korea*

<sup>2</sup>*Department of Physics, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 05029, Republic of Korea*

Carbon and nitrogen oxides (CO, NO, and NO<sub>2</sub>) released during the combustion of fossil fuels, contribute to both smog and acid precipitation and affect both terrestrial and aquatic ecosystems.[1] Additionally, they are central to the formation of fine particles (PM) resulting in a variety of breathing problems, of which are associated with adverse health effects. Sequestration of these gases emitted from coal-fired power stations or motor vehicles is thus one of the most pressing issues in the environmental protection. Due to their intrinsic high surface areas and polarity, boron nitride nanotube (BNNT) could be a good candidate as chemical gas adsorbent.[2-4] However, the pristine BNNT with a large band gap has been widely known to be almost inert to gas molecules. In this study, we chose BNNT with boron antisite (B<sub>N</sub>) as CO, NO, and NO<sub>2</sub> adsorbents, based on our previous work presenting that B<sub>N</sub> in BNNT can capture CO<sub>2</sub> strongly enough to the ambient-condition sequestration.[5] In this congress, let us report that CO, NO, and NO<sub>2</sub> are strongly adsorbed on B<sub>N</sub> in BNNT almost regardless of tube diameter. The geometrical, energetic, and electronic properties of gas-adsorbed B<sub>N</sub>-BNNTs were analyzed via ab initio calculations using plane waves [PAW-PBE] and localized atomic orbitals [ONIAM(ωB97X-D/6-31G\*:AM1)].

[1] I. Sayago, H. Santos, M.C. Horrillo, M. Aleixandre, M.J. Fernandez, E. Terrado, I. Tacchini, R. Aroz, W.K. Maser, A.M. Benito, M.T. Martinez, J. Gutierrez, E. Munoz, *Talanta* **77**, 758 (2008).

[2] C. Zhi, Y. Bando, C. Tang, D. Golberg, *Mater. Sci. Eng.* **70**, 92 (2010).

[3] N.D. Hoa, N. Van Quy, D. Kim, *Sens. Actuators B* **142**, 253 (2009).

[4] D. Ghosh, B. Ghosh, S. Hussain, S. Chaudhuri, R. Bhar, A.K. Pal, *Appl. Surf. Sci.* **263**, 788 (2012).

[5] H. Choi, Y.C. Park, Y.-H. Kim, Y.S. Lee, *J. Am. Chem. Soc.* **133**, 2084 (2011).

## Structural analysis of phthalocyanines dimers using computational methods

Mateus Zanotto, Felipe C. T. Antonio, Paula Homem-de-Mello<sup>1</sup>

*Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Av. dos Estados, 5001, Santo André, São Paulo, Brazil*

Phthalocyanines (Pc's) compounds have widely application in nanotechnology and photodynamic therapy of cancer, besides their common use as dye [1,2]. In phthalocyanines dimers with a face-to-face stacking it is possible to observe  $\pi$ — $\pi$  interaction between the two Pc rings [3] affecting their photophysical and photochemical properties. In order to see how phthalocyanines and naphthalocyanines (Nc's) complexed with Zn(II) have their optical properties changed when stacked in dimers, we have conducted computational studies, as well as verifying the tert-butyl substituent influence.

The computational method employed was based on Density Functional Theory (DFT). The geometry optimization and the TD-DFT were carried out by using the BLYP functional and 6-31G basis set and the dispersion correction was included with the Grimme's approach (D3-BJ). We have evaluated 4 molecules: ZnPc and ZnNc without substituents and both compounds with tert-butyl as substituent. For each optimized molecule, we performed conformational analysis with molecular mechanics approach (using UFF force field) and found 3 to 4 dimers conformations that were more probable. After this procedure, all conformations found were submitted to DFT calculations (geometry optimization and TD-DFT calculations).

The optimized dimers of ZnPc and ZnNc without substituents converged to conformations where monomers were rotated 45° or 90°. The only exception was ZnPc with tert-butyl, whose conformation presented the rings eclipsed, with a torsion angle about 20°. The distances between the Zn-Zn in the dimers with 90° were smaller than their distance in the dimers with 45°, because the Zn(II) from one monomer complex to nitrogen atoms of the other monomer. So, besides  $\pi$ -interaction, aggregation is also driven by complexation.

- [1] R. P. Feynman, *Phys. Rev.* **56**, 340 (1939).
- [2] Nemykin, Victor N., *The Journal of Physical Chemistry.* **111**, 50 (2007)
- [3] Bettanin, F. ; Fontinelles, T. A. ; Maciel, C. D. ; Dias, Lg ; Coutinho Neto, M. D. ; Homem-De-Mello, P. *Theoretical Chemistry Accounts*, **134**, 152 (2015).

## Density Functional Study of [2+1] Radical Cation Cycloaddition

Xinglong Zhang<sup>1</sup>, Robert S. Paton<sup>1, 2</sup>

<sup>1</sup>*Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QZ, United Kingdom*

<sup>2</sup>*Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford, OX1 3TA, United Kingdom*

Radical cation intermediates have been implicated in the oxidation-promoted, electron-transfer catalyzed cycloaddition of two electron-rich alkenes experimentally[1, 2, 3]. Herein, we performed a detailed study of the heterodimeric cycloaddition between two unsymmetrical alkenes using density functional theory (DFT) M062X functional. Concerted [2+1] cycloaddition is ruled out based on our calculations. We found that the first C-C bond formation in the step-wise mechanism is the rate-determining step of the whole reaction. Both 4-membered and 6-membered rings can be accessible under suitable reaction conditions. Conformational effects have been fully explored and it is found that the positive-gauche addition proceeds with the lowest energy barrier. Anti-cyclobutyl ring is found to be the most thermodynamically stable, in accordance with experimental findings. The effects of solvents on the reaction have also been investigated.

[1] A. Ledwith, *Acc. Chem. Res.* **5**, 133 (1972).

[2] R. Pabon, N. Bauld, *J. Am. Chem. Soc.* **105**, 633 (1983)

[3] S. L. Mattes, S. Farid, *J. Am. Chem. Soc.* **104**, 1454, (1982)

## Configurational Bias Monte Carlo method to sample molecular flexibility: The case of octane and 1,2-dichloroethane

Henrique M. Cezar<sup>1</sup>, Sylvio Canuto<sup>1</sup>, Kaline Coutinho<sup>1</sup>

<sup>1</sup>*Institute of Physics, University of São Paulo, São Paulo, Brazil*

Several processes in physics, chemistry and biology are affected by the molecular structure. In computer simulations, structures are usually sampled through either Molecular Dynamics (MD) or Monte Carlo (MC). The method of choice usually depends on the properties of interest. However, to study flexible molecules usually MD is applied, since several efficient implementations are available and MC lacks a standard and established method to sample the molecular internal degrees of freedom of a molecule. This problem arises since the standard Cartesian coordinates atomistic displacements usually applied within MC are very inefficient to generate structures with large conformational changes. In this work we implemented and improved a Configurational Bias Monte Carlo (CBMC) method used to sample molecular conformations in solvent. Based on the work of Shah and Maginn[1, 2] we implemented in the DICE package[3] a CBMC strategy that separates hard and soft degrees of freedom within a fragment scheme. We guarantee that the correct ensemble is sampled by enforcing the detailed balance to obtain the acceptance criteria. We checked and benchmarked our implementation[4] by applying it to octane and 1,2-dichloroethane in different solvents. The trans and gauche populations were compared with experimental data and results from MD simulations. In both cases the results had an excellent agreement. We observe that at least for those systems, the correct population is achieved faster with our CBMC implementation than with MD, being the CBMC less likely to get trapped in local minima.

- [1] J. K. Shah, E. J. Maginn, *J. Chem. Phys.* **135**, 134121 (2011).
- [2] J. K. Shah, E. Marin-Rimoldi, R. G. Mullen, B. P. Keene, S. Khan, A. S. Paluch, N. Rai, L. L. Romanielo, T. W. Rosch, B. Yoo, E. J. Maginn, *J. Comput. Chem.* DOI: 10.1002/jcc.24807 (2017).
- [3] K. Coutinho, S. Canuto, DICE: A Monte Carlo Program for Molecular Liquid Simulation v2.9, University of São Paulo, Brazil (2011)
- [4] H. M. Cezar, S. Canuto, K. Coutinho, (*manuscript in preparation*)

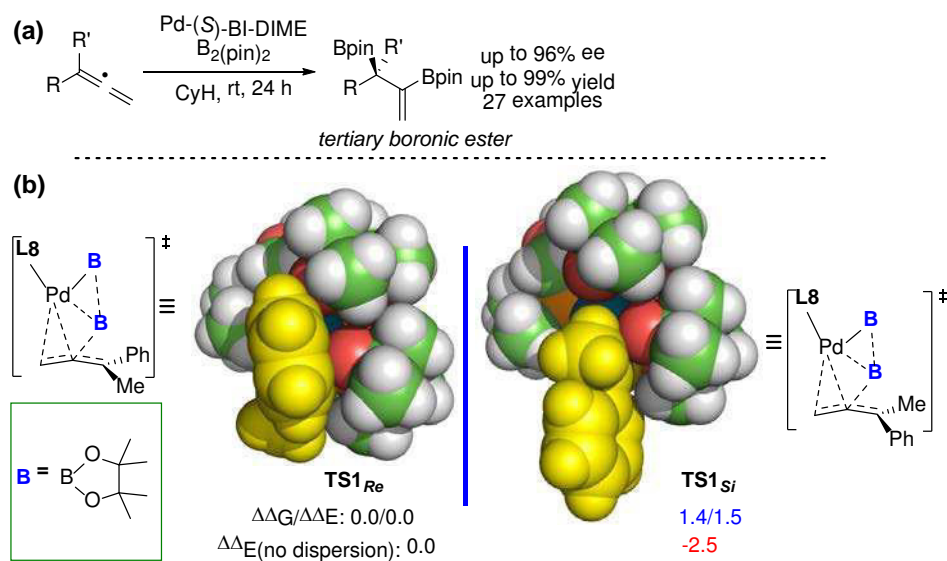
# DFT Calculations on Enantioselective Pd-Catalyzed Diboration of 1,1-Disubstituted Allenes: Dispersion-Drive Eantioselectivity

Qinghai Zhou, Renke Huang, Lung Wa Chung\*

Department of Chemistry, South University of Science and Technology of China, No 1088,xueyuan Rd., Xili, Nanshan District, Shenzhen, Guangdong, People's Republic of China, 518055

oscarchung@sustc.edu.cn

Tang, Ding and coworkers developed the first enantioselective Pd-catalyzed diboration of 1,1-disubstituted allenes to form chiral alkene products with a quaternary carbon (Fig.1(a)).<sup>1</sup> We carried out DFT calculations to study the reaction mechanism and the origin of the enantioselectivity. Our results indicate that the enantioselectivity is dictated by oxidative addition of diboron concerted with allene insertion (Fig.1(b)). Distortion/interaction analysis reveals that a larger interaction energy especially dispersion interaction between the phenyl group on the allene and the two boryl groups in **TS1<sub>Re</sub>** than **TS1<sub>Si</sub>**, is the key factor for the enantioselectivity. Exclusion of the dispersion contribution could reverse the enantioselectivity. Dispersion-drive enantioselectivity is unusual, compared to the common steric-hindrance-driven manner.



**Fig.1 (a). Enantioselective Pd-catalyzed diboration of 1,1-disubstituted allenes. (b) Our key B3LYP-D3 results.**

## Reference

[1] Liu, J.; Nie, M.; Zhou, Q.; Chung, L. W.; Tang, W.; Ding, K. *Chem. Sci.* DOI: 10.1039/C7SC01254C.

## Aluminum interaction with serine and O-phosphoserine

**E. Formoso, and X. Lopez**

*Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU) & Donostia International Physics Center (DIPC), Spain*

e-mail: elena.formoso@ehu.eus

Although, aluminum is the most abundant metal and the third most abundant element in the Earth's crust it has no essential role in any biochemical system in any extant organism[1]. In the last century, human intervention has made aluminum so available for biological systems. Unfortunately, there is increasing evidence that aluminum could be behind of a variety of toxic effects, with significant risks for human health[2].

The toxicity of aluminum is greatly affected by its bioavailability. Additionally, partly independently of the chemical form in which it is absorbed, it will interact with many potential Al binders in the various biofluids and tissues. Accordingly, speciation studies[3] are fundamental to understand the effects of Aluminum in biological systems.

In addition, phosphorylation of proteins is thought to increase their affinity for aluminum[5] and could be a key aspect in understanding the Al promotion of the NFT aggregation process[6]. The alcoholic-OH of Ser and Thr and the phenolic-OH of Tyr are the phosphorylation sites of proteins. Thus, phosphoserine (Pser) molecule serves as a model of phosphorylated protein residues.

The aim of this work is to give insight into the increase in the binding affinity of aluminum to phosphorylated proteins in general. As a first step of this goal, we characterize and compare the binding affinity of aluminum cation to Ser and Pser, by Density Functional Theory studies combined with polarizable continuum models to account for bulk solvent effects. This allows us to estimate the increase in aluminum binding affinity expected by phosphorylation of Ser in peptides.

[1] C. Exley, *Trends Biochem. Sci.*, **34**, 589-593 (2009).

[2] L. Tomljenovic, *J. Alzheimer's Disease*, **23**, 567-598 (2011).

[3] a) T. Kiss, *J. Inorg. Biochem.*, **128**, 156-163 (2013); b) E. Formoso, J.I. Mujika, S. Grabowski, X. Lopez, *J. Inorg. Biochem.*, **152**, 139-146 (2015); c) N.B. Luque, J.I. Mujika, E. Formoso, X. Lopez, *RSC Adv.*, **5**, 63874-63881 (2015); d) E. Formoso, X. Lopez, *RSC Adv.*, **7**, 6064-6079 (2017).

[5] R. Grande-Aztatzi, E. Formoso, J.I. Mujika, J.M. Ugalde, X. Lopez, *Phys. Chem. Chem. Phys.*, **18**, 7197 (2016).

[6] G. Fasman, *Coord. Chem. Rev.*, **149**, 125-165 (1996).

**Preparing a computational database of surface structures  
for investigating catalytic reactions**

**Hyun Woo Kim, Hyunju Chang**

*Center for Molecular Modeling and Simulation,  
Korea Research Institute of Chemical Technology (KRICT),  
141 Gajeongro, Yuseong, Daejeon 34114, Korea*

There is constant need for discovering new materials to yield better solutions of global issues in environment, renewable energy, and human health. To efficiently find candidates of new materials, data-driven researches were proposed in several perspectives. Materials screening based on a huge database can be more important in the future as more computational results are accumulated in both private and public databases with the advances in computational and theoretical methods. Nowadays, physical properties of bulk materials can be found in some open-databases and surface structures and their surface energies are available for elemental crystals. Here, we present our strategy of preparing a new database for studying chemical reactions on catalytic surfaces. Starting from structures in existing databases of elemental crystals, we performed first-principles calculations to generate our database. We will also discuss possible applications of our database for understanding reaction mechanisms on catalytic surfaces.



## Experimental and theoretical investigations of spectroscopic properties of azobenzene derivatives

**Paul Datin<sup>1</sup>, David Carrière<sup>1</sup>, Christophe Fajolles<sup>1</sup>, Jean-Pierre Dognon<sup>1</sup>**

<sup>1</sup>*NIMBE, CEA, CNRS, Université Paris-Saclay, CEA/Saclay, 91190 Gif-sur-Yvette, France*

A series of azobenzenes was studied using ab initio and DFT methods to determine the substituent effects on the ground and electronically excited states. Azobenzene molecule is known to undergo a photoisomerization from trans to cis conformation upon irradiation by light. The aim of the presentation is twofold. Firstly, we analyze different methods of calculations of electronic excitations of azobenzene molecule by comparing the results with experimental data. Secondly, we present the results of calculations of the UV-Visible spectra of azobenzene derivatives (e.g. Figure 1) and analyze the nature of the experimentally observed excitations.

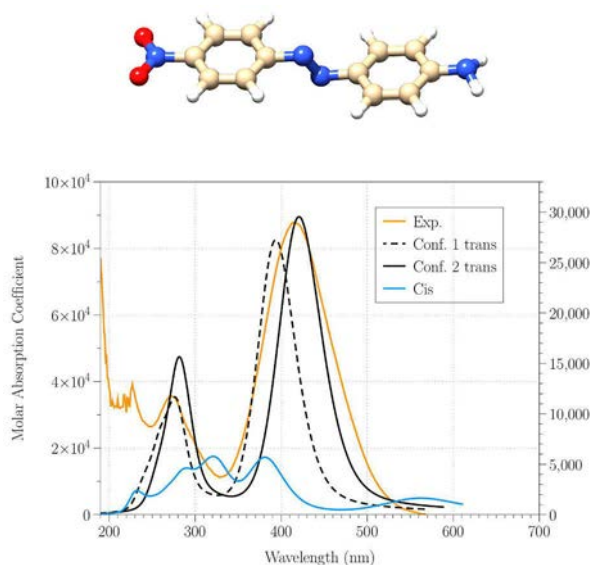


Figure 1: Disperse Orange 3 TD-DFT/CAM-B3LYP vs. experimental UV-Visible spectra

## Computational Thermochemistry of Carbamic Acid and Related Compounds

Zikri Altun<sup>1</sup>, Erdi A. Bleda<sup>1</sup>, and Carl Trindle<sup>2</sup>

<sup>1</sup>*Department of Physics, Marmara University, Ziverbey, Istanbul, Turkey*

<sup>2</sup>*Department of Chemistry, University of Virginia, Charlottesville, USA*

Carbamic acid (H<sub>2</sub>N-COOH, “CA”) has been implicated in the equilibrium between solid ammonium carbamate and gas phase carbon dioxide and ammonia [1], as an intermediate in the production of urea from carbon dioxide and ammonia [2]; and as a participant in processes occurring in ammonia-carbon dioxide ices on interstellar grains [3]. Monomeric CA is not observed in the gas phase but existence of the dimer (CA)<sub>2</sub> and perhaps higher-order clusters is suggested by IR studies [3,4].

Computational modeling of CA and associated species has relied primarily on density functional theory evaluations of molecular structures and harmonic frequencies, and has only rarely [2] been directed toward estimation of thermochemical quantities. Chemical accuracy (ca. 1 kcal/mol) is essential to the evaluation of mechanistic proposals for processes in which carbamic CA or related species may participate [1]. Here we report vibrational frequencies corrected for anharmonicity and estimates of thermochemical quantities of high accuracy derived from CBS-QB3 and Wn calculations. These results can guide experimental studies of kinetics and aid in the search for new species in the interstellar medium.

### Acknowledgement:

The authors are grateful to the Body Foundation and BAPKO of Marmara University for travel and computational support.

[1] B. R. Ramachandran, A. M. Halperin, and E. D. Glendenning, *J. Phys. Chem. A* 102:3934-3941 (1998)

[2] C. A. Tsipis and P. A. Karipidi, *J. Phys. Chem. A* 109:8560-8567 (2005)

[3] J. B. Bossa, P. Theulé, F. Duvernay, F. Borget, and T. Chiavassa, *Astronomy and Astrophysics*, 492:719-724 (2008)

[4] J.-B. Bossa, F. Borget, F. Duvernay, P. Theulé, and T. Chiavassa, *J. Phys. Chem. A* 112:5113-5120 (2008)

**The effect of the environment on the photodynamics of biological chromophores**

**Dmitry Morozov, Satu Mustalahti, Pasi Myllyperkio, Mika Pettersson, Gerrit Groenhof**

*Chemistry Department, University of Jyväskylä, Surfontie 9, Jyväskylä, 40500, Finland  
dmitry.morozov@jyu.fi*

The key step in activation of many photoreceptor proteins is photoisomerization of a conjugated chromophore. Interactions between these chromophores and the protein matrix control the outcome and efficiency of these photoreactions. Understanding how proteins have evolved to mediate those excited state dynamics might be important to controlling photochemistry in artificial systems. As the required time and spatial resolution are notoriously difficult to access experimentally, we use excited-state molecular dynamics simulations with quantum-mechanical description (QM/MD) to simulate the photoisomerization of the chromophore of the prototypical photoreceptor photoactive yellow protein (pCK). Whereas a single isomerization pathway was found in the protein [1], multiple pathways were observed in solution. Our simulations provide a detailed understanding of how solvent viscosity and hydrogen bonding control the isomerization process, which we are currently validating by means of time-resolved spectroscopy measurements.

- [1] K. Pande et al., *Science*. **352**, 725 (2016).

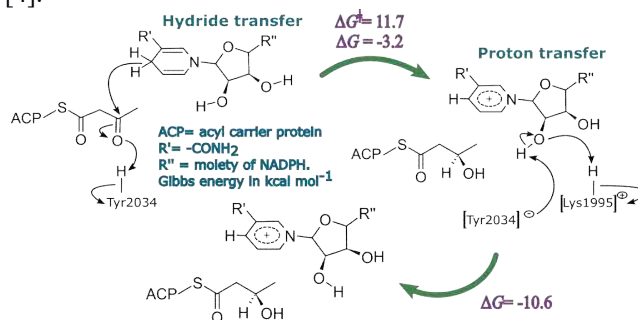
## A QM/MM Study of the Catalytic Mechanism of Human $\beta$ -ketoacyl Reductase

Fabiola E. Medina, Rui P. P. Neves, Maria J. Ramos and Pedro A. Fernandes

UCIBIO, REQUIMTE, *Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169-007, Porto, Portugal*

The  $\beta$ -ketoreductase (KR) is a catalytic domain in the human fatty acid synthase (hFAS) enzyme that catalyzes the reduction of  $\beta$ -ketoacyl to  $\beta$ -hydroxyacyl through a NADPH cofactor. The hFAS is a cytosolic enzyme involved in the synthesis of palmitic acid, and is generally overexpressed in cancer cells. Thus, the catalysis by KR is an intermediate step in the cycle of reactions that elongate the substrate's carbon chain until the final product (palmitic acid) is obtained [1-2].

We conducted hybrid QM/MM calculation to propose the catalytic mechanism of the KR domain, at the ONIOM(B3LYP/6-311+G(2d,2p):AMBER) level of theory [3]. The QM/MM results have shown that the reduction step occurs in two stages; i) nucleophilic attack by the hydrogen in NADPH to the  $\beta$ -carbon of the substrate, with an asynchronous deprotonation of the Tyr2034 to hold the final alcohol product; and ii) an asynchronous deprotonation of the hydroxyl in the NADP<sup>+</sup>'s ribose by Tyr, and of the Lys1995 by the resulting alkoxide in the former ribose. The Gibbs energy barrier for the rate-limiting steps in the first steps was found to be 11.7 kcal·mol<sup>-1</sup> and the Gibbs reactions energy was -10.6 kcal·mol<sup>-1</sup>. These results seem to lead a suitable description of the catalysis by KR. In addition, we found that the oxyanion hole contributes for the TS stabilization through the hydrogen bond formation with the catalytic residues identified as essential for the reduction reaction [4].



- [1] M. A. Hardwicke, *et al.*, *Nat. Chem. Bio.* **10**, 774-779 (2014).
- [2] T. Maier, M. Leibundgut, N. Ban, *Science*, **321**, 1315-1322 (2008).
- [3] L. W. Chung, W. M. C. Sameera, R. Ramozzi, A. J. Page, M. Hatanaka, G. P. Petrova, T. V. Harris, X. Li, Z. F. Liu, H. B. Li, L. Ding, K. Morokuma, *Chem. Rev.* **115**, 5678-5796 (2015).
- [4] F. E. Medina, R. P. P. Neves, M. J. Ramos, P. A. Fernandes, *PCCP*. **19**, 247-355 (2017).

## Sightseeing in the Electronic Structure: Topological Analysis of $|\Psi|^2$

**Michael A. Heuer, Arne Lüchow**

*Institute of Physical Chemistry, RWTH Aachen University,  
Landoltweg 2, 52056 Aachen, Germany*

Local properties of a chemical system (e.g. partial charges, interaction energies) are expressed in its electronic wave function but the perception of the relations is lost with an increasing number of particles due to the high dimensionality. To retrieve these relations and derive chemical concepts and descriptors from them, usually, effective one-electron methods are employed and can be broadly categorized into orbital localization methods (e.g. natural bond orbitals analysis) and electron density methods (e.g. electron localization function, quantum theory of atoms in molecules).

In this work, we present a complementary approach considering the full,  $3N$ -dimensional, electronic wave function  $\Psi$ : A topological analysis of the probability density  $|\Psi|^2$ . By drawing  $|\Psi|^2$ -distributed samples and following the gradient of  $|\Psi|^2$ , we identify statistically significant and highly probable maxima constituting interesting sights in the electronic wave function. The associated electron arrangements, which we exemplarily show for the ethane molecule, exhibit highly ordered motifs that can be rationalized by means of Coulomb interaction and Pauli repulsion and show correlation effects [1]. We show that maxima are interconnected by maximum probability density paths and provide a natural, spatial partitioning of  $|\Psi|^2$  into  $3N$ -dimensional attractor domains, which can be utilized for the definition of local properties. In future works, the results obtained from topological analyses of  $|\Psi|^2$  can be employed to retrieve relations and derive chemical concepts and descriptors from the electronic wave function.

- [1] A. Lüchow, *J. Comput. Chem.* **35**, 854, (2014)

## Mechanistic studies and bonding situation on organometallic chemistry of gold(III) complexes.

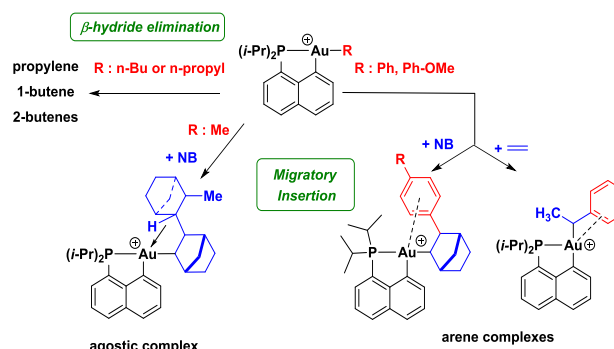
L. Estévez,<sup>1,2</sup> K. Miqueu,<sup>1</sup> F. Rekhroukh,<sup>3</sup> A. Amgoune,<sup>3</sup> D. Bourissou,<sup>3</sup>

<sup>1</sup>IPREM UMR CNRS 5254, UNIV PAU & PAYS ADOUR. Hélioparc 2 avenue P. Angot 64053 Pau Cedex 09 (France). E-mail: karinne.miqueu@univ-pau.fr; <sup>2</sup>Departamento de Química Física, Universidade de Vigo, Galicia (Spain); <sup>3</sup>LHFA UMR CNRS 5069, Equipe LBPB, Université Paul Sabatier, Toulouse Cedex 09 (France).

The organometallic chemistry of gold(III) compounds remained for a long time much less developed than that of their isolobal Pt(II) and Pd(II) counterparts.[1] Very little was known about the structure, stability and reactivity of gold(III) complexes because of the intrinsic instability of gold species in high oxidation state and the challenges associated with their synthesis. However, thanks to the recent development of new synthetic routes, a variety of new organometallic gold(III) compounds have been isolated and important insights have been gained into their intrinsic properties. Reductive elimination, transmetalation, and C–H activation, have been progressively documented. However, two last important elementary reactions were unknown and remained to be highlighted and described : the migratory insertion of unsaturated substrates into gold–carbon bonds and  $\beta$ -hydride elimination at low gold (III) center.

In the frame of our research program on the reactivity of gold complexes, we have obtained by a joint experimental / theoretical approach, precise insights into these unprecedented processes, demonstrating the ability of gold(III) complexes to undergo these two key organometallic transformations, [2] which comprise most of the important catalytic cycles.

This communication will report a detailed picture of the migratory insertion mechanism as well as the comprehensive study of  $\beta$ -hydride elimination at gold(III) by joint DFT and NMR studies. A particular attention will also devote to the description of new bonding situations (agostic interaction,  $\pi$ -complexes with gold(III)) in some intermediates by NBO and AIM analyses and calculations of specific NMR data.



[1] (a) M. Joost, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.*, **54**, 5236 (2015). (b) H. Schmidbaur, A. Schier, *Arab. J. Sci. Eng.*, **37**, 1187 (2012).

[2] (a) F. Rekhroukh, L. Estevez, C. Bijani, K. Miqueu, A. Amgoune, D. Bourissou, *Organometallics*, **35**, 995 (2016) and *Ang. Chem. Int. Ed. Engl.*, **55**(10), 3414 (2016). (c) F. Rekhroukh, L. Estevez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc.*, **138**, 11920 (2016). (d) F. Rekhroukh, C. Blons, L. Estévez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *Chemical Sciences*, just accepted (2017).

## Impact of chosen DFT functionals on one- and two-photon absorption properties of fluorescent proteins chromophores

Dawid Grabarek, Tadeusz Andruniów

*Advanced Materials Engineering and Modelling Group, Department of Chemistry,  
Wroclaw University of Science and Technology, 27 Wyb. Wyspińskiego, Wroclaw, Poland*

Fluorescent proteins (FPs) belong to versatile and modern markers for visualization of various processes taking place *in vivo*. The chromophore – “the heart” of every fluorescent protein – is created in a series of autocatalyzed reactions without a need of external cofactors except for molecular oxygen. The mutagenesis of amino acids residues surrounding the chromophore brings the possibility of constructing novel FPs. In fact since mid-90s, a palette of FPs has been obtained with absorption and emission spectra covering the whole visual spectrum as well as near ultraviolet and near infrared.

One of the most recent and rapidly developing directions of engineering FPs is searching for markers with high two-photon absorption (TPA) cross-section values for TPA-based visualization techniques possessing many advantages over one-photon absorption (OPA) based ones, including lower phototoxicity, higher resolution of images and deeper penetration of living tissues. Due to various drawbacks of experimental techniques for TPA measurements, it seems that theoretical chemistry methods will play a leading role in explaining mechanisms by which the protein environment influences chromophore's TPA spectrum, ultimately allowing for rational and directed design of FPs for TPA-based visualization techniques.

Such investigations will, however, require costly hybrid (QM/MM) calculations with polarizable force fields. Performing such calculations with wavefunction based methods, e.g. within coupled cluster ansatz although possible is extremely costly. For this reason, a computationally cheap yet reliable QM methodology is required. Currently, time-dependent density functional theory (TDDFT) seems to be the method of choice. However, the question remains which DFT functional should be used? In our present contribution, we analyse the gas phase excitation energies, OPA oscillator strengths and TPA cross-sections, calculated with the TDDFT methodology employing the BLYP (0 % of HF exchange), B3LYP (20 %), B1LYP (25 %), BHandHLYP (50 %) and CAM-B3LYP (19 % + 65 %) functionals for a variety of FPs' chromophores in reference to CC2 results. Our choice of DFT functionals is dictated by increasing percentage of the HF exchange energy, providing systematic assessment of this parameter impact on investigated spectral properties. We show a dramatic importance of the HF exchange energy for a qualitative recovery of TPA intensities in reference to *ab initio* CC2 results, while OPA oscillator strengths seem to be less affected. We believe that our work provides a missing, although important, assessment of TDDFT functionals for TPA and OPA properties calculations that also finds its applications for further calculations including protein environment.

**Acknowledgments.** This work was financed by National Science Centre, Poland (grant no. 2016/21/N/ST4/00004). Calculations were performed at the Wroclaw Centre for Networking and Supercomputing.

## Nitrogen doping strategies for modulating the biradicaloid nature of acenes: insights from multireference calculations

Max Pinheiro Jr<sup>1</sup>, Adélia J. A. Aquino<sup>2,3,4</sup>, Francisco B. C. Machado<sup>1</sup>, Hans Lischka<sup>2,3,4</sup>

<sup>1</sup>*Departamento de Química, Instituto Tecnológico de Aeronáutica, São José dos Campos, São Paulo, Brasil*

<sup>2</sup>*School of Pharmaceutical Sciences and Technology, Tianjin University, Tianjin, P.R. China*

<sup>3</sup>*Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas, USA*

<sup>4</sup>*Institute for Theoretical Chemistry, University of Vienna, Vienna, Austria*

Acenes are fascinating polyaromatic compounds that combine impressive semiconductor properties with an open-shell character by varying their molecular size. However, the increasing chemical instability related to their biradicaloid structure poses a great challenge for synthetic chemistry [1, 2]. Modifying the  $\pi$ -bond topology through chemical doping allows modulating the electronic, optical, and physico-chemical properties of graphene-related materials [3, 4]. In spite of the practical importance of these techniques, remarkably little is known about basic question - the extent of the radical character created or quenched thereby. From a theoretical point of view, high-level *multireference methods* (MR) formally provide an adequate approach to address such a question [5]. In this work, we report a computational MR study on two acene oligomers chemically modified with different types of nitrogen defects. Moving the dopants from the terminal rings to the central ones leads to a remarkable variation in the biradicaloid character (and thereby also in the chemical stability). This effect is related to a  $\pi$ -charge transfer involving the dopants and the radical carbon centers at the zigzag edges. Our findings also provide specific guidelines to a rational design of large polyaromatic compounds with enhanced chemical stability.

**Acknowledgments:** Brazilian funding agencies CNPq, CAPES-ITA and FAPESP.

- [1] M. Watanabe, Y. J. Chang, S.-W. Liu, T.-H. Chao, K. Goto, M. M. Islam, C.-H. Yuan, Y.-T. Tao, T. Shinmyozu, and T. J. Chow, *Nat. Chem.* **4**, 574 (2012).
- [2] H. F. Bettinger and C. Tonshoff, *Chem. Rec.* **15**, 364 (2015).
- [3] N. Ketabi, T. de Boer, M. Karakaya, J. Zhu, R. Podila, A. M. Rao, E. Z. Kurmaev, and A. Moewes, *RSC Adv.* **6**, 56721 (2016).
- [4] F. Joucken, Y. Tison, J. Lagoute, J. Dumont, D. Cabosart, B. Zheng, V. Repain, C. Chacon, Y. Girard, A. R. Botello-Méndez, S. Rousset, R. Sporken, J.-C. Charlier, and L. Henrard, *Phys. Rev. B* **85**, 161408 (2012).
- [5] P. G. Szalay, T. Müller, G. Gidofalvi, H. Lischka, and R. Shepard, *Chem. Rev.* **112**, 108 (2012).



Computation of Atom-Atom Electrostatic Energy in RNA Based on Multipolar  
Electrostatics

**Zhuangzhuang Zhang, Yongna Yuan<sup>\*</sup>, Rongjing Hu, Ruisheng Zhang**

*School of Information Science & Engineering, Lanzhou University, Tianshui Road,  
Lanzhou, China*

**Abstract:** Empirical force field calculations on biological molecules (RNA) represent an effective method to obtain atomic detail information on the relationship of their structure to their function. Results from those calculations depend on the quality of the force field. Although state-of-the-art Molecular Dynamics (MD) force fields have been applied widely to simulate the structure and compute the stable free-energy of biological molecules (RNA), the results suggest yet not accuracy enough compared with the experimental results. In this manuscript, optimization of the atom-atom electrostatic energy for force fields is presented. The optimization procedure is based on small molecules from quantum mechanical studies. These small molecules are cut from the pilot RNA (2MVY), including phosphate, pentose, base, phosphate-pentose, pentose-base, or nucleotide, and are then capped by mimicking structure environment in RNA. The atoms in the small molecules are defined though Quantum Chemical Topology (QCT) as finite volume electron density fragments, each endowed with multipole moments. The minimum internuclear distance in the convergent region of all the 15 possible types of atom-atom interactions in RNA (2MVY) that were calculated based on phosphate, pentose and base are close to the values calculated from phosphate-pentose, pentose-base and from nucleotide. Calculations are completed at HF/6-31G(d,p), B3LYP/aug-cc-pVTZ, and MP2/aug-cc-pVTZ levels. Values obtained at these three levels are quite similar and are tested through another RNA (1ELH) which demonstrated the transferable of the convergence behavior. Furthermore, the change of the multipole moments for a selected central atom by varying the system it exists, and how far away this influence can be ignored is determined as well.

**References:**

- [1] I. Yildirim, *J. Phys. Chem. B.*, **7**, 2886 (2011).
- [2] M. Rafat, P.L.A. Popelier, *J. Chem. Phys.*, **123**, 204103 (2005).
- [3] Y. Yuan, M.J.L. Mills, P.L.A. Popelier, *J. Comput. Chem.*, **35**, 343 (2014).
- [4] M. Rafat, P.L.A. Popelier, *J. Comput. Chem.*, **28**, 832 (2007).

## A Computational Study of the Diels-Alder Reaction between 2,3-dibromo-1,3-butadiene and Maleic Anhydride

Uxía Rivero<sup>1</sup>, Markus Meuwly<sup>1</sup>, Stefan Willitsch<sup>1</sup>

<sup>1</sup>*Department Chemie, Universität Basel, Klingelbergstrasse 80, Basel, Switzerland*

The Diels-Alder reaction is one of the most important reactions in organic chemistry. It has been extensively studied in order to elucidate whether or not it is a concerted process and, if so, whether it happens in a synchronous or an asynchronous manner. The general picture has emerged that neutral reactions usually occur in a concerted fashion while cationic systems react in a non-concerted way [1, 2]. However, the border between asynchronous, concerted and stepwise mechanisms is not yet clear [3, 4].

Recent advances in molecular-beam experiments allow now conformational separation of isomers by electrostatic deflection of a molecular beam based on their different dipole moments [5]. Hence, the separation of the s-cis and s-trans conformers of a diene is possible as long as they meet the experimental requirements for this technique.

We aim to experimentally and computationally explore the detailed mechanism of the Diels-Alder reaction between conformationally selected 2,3-dibromo-1,3-butadiene and supersonically cooled maleic anhydride both in its neutral and cationic states. Here, we present computational results on this particular reaction. Density functional theory calculations show that the neutral reaction is concerted while the cationic reaction can be either concerted or stepwise. Further isomerizations of the Diels-Alder products have been explored in order to predict possible fragmentation routes that would be important for the interpretation of the experimental results. Rice-Ramsperger-Kassel-Marcus (RRKM) calculations suggest that under typical single-collision experimental conditions the neutral product may reform the reactants and the cationic product will most likely eliminate CO<sub>2</sub> [6]. We are currently working on the parametrization of a force field that will allow us to run reactive dynamics in this system [7].

- [1] K. N. Houk, J. González, Y. Li, *Acc. Chem. Res.* **28**, 81 (1995).
- [2] P. J. Donoghue, O. Wiest, *Chem. Eur. J.* **12**, 7018 (2016).
- [3] D. A. Singleton et al., *Tetrahedron* **57**, 5149 (2001).
- [4] L. R. Domingo, J. A. Sáez, *Org. Biomol. Chem.* **7**, 3576 (2009).
- [5] Y.-P. Chang et al., *Science* **342**, 98 (2013).
- [6] U. Rivero, Markus Meuwly, Stefan Willitsch, *Chem. Phys. Lett.* 10.1016/j.cplett.2017.03.063 (2017).
- [7] T. Nagy, J. Yosa Reyes and M. Meuwly, *J. Chem. Theory Comput.* **10**, 1366 (2014).

## Improved partitioning of biomolecules for quantum-chemical embedding calculations based on graph theory

Mario Wolter<sup>1</sup>, Moritz von Looz<sup>2</sup>, Henning Meyerhenke<sup>2</sup>, Christoph R. Jacob<sup>1</sup>

<sup>1</sup>*TU Braunschweig, Institute of Physical and Theoretical Chemistry,  
Gaußstr. 17, 38106 Braunschweig, Germany*

<sup>2</sup>*Karlsruhe Institute of Technology (KIT), Institute of Theoretical Informatics,  
Parallel Computing Group, Postfach 6980, 76128 Karlsruhe, Germany*

Quantum-chemical subsystem methods [1] allow for the efficient calculations of local molecular properties, such as local excitation energies in biomolecular systems. To this end, the system is partitioned into a subsystem of interest (e.g., the chromophore) and its environment. This environment is usually further partitioned into smaller fragments.[2] For protein environments, a partitioning into fragments containing a fixed number of amino acids has so far been employed.[3]

Here, we employ methods from graph theory to determine the partitioning of protein environments for quantum-chemical embedding calculations of local molecular properties. The main challenge is to map the protein structure onto a graph in which the nodes are the amino acid residues connected by edges. Depending on the strength of interaction and distance to the subsystem of interest, weighting factors are assigned to the edges. These have to be chosen in a way that they estimate the error in the property of interest that is expected when assigning its two nodes to different subsystems. To obtain these weighting factors, we employed DFT calculations for all pairs of amino acids in small proteins. Based on these graphs we use heuristics and cut-offs for larger protein test cases where the direct calculation becomes computationally unfeasible.[4]

We then apply graph partitioning algorithms for partitioning the protein graphs into clusters with the lowest cut weights, i.e., the partitioning for which the estimated error in the local molecular property is low for a given number of fragments. Established graph partitioning tools had to be modified to be applied directly to such protein graphs, as some additional constraints had to be introduced due to chemical idiosyncracies.[5]

- [1] A. S. P. Gomes, Ch. R. Jacob, *Ann. Rep. Prog. Chem. C*, **108**, 222 (2012).
- [2] Ch. R. Jacob, L. Visscher, *J. Chem. Phys.* **128**, 155102 (2008).
- [3] A. Goez, Ch. R. Jacob, J. Neugebauer, *Comput. Theor. Chem.* **1040–1041**, 34–359 (2014).
- [4] M. Wolter, M. von Looz, H. Meyerhenke, Ch. R. Jacob, *to be submitted* (2017)
- [5] M. von Looz, M. Wolter, Ch. R. Jacob, H. Meyerhenke, *Experimental Algorithms. SEA 2016. Lecture Notes in Computer Science*, **9685**, 353–368. Springer, Cham (2016)

## PEGylation of Temozolomide (TMZ): A Molecular Dynamics study

**Tatiana F. Vieira<sup>1</sup>, Sérgio F. Sousa<sup>2</sup>, Joana Peres<sup>1</sup>, Manuel Coelho<sup>1</sup>**

<sup>1</sup>LEPABE, Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

<sup>2</sup>UCIBIO, REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal

There has been a great interest in PEGylation of small drugs, mainly antitumor agents because of their low solubility, high toxicity, rapid excretion or untargeted biodistribution [1]. PEGylation can increase the circulating half-life of the drugs and also lead to a continued drug release [2]. However, the exact interaction between small drug molecules and PEG is still not clearly understood.

Imidazotetrazine compounds presented promising results as antitumor agents, but, only temozolomide is currently used [3]. However, there are some limitations, namely poor uptake and tumour cell resistance. PEGylation can help overcome these constraints by promoting drug delivery *in situ*, protecting against proteolytic enzymes and reticuloendothelial system (RES) uptake, leading to an increase in the circulating half-life.

In this study we performed several all atom molecular dynamic simulations with systems containing different poly(ethylene) glycol (PEG) molecules, the active form of an imidazotetrazine drug, temozolomide (TMZ) and salt at physiological conditions.

Based on the results we are able to evaluate the influence of type of functional group, molecular weight, presence of drug molecules and Na<sup>+</sup> and Cl<sup>-</sup> ion concentration in the behaviour of PEG as well as provide atomic-scale insight into its interaction with other molecules and complement experimental findings. This is an on-going work and we plan to expand this study to other drugs, proteins and nanocarriers such as dendrimers and liposomes.

[1] F. M. Veronese, G. Pasut, *Drug Discov. Today* **10**, 1451–1458 (2005).

[2] J. S. Kang, P. P. Deluca, K. C. Lee, *Expert Opin. Emerg. Drugs* **14**, 363–80 (2009).

[3] C. L. Moody, R. T. Wheelhouse, *Pharmaceuticals*, **7** (2014).

## Decoherence of Electron Dynamics upon Ionization of Polyatomic Molecules

Morgane Vacher<sup>1</sup>, Michael J. Bearpark<sup>2</sup>, Michael A. Robb<sup>2</sup>, João P. Malhado<sup>2</sup>

<sup>1</sup>*Department of Chemistry – Ångström, Uppsala University, Uppsala, Sweden*

<sup>2</sup>*Department of Chemistry, Imperial College London, London, United Kingdom*

Knowledge about the electronic motion in molecules is essential for our understanding of chemical reactions. The advent of attosecond techniques opens up the possibility to induce electronic motion, observe it in real time, and potentially steer it. Many theoretical studies so far treated molecular electron dynamics upon ionisation as a purely electronic process: by neglecting the nuclear coordinates, long-lived oscillations in the electronic density are then predicted. There has been an enormous experimental effort dedicated to observe the predicted oscillations in the electronic density of molecules [1], unsuccessful so far. But what does the oscillatory electronic motion actually become when the nuclear coordinates are taken into account? Here, we simulate the dynamics upon ionization of paraxylene (Figure 1a) and modified bis-methylene-adamantane, with a quantum mechanical treatment of both electron and nuclear dynamics using the direct dynamics variational multiconfigurational Gaussian method [2]. Our simulations give new important physical insights about the expected decoherence process. In particular, we show that the decoherence of electron dynamics happens on the time scale of a few femtoseconds (Figure 1b), with the interplay of different mechanisms [3].

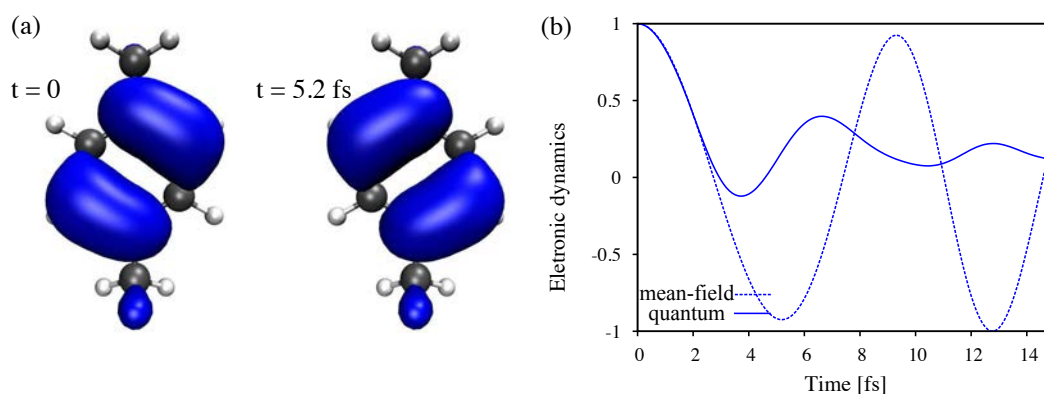


Figure 1: (a) Time-dependent hole density in paraxylene cation. (b) Electron dynamics with a mean-field nuclear motion (dashed line) and with quantum nuclear motion (solid line).

[1] F. Calegari et al., *Science* **346**, 336 (2014).

[2] M. Vacher, M. Bearpark and M. Robb, *Theor. Chem. Acc.* **135**, 187 (2016).

[3] M. Vacher, M. Bearpark, M. Robb and J. Malhado, *Phys. Rev. Lett.* **118**, 083001 (2017).

## Investigation of the degradation process of chlorhexidine using Density Functional Theory calculations

**Michele Aparecida Salvador<sup>1</sup>, Camila Pinheiro Sousa<sup>2</sup>, Simone Morais<sup>3</sup>, Pedro de Lima-Neto<sup>2</sup>, Adriana Nunes Correia<sup>2</sup>, Paula Homem-de-Mello<sup>1</sup>**

<sup>1</sup> *Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Av. dos Estados, 5001, Bloco B, sala 1017, 09210-580, Santo André - SP, Brazil*

<sup>2</sup> *Departamento de Química Analítica e Físico-Química, Centro de Ciências, Universidade Federal do Ceará, Bloco 940, Campus do Pici, 60440-900, Fortaleza – CE, Brazil*

<sup>3</sup> *REQUIMTE-LAQV, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, R. Dr. António Bernardino de Almeida 431, 4200-072, Porto, Portugal*

Chlorhexidine (CHD) is a germicidal drug which has hemotoxic and carcinogenic degradation products. Although the descriptions of the main degradation products have been reported through experimental studies [1, 2, 3], there is no consensus either about the degradation pathway, or the molecule's structure in its neutral form. In order to shed light on that mechanism, we have employed Density Functional Theory calculations to study reactants (both conformers), in different protonation states, its degradation products and some intermediates involved in the different pathways. Based on free energy values comparison and frontier molecular orbital analysis in terms of energy and form/localization, we have obtained the most stable structures in each protonation state. CHD in saturated form was found as the most stable: it has HOMO localized in one *p*-chloroaniline, and, due to molecule's symmetry, HOMO-1 has contributions from the other side of the molecule, but mainly from the biguanide portion of the molecule, instead of from the *p*-chloroaniline. Also, for the saturated form we have studied two possible degradation pathways, starting from the monoprotonated structure, and three pathways starting from the neutral structure. We found out that the mechanisms proposed in literature, whose pathways lead to *p*-chloroaniline (PCA) formation in a smaller number of steps, are more likely than the mechanisms with more intermediate steps or pathways that do not predict PCA formation. Also, based on free energy results, we have found that the formation of another sub-product (PBG-AU) is favorable as well, being it our main result.

[1] Y. Ha, A. P. Cheung, *J. Pharm. Biom. Analysis*, vol 10, n. 12, p. 1327–1334, 1996.

[2] L. K. Reville, W. H. Doub, R. T. Wilson, M. H. Harris, A. M. Rutter, *Pharm. Res. An Off. J. Am. Assoc. Pharm. Sci.*, vol 10, n. 12, 1993.

[3] Z. Zong e L. E. Kirsch, *J. Pharm. Sci.*, vol. 101, n. 7, 2417 – 2427, 2012.

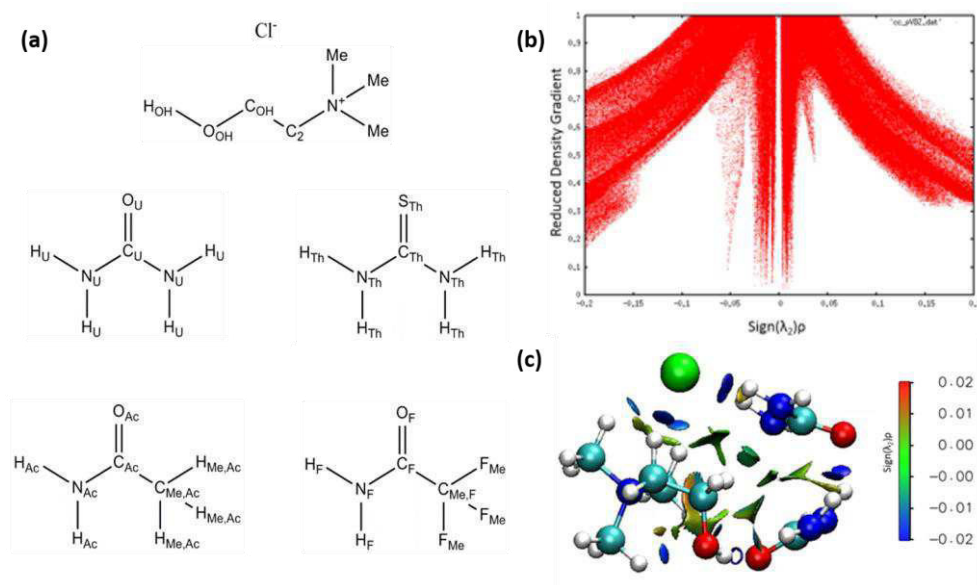
## Deep Eutectic Solvents: The Effect of the Hydrogen Bond Donor on Structure

Ryan Stefanovic<sup>1</sup>, Grant B. Webber<sup>1</sup>, Alister J. Page<sup>1</sup>

<sup>1</sup>University of Newcastle, University Drive, Newcastle, Australia

Deep Eutectic Solvents (DES) are a relatively new class of solvent, formed from mixtures of a salt and molecular hydrogen bond donor (HBD). At a certain molar ratio, the mixture of these two components exhibits a melting temperature far reduced compared to the pure components themselves. The archetypal DES is a 1:2 molar ratio mixture of choline chloride (ChCl, mp: 302 °C) and urea (mp: 133 °C), which is liquid at room temperature.<sup>1</sup>

The temperature depression in DES is thought to be the result of the intercalation of the HBD in the ionic salt lattice. However, this qualitative picture does not explain why different HBD species lead to different temperature depressions. Recently, we have presented the first structural model of bulk DES, based on QM/MD simulations,<sup>2</sup> which demonstrated that the structural ordering of the urea HBD determines the melting point depression. In this work, we present ab initio calculations of DES formed between ChCl and four HBDs - urea, thiourea, acetamide, and 2,2,2-trifluoroacetamide, to systematically probe the relationship between the HBD and the bulk DES structure. Analysis of non-covalent interactions (via the reduced density gradient<sup>3</sup> analyses) within (ChCl)<sub>x</sub>HBD<sub>2x</sub> (x=1...5) clusters reveals for the first time the dominant intermolecular forces acting in DES, and how the HBD controls these interactions. Our results provide a new and fundamental understanding of the origins of solvation in this interesting class of solvents.



**Figure 1.** (a) Structure of parent salt (choline chloride, top) and HBDs studied (clockwise from top left; urea, thiourea, 2,2,2-trifluoroacetamide, and acetamide), (b) plot of reduced density gradient vs. electron density for ChCl:Urea<sub>2</sub> produced using NCIPLOT,<sup>4</sup> and (c) the graphical representation of structure and RDG isosurface (right).

[1] A.P. Abbott *et al*, *Chemical Communications*. **1**, 70-71 (2003).

[2] R. Stefanovic *et al*, *Physical Chemistry Chemical Physics*. **19**, 3297-3306 (2017).

[3] E.R. Johnson *et al*, *Journal of the American Chemical Society*. **132**, 6498-6506 (2010).

[4] J. Contreras-Garcia *et al*, *Journal of Chemical Theory and Computation*. **7**, 625-632 (2011).

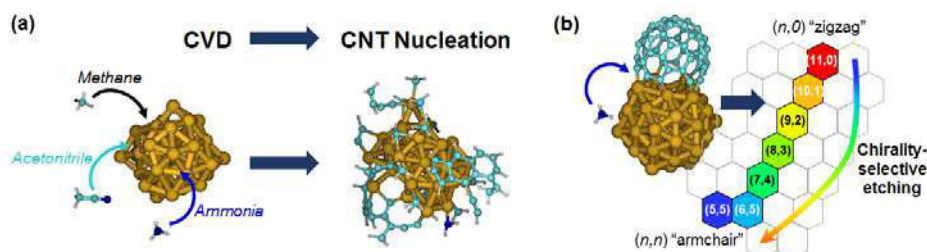
## How does Nitrogen Change Carbon Nanotube Chirality? Insights from Quantum Chemistry.

Clothilde A. Eveleens<sup>1</sup>, Stephan Irle<sup>2</sup>, Alister J. Page<sup>1</sup>

<sup>1</sup>*Discipline of Chemistry, University of Newcastle, University Drive, Callaghan, Australia.*

<sup>2</sup>*Department of Chemistry, Graduate School of Science, Nagoya University, Nagoya, Japan.*

The chirality ( $n, m$ )-controlled growth of carbon nanotubes (CNTs) on a commercial scale is an ongoing challenge. Chemical vapour deposition (CVD) is the preferred method for the synthesis of CNTs though ( $n, m$ ) product mixtures are obtained. Recent studies have shown that the addition of an etchant to the feedstock gas can alter the chirality and diameter during CVD [1]. However, the mechanism explaining how nitrogen changes CNT chirality during growth remains largely unexplored. Here, we present first principles density functional theory (DFT) calculations and non-equilibrium density functional tight binding molecular dynamics (DFTB/MD) simulations that reveal how nitrogen etchants, e.g. ammonia and acetonitrile, influence the CVD mechanism and change CNT nucleation during growth [2, 3]. We propose that particular chirality CNTs can be removed from CVD-produced distributions via “chirality-selective etching” [2]. DFTB/MD simulations additionally show that ammonia is selectively activated by the CVD catalyst, providing a sustained source of hydrogen during growth. These simulations reveal for the first time that nitrogenous species influence CNT nucleation and growth in new, unexpected ways.



**Figure 1.** (a) DFTB/MD simulations show how ammonia and acetonitrile influence CNT nucleation on transition metal nanoparticles, (b) DFT calculations demonstrate CNT reactive selectivity is a function of ( $n,m$ ) chirality.

[1] Z. Zhu, H. Jiang, T. Suzi, A. G. Nasibulin, E. I. Kauppinen, *J. Am. Chem. Soc.* **133**, 1224 (2011).

[2] C. A. Eveleens, Y. Hijikata, S. Irle, A. J. Page, *J. Phys. Chem C* **120**, 19862, (2016).

[3] C. A. Eveleens, A. J. Page, *Nanoscale* **9**, 1727, (2017).



## Development and Application of ReaxFF for Describing Catalytic Boron Nitride Nanotube Growth

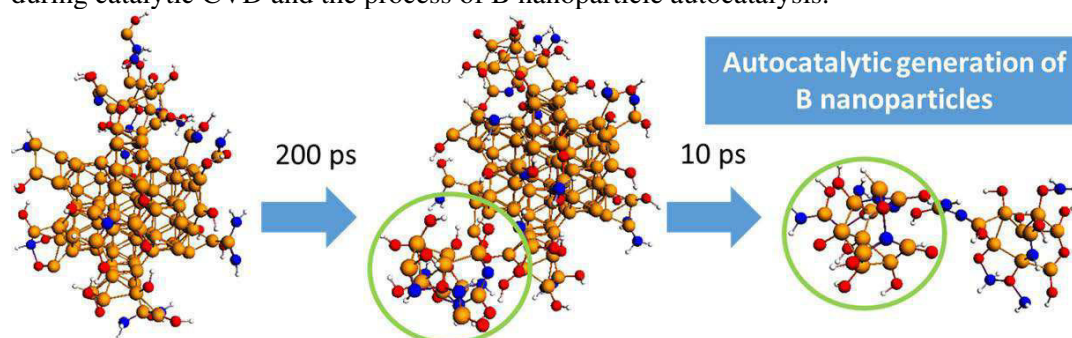
B. McLean<sup>1</sup>, G. B. Webber<sup>2</sup>, and A. Page<sup>1</sup>

<sup>1</sup>*Discipline of Chemistry and* <sup>2</sup>*Discipline of Chemical Engineering, The University of Newcastle, Callaghan, NSW, Australia*  
*University Road, Callaghan, NSW, Australia*

Boron nitride nanotubes (BNNTs), first predicted in 1994 [1] and experimentally realised in 1995 [2], are structural analogues to carbon nanotubes (CNTs). Unlike CNTs, BNNTs exhibit the same physical properties independent of the tube chirality, with a wide band gap of 5-6 eV [3]. Among other techniques [4], BNNTs can be synthesised effectively via boron oxide chemical vapour deposition (BOCVD) [5-8]:



The mechanism explaining this self-assembly process remains essentially unexplored. Here we report an atomistic mechanism to explain BOCVD and BNNT growth, using nonequilibrium ReaxFF molecular dynamics simulations [9]. ReaxFF parameters to describe B/N-transition metal interactions have additionally been developed for transition metals including Co, Cu, Fe and Ni. These simulations reveal, for the first time, the fundamental steps towards BN nanomaterial nucleation from  $\text{B}_2\text{O}_3$  and  $\text{NH}_3$  precursors during catalytic CVD and the process of B nanoparticle autocatalysis.



**Figure: Non-equilibrium ReaxFF MD simulations reveal autocatalytic generation of boron nanoparticles during simulated CVD**

1. Rubio, A., J.L. Corkill, and M.L. Cohen, *Phys. Rev. B.*, **1994**. 49 5081-5084.
2. Chopra, N.G., et al., *Science*, **1995**. 269 966.
3. Blase, X., et al., *EPL (Europhysics Letters)*, **1994**. 28 335.
4. Lee, C., et al., *Molecules*, **2016**. 21 922.
5. Lourie, O.R., et al., *Chem. Mater.*, **2000**. 12 1808-1810.
6. Tang, C., et al., *Chem. Commun.*, **2002** 1290-1291.
7. Tang, C.C., et al., *Chem. Phys. Lett.*, **2002**. 356 254-258.
8. Zhi, C., et al., *Solid State Commun.*, **2005**. 135 67-70.
9. Senftle, T.P., et al., *Npj Comp. Mater.*, **2016**. 2 15011.

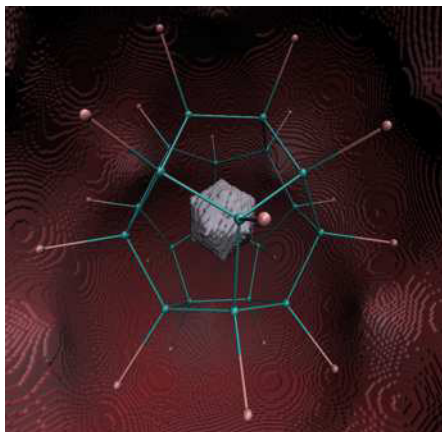
**The electronic structure of the  $[\text{C}_{20}\text{X}_{20}]^-$ ,  $[\text{C}_{20}\text{X}_{20}]^{2-}$ ,  $[\text{Si}_{20}\text{F}_{20}]^-$ ,  $[\text{Si}_{20}\text{F}_{20}]^{2-}$  (X= F, Cl, Br, I) anions.**

**Śławomir Berski<sup>1</sup>, Agnieszka Gordon<sup>1</sup>, Roma Musik<sup>2</sup> and Szczepan Roszak<sup>2</sup>**

<sup>1</sup>*Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland*

<sup>2</sup>*Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wrocław University of Science and Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland*

Following the strategy of Irikura [1] for design of electron boxes on the basis of fluorocarbon cages, we have studied three problems related to the localisation of electron density inside atomic cages: 1) a possibility to increase an amount of electron density inside the cage going from the  $[\text{C}_{20}\text{X}_{20}]^-$  to  $[\text{C}_{20}\text{X}_{20}]^{2-}$  anion 2) how the decreasing electronegativity of halogen in  $[\text{C}_{20}\text{X}_{20}]^-$  and  $[\text{C}_{20}\text{X}_{20}]^{2-}$  cages influences properties of electron density localised inside the cage and local electronic nature of C-C and C-X bonds, 3) a possibility of electron localisation inside the cage, where carbon is replaced by silicon for  $[\text{Si}_{20}\text{F}_{20}]^-$  and  $[\text{Si}_{20}\text{F}_{20}]^{2-}$  clusters. The analysis of molecular electronic structure is performed in real space using topological analysis of Electron Localisation Function (ELF) [2]. Above methodology is free from the arbitrary selection of molecular orbitals. This study is a continuation of our previous research [3] where we have shown that among the following radical anions:  $\text{C}_4\text{F}_4$ ,  $\text{C}_8\text{F}_8$ ,  $\text{C}_{10}\text{F}_{16}$ ,  $\text{C}_{20}\text{F}_{20}$ , the local maximum of ELF inside the cage is observed only for the  $[\text{C}_{20}\text{F}_{20}]^-$  cage. We believe that our results will contribute to the synthesis of new materials from molecular electrides group.



- [1] K. K. Irikura, *J. Phys. Chem. A* **112**, 983 (2008).
- [2] B. Silvi, A. Savin, *Nature*, **371**, 683 (1994).
- [3] S. Berski, A. J. Gordon, Z. Latajka, *J. Phys. Chem. A*, **118**, 4147 (2014).

## From functional mechanism to new therapeutic tools: reaction modelling and computational design of PDC inhibitors.

**Jacopo Sgrignani<sup>1</sup>, JingJing Chen<sup>2</sup>, Alessio Ferrari<sup>3</sup>, Giovanni Grazioso<sup>4</sup>, Maura Garofalo<sup>1</sup>, Alessandra Silvani<sup>3</sup>, Andrea Alimonti<sup>2</sup>, and Andrea Cavalli<sup>1</sup>.**

<sup>1</sup> *Institute for Research in Biomedicine (IRB), Università della Svizzera Italiana (USI), Via Vela 6, Bellinzona.*

<sup>2</sup> *Institute of Research in Oncology (IOR), Università della Svizzera Italiana (USI), Bellinzona, Switzerland.*

<sup>3</sup> *Department of Chemistry, Università degli Studi di Milano, Milano, Italy.*

<sup>4</sup> *Department of Pharmaceutical Sciences, Università degli Studi di Milano, Milano, Italy.*

Pyruvate (PYR) dehydrogenase complex (PDC) is a multi-subunits molecular machine responsible of the conversion of PYR into acetyl-CoA by a process known as pyruvate decarboxylation. From the biochemical point of view PDC is the gatekeeper controlling the entry of carbon in the TCA cycle (also known as Krebs cycle) from two main sources: carbohydrates and gluconeogenic amino acids.

Metabolic modifications of cancer cells were firstly described by Otto Warburg in 1930, and subsequently confirmed by several studies. In particular, cancer cells have a higher rate of glycolysis than normal cells, however, according to the Warburg interpretation, this is mainly followed by lactic fermentation rather than mitochondrial PYR oxidation, as it happens in normal cellular conditions. In spite of this, recent investigations pointed out the importance of oxidative phosphorylation in some specific cancers [1-2]. Other studies, also carried out by some of us, highlighted a key role for the PDC activity in the progression of prostate cancer and glioblastoma. These observations confirmed that PDC inhibition, for a long time scarcely considered as target for the development of new anti-cancer drugs, could be a viable strategy for the design of new antineoplastic molecules.

In our studies, starting from the available structural information, we used multiple computational techniques to (1) improve our knowledge about the functional mechanisms of PDC and (2) identify new drug-like inhibitors.

These efforts lead to the identification of one lead compound able to inhibit both the enzyme and the prostate cancer cellular growth.

Moreover, applying different QM/MM calculations (geometrical optimization of relevant intermediates or Umbrella Sampling calculations) on specific structural models, we were able to estimate a free energy profile of the enzymatic reaction fully consistent with the available experimental data.

In strict collaboration with synthetic organic chemists and molecular oncologists, we are using the acquired knowledge about the PDC functional mechanism and computer simulations to design new molecules with improved affinity and bioavailability with respect to identified lead compound, obtaining encouraging results.

- [1]. Z. Zachar, et al., *J. Mol. Med.*, **89**, 1137 (2011)
- [2]. V. I. Bunik et al., *Oncotarget*, **6**, 40036 (2015)

## Towards the description of non-covalent interactions in AP1roG model

**F. Brzęk<sup>1</sup>, P. Tecmer<sup>1</sup>, K. Boguslawski<sup>1</sup>, P. Żuchowski<sup>1</sup>**

<sup>1</sup>*The Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University,  
Gagarina 11, Torun, Poland*

Geminal-based methods are a promising alternative to standard multireference methods because they allow us to efficiently model strongly-correlated systems, like bond-breaking processes and heavy-element chemistry [1–3]. One example is the Antisymmetric Product of 1-reference orbital Geminals (AP1roG) [1–4]. However, in order to reach chemical accuracy when predicting molecular properties, the missing correlation effects that cannot be described by electron-pair states have to be included in the electronic wave function. Different a posteriori corrections with an AP1roG reference function have been developed that aim at including dynamic electron correlation effects (see for instance Refs. [5, 6]).

In this work, we discuss a different approach to account for dynamic correlation on top of AP1roG in weakly interacting dimers that will allow us to model dispersion energies. Specifically, we apply Symmetry Adapted Perturbation Theory (SAPT)[7] to approximate the dispersion energy between two interacting monomers.

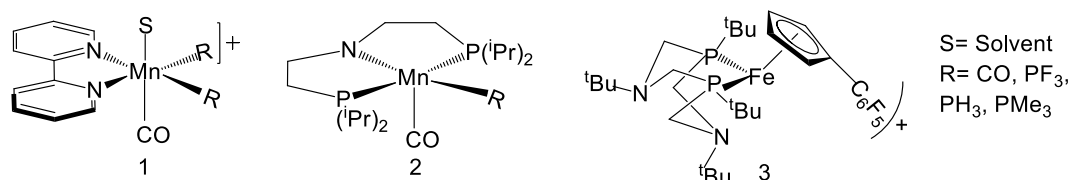
- [1] K. Boguslawski, P. Tecmer, P.W. Ayers, P. Bultinck, S. De Baerdemacker, D. Van Neck, *Phys. Rev. B* **89**, 201106(R) (2014)
- [2] P. Tecmer, K. Boguslawski, P.A. Limacher, P.A. Johnson, M. Chan, T. Verstraelen, P.W. Ayers, *J. Phys. Chem. A* **118**, 9058 (2014)
- [3] K. Boguslawski, P. Tecmer, P. W. Ayers, *Phys. Chem. Chem. Phys.* **17**, 14427-14436 (2015)
- [4] K. Boguslawski, P. Tecmer, Ö. Legeza, *Phys. Rev. B* **94**, 155126 (2016)
- [5] K. Boguslawski, P. W. Ayers, *J. Chem. Theory Comput.* **11**, 5252 (2015)
- [6] A. J. Garza, I. W. Bulik, T. M. Henderson, G. E. Scuseria, *J. Chem. Phys.* **142**, 044109 (2015)
- [7] B. Jeziorski, R. Moszyński, K. Szalewicz, *Chem. Rev.* **94**, 1887-1930 (1994)

## CO<sub>2</sub> Hydrogenation using Earth Abundant Metal Catalysts: Role of Ligand

Kuber Singh Rawat, Arup Mahata, Biswarup Pathak\*

*Discipline of Chemistry, Indian Institute of Technology (IIT) Indore, Indore, Madhya Pradesh 453552, India*

**Abstract:** The catalytic conversion of CO<sub>2</sub> into useful products is highly desirable as CO<sub>2</sub> is a promising feedstock for one-carbon building block based organic products. In the CO<sub>2</sub> hydrogenation reaction, heterolytic H<sub>2</sub> cleavage and hydride transfer are usually the rate-determining steps. Using the density functional theory (DFT) calculations, earth abundant metal (Mn and Fe) based complexes (Figure 1) have been studied for CO<sub>2</sub> hydrogenation reaction. We show that the role of  $\sigma$  and  $\pi$  acceptor ligands is important to improve the rate determining steps. A base free CO<sub>2</sub> hydrogenation mechanism is possible in the presence of flexible ligands. Here, we will present a series of earth abundant metal-based catalysts with different set of ligands to show that earth abundant metal-based catalysts are very promising for CO<sub>2</sub> hydrogenation reaction.



**Figure 1.** Different types of metal Catalysts have been studied for the CO<sub>2</sub> hydrogenation using different nature of the ligands.

- [1] K. S. Rawat, A. Mahata, I. Choudhuri, B. Pathak, *J. Phys. Chem. C* **120**, 8821 (2016).
- [2] K. S. Rawat, A. Mahata, I. Choudhuri, B. Pathak, *J. Phys. Chem. C* **120**, 16478 (2016).
- [3] K. S. Rawat, A. Mahata, B. Pathak, *J. Phys. Chem. C* **120**, 26652 (2016).
- [4] K. S. Rawat, B. Pathak, *Catal. Sci. Technol.* (2017) DOI: 10.1039/C7CY00737J

## Instantaneous absorption spectra of firefly oxyluciferin using the first principle molecular dynamics simulations

Miyabi Hiyama<sup>1</sup>, Yoshifumi Noguchi<sup>1</sup>, Motoyuki Shiga<sup>2</sup>,

Osamu Sugino<sup>1</sup>, Hidefumi Akiyama<sup>1,3</sup>, Nobuaki Koga<sup>4</sup>

<sup>1</sup> *Institute for Solid State Physics, The University of Tokyo, Kashiwa 277-8581, Japan*

<sup>2</sup> *Center for Computational Science and E-Systems, Japan Atomic Energy Agency, Kashiwa 277-0871, Japan*

<sup>3</sup> *AIST-UTokyo Advanced Operando-Measurement Technology Open Innovation Laboratory (OPERANDO-OIL), Kashiwa 277-8581, Japan*

<sup>4</sup> *Graduate School of Informatics, Nagoya University, Nagoya 464-8601, Japan*

The spectroscopic characteristics of oxyluciferin and its conjugate bases, the emitters of firefly bioluminescence, are critical for understanding firefly bioluminescence. In our studies, first, we elucidated the vibronic effect on the absorption and fluorescence spectra of the firefly oxyluciferin and its conjugate bases. While the energies of the excited states were calculated with the time-dependent density functional theory (TD-DFT), the solvent effect was incorporated using the polarized continuum model (PCM). The calculated absorption energies are slightly lower than the experimental ones. The calculated spectral shapes well reproduce the experimental shapes except for the case of keto type of oxyluciferin anion of which theoretical spectra peak is very sharp, different from the experimental broad shape. Then, the effects of hydrogen bonding interactions were clarified through a theoretical study on the stability of the oxyluciferin anions with explicit water molecules using the first-principles molecular dynamics (FPMD) simulations [1]. These simulations showed that enol type of anion is more stable than keto type because of the unique features of the static and dynamical hydration structures, which are difficult to capture using the PCM solvation model. Next, the absorption spectra of aqueous oxyluciferin anions were derived using the structures obtained from the FPMD simulations at room temperature for each isomeric form, in order to account for the effects of vibrations of oxyluciferin anions and dynamical fluctuations of their hydration structures [2].

[1] Y. Noguchi, M. Hiyama, M. Shiga, O. Sugino, H. Akiyama, *J. Phys. Chem. B*, **120**, 8776 (2016)

[2] M. Hiyama, M. Shiga, N. Koga, O. Sugino, H. Akiyama, Y. Noguchi, *Phys. Chem. Chem. Phys.*, **19**, 10028 (2017)

## Low-lying excited states and diradical nature of conjugated dicarbonyl compounds

**Diego López-Carballeira<sup>1</sup>, David Casanova<sup>2,3</sup> and Fernando Ruipérez<sup>1</sup>**

<sup>1</sup>*POLYMAT, University of the Basque Country UPV/EHU, Joxe Mari Korta Center, Avda. Tolosa 72, 20018 Donostia-San Sebastián (Spain)*

<sup>2</sup>*Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU) and Donostia International Physics Center (DIPC), P.K. 1072, 20080, Donostia, Euskai, Spain*

<sup>3</sup>*IKERBASQUE, Basque Foundation for Science, Bilbao 48013, Spain*  
*diego.lopez@polymat.eu*

The open-shell electronic structure of certain organic systems has demonstrated to be fundamental for the comprehension of their remarkable physico-chemical properties, leading to applications in a broad range of fields of materials science.<sup>1</sup> As a general observation, this kind of systems are usually characterized by a small energy gap between the open-shell singlet ground state and the lowest triplet state. Thus, these systems are promising candidates to host the singlet fission (SF) process, a mechanism that may enhance the efficiency of conventional solar cells, by which a singlet excited state splits into two triplets, following the condition  $E(S_1) \geq 2E(T_1)$ . Despite the scientific effort carried out, additional molecular design protocols are required to achieve a system with real application. In such a way, diradicals has been proposed as a class of promising SF sensitizers.<sup>2</sup> As a representative part of a larger investigation, in this communication we present an analysis of the diradical character and the low-lying excited states of 19 quinone-like molecules, classified as benzoquinones (BQ), pentaloquinones (PQ), naphtoquinones (NQ) and anthraquinones (AQ), in the pursuit of new efficient SF molecules.

Due to the inherent difficulties in the proper description of diradicaloids, a previous benchmark has been performed assessing TDDFT and spin-flip TDDFT (SF-TDDFT) methods. The diradical character is evaluated by means of the spin-projected UHF (PUHF) method. While the diradical character ranges between 0 and 0.8, the optimal structures are characterized by a moderate diradical character (0.1-0.4). Both TDDFT and SF-TDDFT demonstrate to work well depending on the diradical character. Several molecules fulfill the aforementioned conditions, and those labeled as 1,4-PQ, 1,6-PQ, 1,5-NQ, 1,7-NQ, 2,6-AQ, 1,10-AQ, and 2,9-AQ seem to be promising for their application as singlet fission sensitizers.

[1] C. Lambert, *Angew. Chem., Int. Ed.*, **50**, 1756 (2011)

[2] M. B. Smith and J. Michl, *Chem. Rev.*, **110**, 6891 (2010)



## Energetics and dynamics of a light-driven sodium-pumping rhodopsin

Carl-Mikael Suomivuori<sup>1,2</sup>, Ana P. Gamiz-Hernandez<sup>2</sup>, Dage Sundholm<sup>1</sup>, and Ville R. I. Kaila<sup>2</sup>

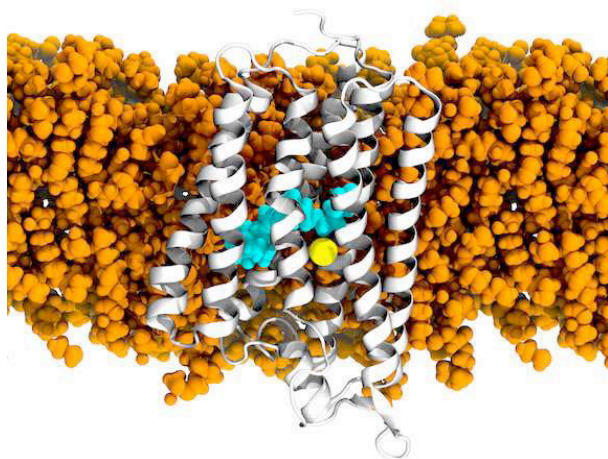
<sup>1</sup>Department of Chemistry, University of Helsinki, A. I. Virtasen Aukio 1, Helsinki, Finland

<sup>2</sup>Department of Chemistry, Technical University of Munich, Lichtenbergstrasse 4, Garching, Germany

The conversion of light energy into ion gradients across biological membranes is one of the most fundamental reactions in primary biological energy transduction. Recently, the structure of the first light-activated Na<sup>+</sup> pump, *Krokinobacter eikastus* rhodopsin 2 (KR2), was resolved at atomic resolution [2]. In order to elucidate its molecular mechanism for Na<sup>+</sup> pumping, we perform extensive classical molecular dynamics (MD) simulations and hybrid quantum mechanics/molecular mechanics (QM/MM) calculations of transient photocycle states. Our simulations show how the dynamics of key residues regulate water and ion access between the bulk and the buried light-triggered retinal site. We identify putative Na<sup>+</sup> binding sites and show how protonation and conformational changes gate the ion through these sites toward the extracellular side. We further show by correlated *ab initio* quantum chemical calculations that the obtained putative photocycle intermediates are in close agreement with experimental transient optical spectroscopic data. The combined results of the ion translocation and gating mechanisms in KR2 may provide a basis for the rational design of novel light-driven ion pumps with optogenetic applications.

[1] C. -M. Suomivuori, A. P. Gamiz-Hernandez, D. Sundholm, V. R. I. Kaila, (in press) *Proc. Natl. Acad. Sci. U. S. A.* (2017).

[2] H. E. Kato *et al.*, *Nature* **521**, 48 (2015).





## Mechanistic Study on Photocatalytic Water Splitting with Carbon Nitride Materials

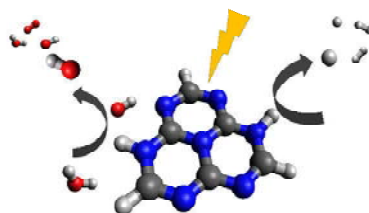
Johannes Ehrmaier<sup>1</sup>, Andrzej L. Sobolewski<sup>2</sup>, Tolga N. V. Karsili<sup>1</sup>,  
Wolfgang Domcke<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Technical University of Munich, Lichtenbergstraße 4,  
85748-Garching, Germany*

<sup>2</sup>*Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa,  
Poland*

Impressive progress has recently been achieved in photocatalytic water splitting with so-called graphitic carbon nitride materials consisting of heptazine (tri-*s*-triazine) building blocks [1]. In addition to efficient hydrogen evolution in the presence of sacrificial electron donors, stoichiometric splitting of pure water with doped C<sub>3</sub>N<sub>4</sub> materials has been reported [2,3]. However, the fundamental mechanistic principles of the photoinduced reaction and the catalytic cycle are, as yet, poorly understood.

We provide first-principles computational evidence that water splitting with carbon-nitride based materials can be understood as a molecular photochemical reaction taking place in hydrogen-bonded chromophore-water complexes. The oxidation of water occurs homolytically via a light-driven concerted electron/proton transfer from water to heptazine. Via a conical intersection of the potential-energy surface of the charge transfer state with the electronic ground state, ground-state heptazinyl and OH radicals are generated. It is shown that the excess hydrogen atom of the chromophore radical can be photodetached by a second photon, which regenerates the chromophore. A water molecule is thus catalytically split into H and OH radicals by the sequential absorption of two photons. Alternatively to the photodetachment reaction, two heptazinyl radicals can recombine in an exothermic dark reaction to form H<sub>2</sub> and two heptazine molecules. The recombination of OH radicals is also exothermic and may yield H<sub>2</sub>O<sub>2</sub> and eventually O<sub>2</sub> and H<sub>2</sub>O in catalyzed dark reactions. The proposed photochemical reaction scheme within hydrogen-bonded chromophore-water complexes is complementary to the traditional paradigm of photocatalytic water splitting, which requires the separation of electrons and holes over substantial time scales (microseconds) and distances (micrometers).



- [1] X. Wang, K. Maeda, et al., *Nat. Mater.* **8**, 76 (2009).
- [2] J. Liu, Y. Liu, et al., *Science*, **347**, 970 (2015)
- [3] J. Liu, N. Y. Liu, et al., *Nanoscale*, **8**, 11956 (2016)

## Fluorescent markers for the detection of amyloid- $\beta$ in Alzheimer's disease

**Francesca Peccati<sup>1</sup>, Stefano Pantaleone<sup>1</sup>, Jordi Hernando<sup>1</sup>, Xavier Solans-Monfort<sup>1</sup>, Marion Sodupe<sup>1</sup>**

<sup>1</sup>*Departament de Química, Unitat de Química-Física, UAB, Bellaterra, 08193, Barcelona.*

Alzheimer's disease is a progressive disorder of the central nervous system showing several pathological hallmarks, including plaques caused by aggregation of the peptide amyloid- $\beta$  ( $A\beta$ ) into fibrils. According to the amyloid cascade hypothesis, deposition of  $A\beta$  in the brain is the central event of Alzheimer's pathology and thus, detection of these deposits is crucial to monitor the evolution of this disease.[1]

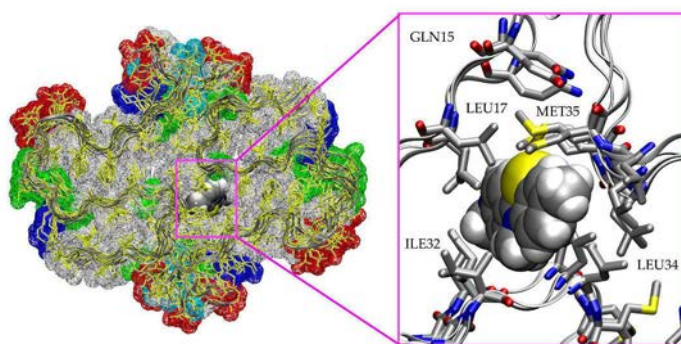


Figure 1: Binding pose of a marker on a model of  $A\beta$ 42 fibril.

Several  $A\beta$  fluorescent markers have been studied with TDDFT and fit-induced docking techniques with the aim of optimizing their optical properties and affinity for  $A\beta$  fibrils. Results indicate that  $A\beta$  fibrils affect the fluorescence properties of these markers through a number of mechanisms, such as reducing the efficiency of non-radiative decay pathways through hindering of molecular flexibility and disaggregation of quenched aggregates spontaneously forming in aqueous solution. Additionally, the binding of these markers to  $A\beta$  fibrils has been shown to be aspecific and driven by geometric complementarity and weak interactions.[2,3]

- [1] T. J. Eckroat, A. S. Mayhoub, S. Garneau-Tsodikova, *Beilstein J. Org. Chem.*, **9**, 1012 (2013).
- [2] F. Peccati, J. Hernando, L. Blancafort, X. Solans-Monfort, M. Sodupe, *Phys. Chem. Chem. Phys.*, **17**, 19718 (2015).
- [3] F. Peccati, M. Wiśniewska, X. Solans-Monfort, M. Sodupe *Phys. Chem. Chem. Phys.*, **18**, 11634 (2016).

# DFT Study of Cp\*Co<sup>III</sup>-Catalyzed C–H Alkenylation/Annulation Reactions of Indoles with Alkynes

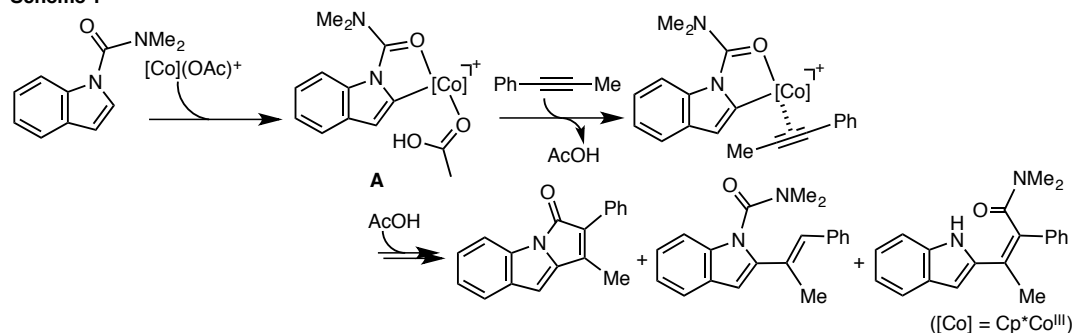
Ken Sakata<sup>1</sup>, Masami Eda<sup>1</sup>, Yuri Kitaoka<sup>1</sup>, Tatsuhiko Yoshino<sup>2</sup>, and  
Shigeki Matsunaga<sup>2</sup>

<sup>1</sup>Faculty of Pharmaceutical Sciences, Hoshi University, Shinagawa-ku, Tokyo, Japan

<sup>2</sup>Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo, Japan

In Cp\*Co<sup>III</sup>-catalyzed C–H functionalization reaction of indoles with alkynes, pyrroloindolone synthesis as well as C2-selective C–H alkenylation of indoles has been reported [1]. In this study, the reaction pathways were examined by using M06-level DFT calculations. After the C≡C bond in the alkyne is inserted into the Co–C bond at an intermediate alkenyl-Co complex (**A**) given by the C–H bond activation step, the reaction pathway bifurcates into alkenylation and annulation pathways (**Scheme 1**). When AcOH coordinates to the Co atom, alkenylation proceeds via proton transfer. On the other hand, the annulation pathway to give pyrroloindolone proceeds in the case where the ring-closure C–C bond formation is followed by the attachment of AcOH. At a high temperature (393K), the difference in the Gibbs free energy between the transition state for proton transfer in the alkenylation pathway and that for the attack of the alkenyl carbon to the carbamoyl carbon in the annulation pathway is relatively small, so both pathways are significant. We further found another pathway to provide the directing-group migration on the way to annulation. This finding well elucidates the recent experimental report that tetrasubstituted alkenes were obtained as the major product under different conditions [2].

**Scheme 1**



[1] H. Ikemoto, T. Yoshino, K. Sakata, S. Matsunaga, M. Kanai, M. *J. Am. Chem. Soc.* **136**, 5424 (2014).

[2] H. Ikemoto, R. Tanaka, K. Sakata, M. Kanai, T. Yoshino, S. Matsunaga, *Angew. Chem., Int. Ed. early view*.

## Ab Initio Crystal Orbital Calculation of Electronic Structure of B-type model-DNA

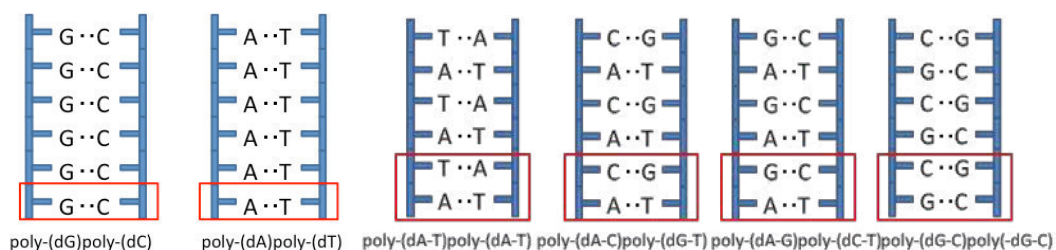
Hiroyuki Teramae<sup>1</sup> and Yuriko Aoki<sup>2</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Josai University,  
1-11 Keyakidai, Sakado, Saitama, Japan

<sup>2</sup>Department of Molecular and Material Sciences, Interdisciplinary Graduate School of  
Engineering Sciences, Kyushu University, 6-1 Kasuga-koen, Kasuga, Fukuoka, Japan

**Abstract:** As an attempts at the electronic structure calculations of the B-type model-DNA, the double helix polymers including sodium atoms as counter cation are performed by means of *ab initio* Hartree-Fock crystal orbital method adapting the screw axis-symmetry[1-3]. All sugar backbones and ions are included in the calculations. The calculation levels are at 3-21G and 6-31G levels.

The simplest DNA model is polymononucleotide, just using guanine and cytosine (or adenine and thymine) base pair. The dG and dC pair repeats with 3.38 angstrom translation and 36 degrees rotation becoming a double helix polymer. The base sequences of two polymononucleotides and four polydinucleotides are shown in Fig. 1. We hereafter use the abbreviations AT, AC, AG, and GC for poly-(dA-T)poly-(dA-T), poly-(dA-C)poly-(dG-T), poly-(dA-G)poly-(dC-T), and poly-(dG-C)poly-(dG-C) in Figure 1, respectively. In addition we use GG and AA for poly-(dG-G)poly-(dC-C) and poly-(dA-A)poly-(dT-T), respectively. These are really polymononucleotides, however, for the comparison of the results of polymononucleotides with those of polydinucleotides, a double-sized unit cell is applied for polymononucleotide for easy comparison with the results of polydinucleotides.



**FIGURE 1.** The structures of base sequences of polymononucleotides and polydinucleotides.

Hole conductions could be expected better in the G-C pair rich environment, while electron conductions could be expected for all the environments. The next step of the present work are; (1) re-calculate with more larger N values, the convergence of properties would not be sufficient, (2) calculate all poly-monomonucleotide and di-nucleotide with and without ions, and (3) calculations of poly-trinucleotide. Such a calculation is in progress and will be published elsewhere.

[1] P. Otto, E. Clementi, J. Ladik, *J. Chem. Phys.* **78**, 4547 (1983).

[2] P. Xie, H. Teramae, K. Liu, and Y. Aoki, *Int. J. Quantum Chem.*, **113**, 489 (2013)

[3] H. Teramae, *Theoret. Chim. Acta* **94**, 311 (1996)

## COMPUTATIONAL MODELING OF VERSATILE PHOTOSENSITIZERS

**Irene Casademont,<sup>1</sup> Carla Casadevall,<sup>2</sup> Arnau Call,<sup>2</sup> Julio Lloret,<sup>2,3</sup>  
Eloy Ramos-Cordoba,<sup>1,4</sup> Eduard Matito<sup>1,5</sup>**

<sup>1</sup>*Kimika Fakult., Euskal Herriko Unib. UPV/EHU, and Donostia Int. Phys. Center (DIPC), Euskadi (Spain).*

<sup>2</sup>*Inst. Chem. Res. of Catalonia (ICIQ), The Barcelona Institute of Science and Technology (Spain).*

<sup>3</sup>*Catalan Institution for Research and Advanced Studies (ICREA), Barcelona (Spain).*

<sup>4</sup>*Departament of Chemistry, Kenneth S. Pitzer Center for Theor. Chem., Univ. Cal. Berkeley (USA).*

<sup>5</sup>*IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Euskadi (Spain).  
e-mail: irenecasre@gmail.com*

Nowadays, the most available renewable energy source on the planet is sunlight. Therefore, one of the most prolific chemical research lines in photovoltaics cells consists in the search for dyes, molecules to be used in the so-called Dye-Sensitized Solar Cells (DSSC). Solar cells are a promising alternative to the silicon photovoltaic cells because they are easier to build and very economical. The challenge today is to improve the yield of DSSC in the transformation of sunlight into electricity.<sup>[1]</sup> Dyes used in DSSC can also be used in Organic Light Emitting Diodes (OLEDs) devices and in the water splitting process.<sup>[2]</sup>

In this project, we have studied the electronic structure of sixteen copper photosensitizers (three have been synthesized and characterized in the lab) using different density functionals in the framework of Time-Dependent Density Functional Theory (TDDFT).<sup>[3]</sup> We have analyzed LC- $\omega$ PBE functional by optimizing the attenuating parameter ( $\omega$ ).<sup>[4]</sup> Our results show the importance of the improvement of several properties upon optimization of  $\omega$ , such as the simulation of UV-Vis absorption spectra and REDOX potentials. Research is underway in our laboratories to improve the adjustment of the computationally simulated absorption spectra and find new molecules that present a wider range of absorption.

[1] Zhang, S. *et al. Sci.* **6**, 1443, (2013).

[2] Fillol, J. *et al. Nat. Chem.* **3**, 807, (2011).

[3] Latouche, C., *et al., J. Chem. Theory Comput.* **11**, 3281, (2015).

[4] Bokareva, O. S., *et al., J. Chem. Theory Comput.* **11**, 1700, (2015).

## Multistructural microiteration technique for geometry optimization and reaction path calculation in large systems

Kimichi Suzuki<sup>1,2</sup>, Keiji Morokuma<sup>2</sup>, and Satoshi Maeda<sup>1</sup>

<sup>1</sup> Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan

<sup>2</sup> Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto 606-8103, Japan

To efficiently explore reaction paths accompanied by a large scale structural transition in the surrounding part of large systems, we have proposed a multistructural microiteration (MSM) technique [1]. In the MSM method, the surrounding part is described as the weighted sum of multiple structures to account for a large-scale structural change along the reaction path. Each surrounding structure is independently optimized with fixing atoms in the reaction center part, and then, geometrical displacements of the reaction-center atoms are computed in the mean field generated by the weighted sum of the multiple surrounding structures. In this study, the MSM technique combined with the ONIOM method [2] was applied to organic reactions in water solution and also to enzyme reactions.

Figs. 1a) and 1b) show relative energy and weight factors of surrounding structures along the AFIR path [3]. Relative energy found by the MSM method was lower than that by ONIOM-microiteration, showing that favorable surrounding structures changed along the AFIR path. In Fig 1b), the weight factor of “Surrounding 1” was the largest among the five surrounding structures for both reactant and product, while that of “Surrounding 2” was the largest around the highest-energy point on the AFIR path. From Fig1c), energy barriers of ONIOM-microiteration and MSM were 41.4 and 32.3 kcal/mol, respectively, where the total energies of the reactant structure by the ONIOM-microiteration and MSM methods were  $-293.89394$  and  $-293.89670$  (a.u.), respectively. The energy profile determined by the MSM method was lower in absolute energy over the entire IRC profile than that determined by the ONIOM-microiteration method.

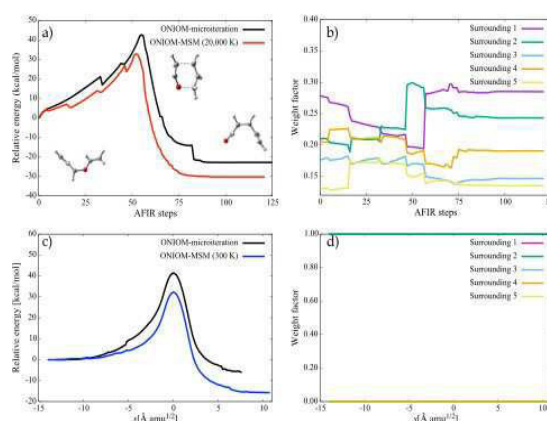


Figure 1. Relative energy (a) and weight factors of the ONIOM-MSM method at  $T^{\text{MSM}} = 20,000$  K (b) along the AFIR paths, and relative energy (c) and weight factors at  $T^{\text{MSM}} = 300$  K along the IRC paths, for Claisen rearrangement in aqueous solution.

[1] K. Suzuki, K. Morokuma, and S. Maeda., *accepted*.

[2] T. Vreven, K. Morokuma, O. Farkas, H. B. Schlegel, M. J. Frisch, *J. Comput. Chem.*, **24**, 760 (2003).

[3] S. Maeda, Y. Harabuchi, M. Takagi, T. Taketsugu, and K. Morokuma, *Chem. Rec.*, **15**, 2232(2016).

## **Nuclear motion is classical**

**Irmgard Frank<sup>1</sup>**

<sup>1</sup>*University of Hannover, Theoretische Chemie, Callinstr. 3A, 30167 Hannover*

The Born-Oppenheimer approximation can be replaced by a better approximation in a very simple way. The consideration starts from the notion that it is problematic to describe the nuclei and the electronic cloud in a similar way, hoping that quantum mechanics will somehow generate meaningful results for these two different types of objects. This is not the case. In the end one wants to have well localized nuclei, eventually smeared out a bit due to temperature. The only consistent way to achieve this is by treating the motion of the nuclei classically right from the beginning. The result is the ab-initio molecular dynamics (AIMD) energy expression. Movies of chemical reactions generated with AIMD show clearly that this approach is working well. Failures of the Born-Oppenheimer approximation are reduced to a technical problem.

[1] I. Frank, arXiv: 1402.1133 (2014)

[2] I. Frank, arXiv: 1605.06954 (2016)

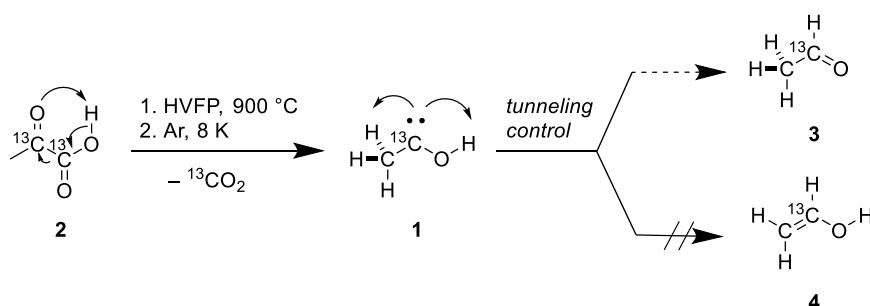


## Heavy Atom Secondary Kinetic Isotope Effect on Tunneling

**André K. Eckhardt, Dennis Gerbig, and Peter R. Schreiner\***

*Institute of Organic Chemistry, Justus-Liebig University, Heinrich-Buff-Ring 17, D-35392 Giessen, Germany*

Methylhydroxycarbene **1** can be generated by high-vacuum flash pyrolysis (HVFP) of pyruvic acid **2** and trapped in a solid noble gas matrix at 3 K.<sup>[1]</sup> The hydroxycarbene rearranges through a tunneling controlled [1,2]H-shift reaction to the thermodynamic product acetaldehyde **3** with a half-life  $\tau$  of 1 h in argon. The expected kinetic product vinyl alcohol **4** does not form under matrix isolation conditions.



Here we investigate the effect of heavy atom  $^{13}\text{C}$  labelling of the carbene center on the rate of H-tunneling experimentally and computationally. Isotope substituted 1- $^{13}\text{C}$ -**1** was prepared by HVFP of 1,2- $^{13}\text{C}$ -**2** and the tunneling half-life determined in noble gases (Ne, Ar, Kr, and Xe). The secondary tunneling kinetic isotope effect (KIE) was determined and compared with the computations. The latter utilized the one-dimensional WKB<sup>[2-4]</sup> approach as well as the multidimensional instanton<sup>[5-7]</sup> and CVT/SCT<sup>[8]</sup> tunneling models.

- [1] Schreiner, P. R.; Reisenauer, H. P.; Ley, D.; Gerbig, D.; Wu, C. H.; Allen, W. D. *Science* **332**, 1300 (2011).
- [2] Wentzel, G. Z. *Physik* **38**, 518 (1926).
- [3] Kramers, H. A. Z. *Physik* **39**, 828 (1926).
- [4] Brillouin, L. *CR Acad. Sci* **183**, 24 (1926).
- [5] Meisner, J.; Rommel, J. B.; Kästner, J. J. *Comput. Chem.* **32**, 3456 (2011).
- [6] Rommel, J. B.; Goumans, T. P. M.; Kästner, J. J. *Chem. Theory Comput.* **7**, 690 (2011).
- [7] Kästner, J. *Chem. Eur. J.* **19**, 8207 (2013).
- [8] Skodje, R. T.; Truhlar, D. G.; Garrett, B. C. *J. Phys. Chem.* **85**, 3019 (1981).



## Why Lead(II) Hydride Complex Would be Better for CO<sub>2</sub> Activation than Its 14 Group Analogues?

**Nery Villegas-Escobar<sup>1</sup>, Daniela E. Ortega<sup>1</sup>, Diego Cortés-Arriagada<sup>2</sup>, Rocio Durán<sup>1</sup>, Diana Yepes<sup>3</sup>, Soledad Gutiérrez-Oliva<sup>1</sup>, Alejandro Toro-Labbé<sup>1, 4</sup>**

<sup>1</sup>*Laboratorio de Química Teórica Computacional (QTC), Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Correo 22 Santiago, Chile.*

<sup>2</sup>*Programa Institucional de Fomento a la Investigación, Desarrollo e Innovación, Universidad Tecnológica Metropolitana, Ignacio Valdivieso 2409, P.O. Box 8940577, San Joaquín, Santiago, Chile.*

<sup>3</sup>*Departamento de Ciencias Químicas, Facultad de Ciencias Exactas, Universidad Andres Bello, Avenida República 275, Santiago, Chile.*

<sup>4</sup>*Freiburg Institut for Advanced Studies (FRIAS), Albert-Ludwigs-Universität Freiburg, Albertstrasse 19, D-79104, Germany.*

A low valent Pb<sup>(II)</sup> hydride complex with NacNac ligand (NacNac = [ArNC(Me)CHC(Me)NAr]<sup>−</sup> with Ar = 2,6-iPr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) is predicted to be the best catalyst for CO<sub>2</sub> activation compared to its Ge<sup>(II)</sup> and Sn<sup>(II)</sup> analogues, which have been experimentally reported[1, 2]. The CO<sub>2</sub> activation mechanism was studied in toluene using density functional theory calculations mediated by Ge<sup>(II)</sup>, Sn<sup>(II)</sup> and Pb<sup>(II)</sup> catalysts. The results show that the activation can be carried out through two reaction pathways, giving rise to two different conformers which have been computationally predicted for the first time. In all the cases, the activation process was thermodynamically favored, in addition, the Pb<sup>(II)</sup> catalyst exhibited the lowest activation energy compared with Ge<sup>(II)</sup>, Sn<sup>(II)</sup>, and even Si<sup>(II)</sup>. Thus, it was found that, going down in group 14, the reactivity of the NacNac based complexes toward CO<sub>2</sub> activation increases considerably. Additionally, a detailed characterization of possible interconversions between the products of activation helps to explain the X-ray structures obtained to date. Our calculations suggest that the CO<sub>2</sub> activation catalyzed by Pb<sup>(II)</sup>NacNac hydride complex would be both thermodynamically and kinetically viable. The reactivity trend found in this work contributes to the growing development of CO<sub>2</sub> activation by transition metal-free catalysts.

[1] Jana, A.; Ghoshal, D.; Roesky, H. W.; Objartel, I.; Schwab, G.; Stalke, D. *J. Am. Chem. Soc.*, **131**, 1288- 1293 (2009).

[2] Jana, A.; Roesky, H. W.; Schulzke, C.; Döring, A. *Angew. Chem. Int. Ed.* **48**, 1106-1109 (2009).

## Ab initio Molecular Dynamics Simulations of the Ion Irradiation on CH<sub>4</sub> Ice

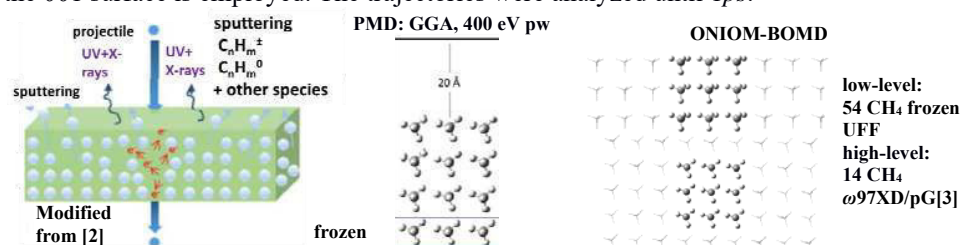
Lenin Díaz<sup>1</sup>, Leonardo Baptista<sup>2</sup>, Rafael Añez<sup>3</sup>, E. F. da Silveira<sup>1</sup>

<sup>1</sup> Departamento de Física, Pontifícia Universidade Católica do Rio de Janeiro, RJ, Brazil

<sup>2</sup> Departamento de Química e Ambiental, Faculdade de Tecnologia, Universidade do Estado do Rio de Janeiro, Resende, RJ, Brazil

<sup>3</sup> Laboratorio de Química-Física y Catálisis Computacional, Centro de Química, Instituto Venezolano de Investigaciones Científicas, Caracas

The occurrence of methane (CH<sub>4</sub>) in the solar system and interstellar medium is of particular significance: interstellar body surfaces containing condensed CH<sub>4</sub> are continuously modified by physicochemical processes, such as: heating, radiolysis (cosmic rays and stellar winds) and photolysis (UV and X-rays). Laboratory simulations of ices bombarded with MeV heavy ions (projectiles) may help to understand the formation and destruction of molecular species in interstellar icy mantles. It is well established that ions, radicals, and atomic species are released, generating new molecular species. In this work, the temporal behavior of the fcc-CH<sub>4</sub> under the influence of projectile impacts is modeled. The projectile effect is considered in two ways: i) by including an initial velocity (corresponding to 0.02 eV [1]) in various H atoms, or ii) by increasing the sample temperature (298 K, 600 K and 900 K); in a neutral, cationic and anionic potential energy surface (PES). DFT molecular dynamics (MD) implemented in G09 [Born–Oppenheimer MD (BOMD)] and VASP [Periodical MD (PMD)] programs are employed. In the case of BOMD simulations the ONIOM-BOMD variation is utilized, while in the PMD approach, the 001 surface is employed. The trajectories were analyzed until 1ps.



Only CH<sub>4</sub> desorption from the sample is obtained with PMD, irrespectively of the temperature used or the PES considered. In the ONIOM-BOMD no desorption is observed, and the amorphization of the sample is predicted. In the cationic PES, one of the C-H bond increased its length in two CH<sub>4</sub> molecules, triggering the H-H interaction to form the H<sub>3</sub>C---H---H---CH<sub>3</sub> complex. Repetition of this process may generate the desorption of H<sub>2</sub> and C<sub>n</sub>H<sub>m</sub> molecules in concordance with experimental results [4].

[1] C. F. M. Guamán, *Thesis*, PUC-Rio (2013). [2] A. Vasconcelos et al., *Phys. Chem. Chem. Phys.* (2017). [3] M. Guerra, *J. Phys. Chem. A*, **103**, 5983 (1999). [4] F. Fantuzzi et al., *Chem. Phys.* **410**, 109 (2013).

## Second-Order Perturbation Theory Based on Density Matrix Renormalization Group: Applications for Transition Metal Complexes

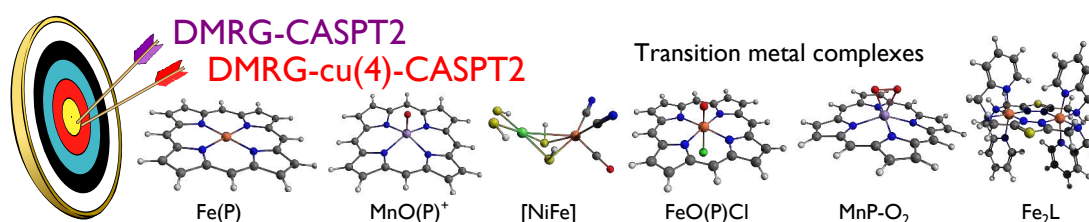
Quan Manh Phung<sup>1</sup>, Sebastian Wouters<sup>2</sup>, Kristine Pierloot<sup>1</sup>

<sup>1</sup>Department of Chemistry, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium

<sup>2</sup>Brantsandpatents, Pauline van Pottelsberghelaan 24, 9051 Sint-Denijs-Westrem, Belgium

The density matrix renormalization group (DMRG) [1] is considered one of the most promising methods to study strongly correlated molecular systems (e.g. transition metal complexes) because of its compact parametrization of the wave function. However, DMRG only includes static correlation and inefficiently treats dynamic correlation, hindering its applications for quantitatively studying transition metal (TM) complexes. To circumvent this biggest problem of DMRG, perturbative approaches on top of DMRG [2, 3, 4, 5] have been used to account for dynamic correlation.

In this work, we demonstrate the applications of DMRG-CASPT2 [5] to study a series of important chemical properties in TM complexes. We first discuss the accuracy and limitations of an approximation of DMRG-CASPT2, in which calculations of the 4-particle reduced density matrix 4-RDM is avoided (DMRG-cu(4)-CASPT2 [2]), to study spin state energetics of iron porphyrin Fe(P), NiFe hydrogenase, and manganese-oxo porphyrin MnO(P)<sup>+</sup> [6]. More challenging problems were studied with the exact solution of DMRG-CASPT2, as implemented in our recent Molcas-CheMPS2 interface. Employing an efficient contraction of the generalized Fock matrix with the 4-RDM, reliable DMRG-CASPT2 calculations with an active space of ~30 active orbitals can be performed. We employed DMRG-CASPT2 to study spin state energetics of a model for compound I (FeO(P)Cl), new families of dinuclear Fe(II) spin-crossover compounds, and binding energy of O<sub>2</sub> to metal porphyrin anions.



- [1] S. R. White, *Phys. Rev. Lett.* **69**, 2863 (1992).
- [2] Y. Kurashige, J. Chalupský, T. N. Lan, T. Yanai, *J. Chem. Phys.* **141**, 174111 (2014).
- [3] M. Roemelt, S. Guo, G. K.-L. Chan, *J. Chem. Phys.* **144**, 204113 (2016).
- [4] L. Freitag, S. Knecht, C. Angeli, M. Reiher, *J. Chem. Theory Comput* **13**, 451 (2017).
- [5] S. Wouters, V. Van Speybroeck, D. Van Neck, *J. Chem. Phys.* **145**, 054120 (2016).
- [6] Q. M. Phung, S. Wouters, K. Pierloot, *J. Chem. Theory Comput* **12**, 4352 (2016).

## XMCQDPT2 calculations elucidated the origin of red to far-red spectral tuning in light-sensitive proteins phytochromes

Egle Maximowitsch<sup>1</sup>, Tatiana Domratcheva<sup>1</sup>

<sup>1</sup>*Department of Biomolecular Mechanisms/Max Planck Institute for Medical Research,  
Jahnstraße 29, 69120 Heidelberg, Germany*

Photoswitchable photoreceptor proteins phytochromes reversibly photoconvert between two thermally stable Pr (red light absorbing) and Pfr (far-red light absorbing) forms. The interconversion is driven by the photochemical isomerization of the tetrapyrrole chromophore covalently bound to the protein via its pyrrole ring A. Upon the C15=C16 double-bond isomerization [1], the pyrrole ring D changes its hydrogen bonding; it interacts with the conserved histidine in the Pr form [2] and with the conserved aspartate in the Pfr form [3]. Because of the rather large molecular size of the chromophore, the origin of the spectral tuning in phytochromes has not yet been investigated using quantum-chemical calculations. For the first time, we performed excited-state calculations of the phytochrome models using the state of the art multi-configurational multi-reference XMCQDPT2 method [4]. These calculations allowed identifying intermolecular interactions of the chromophore with the protein that induce the red shift in the Pfr form as compared to the Pr form [5]. We demonstrated that interactions between ring D and the carboxylate group of the conserved aspartate lead to bond-length alternation of the tetrapyrrole. The geometry change reflects on the change in the electronic structure, which translates to the red shift of the absorption spectrum of the Pfr form. Further, we tested performance of the widely used TD-DFT method in the calculations of the phytochrome color tuning. Understanding the role of hydrogen bonding in control of the tetrapyrrole color provided by our calculations and analysis may facilitate engineering of phytochromes and other tetrapyrrole binding proteins as photoswitches and fluorescent proteins operating in the red spectral region.

- [1] C. Song, G. Psakis, J. Kopycki, C. Lang, J. Matysik, J. Hughes., *J. Biol. Chem.* **289**, 2552 (2014).
- [2] J. R. Wagner, J. S. Brunzelle, K. T. Forest, R. D. Vierstra, *Nature*. **438**, 325 (2005).
- [3] X. Yang, J. Kuk, K. Moffat, *PNAS*. **105**, 14715 (2008).
- [4] A. A. Granovsky, *J. Chem. Phys.* **134**, 214113 (2011).
- [5] E. Maximowitsch and T. Domratcheva, *in preparation*.

## How do oxidised phospholipids affect the properties of a lipid bilayer?

**Alexandra Schumann-Gillett<sup>1</sup> and Megan L. O'Mara<sup>1</sup>**

*<sup>1</sup>Research School of Chemistry, The Australian National University, Building 137  
Sullivans Creek Road, Canberra ACT 2601, Australia*

Oxidative stress continues to be associated with aging and disease. It is known to affect the pathophysiology of lipids in conditions including, but not limited to, Alzheimer's disease, cystic fibrosis, atherosclerosis, cardiovascular disease and cancer. Lipid peroxidation has a wide and varied impact on cells, and little is known about the effects of oxidative stress on the integrity and biophysical properties of the cell plasma membrane. To address this, we performed a series of microsecond-timescale atomistic molecular dynamics simulations of bilayers containing standard and oxidised phospholipids. We studied the following bilayers: 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC), POPC + cholesterol, POPC + oxidised POPC (1-palmitoyl-2-(9'-oxononanoyl)-*sn*-glycero-3-phosphocholine (PoxnoPC) or 1-palmitoyl-2-azelaoyl-*sn*-glycero-3-phosphocholine (PazePC)) and POPC + cholesterol + oxidised POPC (PoxnoPC or PazePC). Our results suggest that membrane composition influences the basic biophysical properties of bilayer systems, including bilayer thickness, permeability to water, area per lipid, bilayer phase and ordering. This is fundamental to our understanding of the effect of lipid peroxidation on biological membranes.

## Computational study of hydrogen shift reaction catalysed by sulphuric acid in Criegee intermediate

Farzaneh Sarrami, Amir Karton

*School of Molecular Sciences, The University of Western Australia,  
Perth, WA 6009, Australia*

**Abstract:** The Criegee intermediates (CIs) are formed during ozonolysis of unsaturated hydrocarbons in the troposphere. The fate of the CIs is of critical importance to troposphere oxidation chemistry, particularly in the context of secondary aerosol formation. Using the high-level G4(MP2) *ab initio* method, we investigate the 1,4 hydrogen shift reaction in all CIs of two common biogenic hydrocarbons: isoprene and  $\alpha$ -pinene. We consider the uncatalyzed reaction as well as the reaction catalyzed by a single water molecule and by sulphuric acid. We find that sulphuric acid is a very effective catalyst leading to a barrierless process relative to the free reactants. In contrast, the water-catalyzed mechanism is associated with a significantly higher reaction barrier. The present findings provide insights into the reaction mechanisms by which larger and less volatile organic compounds are generated in the troposphere from smaller components as required for aerosol growth.

- [1] R. P. Feynman, *Phys. Rev.* **56**, 340 (1939).

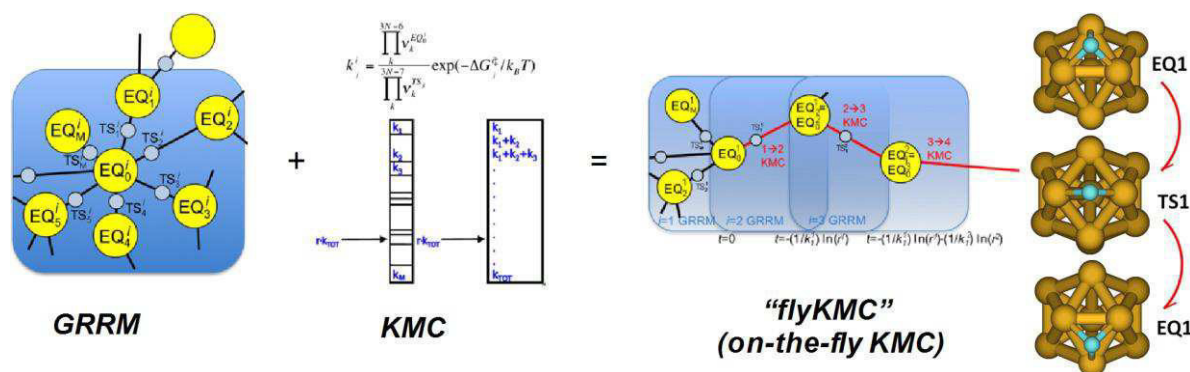
# On-the-fly Kinetic Monte Carlo based on Global Reaction Route Mapping

Izaak Mitchell,<sup>1</sup> Stephan Irle,<sup>2</sup> Alister Page <sup>1</sup>,

<sup>1</sup>The University of Newcastle, Callaghan 2308, Australia.

<sup>2</sup>Department of Chemistry, Graduate School of Science, Nagoya University, Nagoya 464-8602, Japan.

Molecular dynamics simulations of chemical systems and reactivity are plagued by the timescale issue: very small timesteps require prohibitively long simulations to achieve experimentally relevant timescales, even for classical force fields. This problem is exacerbated for systems characterized by infrequent state-to-state transitions (i.e. "rare events"). Kinetic Monte Carlo (KMC) [1-3] can overcome this problem, however is based on the assumption that the complete set of the state-to-state transitions and associated rate constants (the "move table") is known *a priori*. Ideally, the move table should be constructed "on-the-fly" at each successive equilibrium point as the system evolves [4-6]. Here, we describe a new on-the-fly KMC algorithm [10] that uses global reaction route mapping (GRRM) [7-9] to determine all possible reactive pathways around an equilibrium point, and demonstrated its capabilities in describing intramolecular proton transfer, nanoscale surface diffusion and intramolecular rearrangement.



**Figure 1:** GRRM-KMC algorithm for determining the KMC move table on-the-fly. This can allow us to simulate diffusion

<sup>1</sup> S. Maeda, K. Ohno and K. Morokuma, *J. Chem. Theory Comput.* **5**, 2734-2743, (2009)

<sup>2</sup> W. M. Young and E. W. Elcock, *Proc. Phys. Soc.* **89**, 735, (1966)

<sup>3</sup> A. F. Voter, A. Francesco Montalenti and T. C. Germann, *Annu. Rev. Mater. Res.* **32**, 321-346, (2002)

<sup>4</sup> G. Henkelman and H. Jónsson, *J. Chem. Phys.* **115**, 9657-9666, (2001)

<sup>5</sup> G. Henkelman and H. Jónsson, *J. Chem. Phys.* **111**, 7010-7022, (1999)

<sup>6</sup> X. Guo, D. Minakata and J. Crittenden, *Environ. Sci. Technol.* **49**, 9230-9236, (2015)

<sup>7</sup> S. Maeda and K. Ohno, *Chem. Phys. Lett.* **381**, 177-186, (2003)

<sup>8</sup> K. Ohno and S. Maeda, *Chem. Phys. Lett.* **384**, 277-282, (2004)

<sup>9</sup> S. Maeda and K. Ohno, *J. Phys. Chem. A* **109**, 5742-5753, (2005)

<sup>10</sup> I. Mitchell, S. Irle and A. Page, *J Chem. Phys.* **145**, 24105, (2016)

## Serenity: A Subsystem Quantum Chemistry Program

**Jan P. Unsleber<sup>1,3</sup>, Thomas Dresselhaus<sup>1</sup>, Kevin Klahr<sup>1</sup>, David Schnieders<sup>1</sup>,  
Michael Böckers<sup>1</sup>, Dennis Barton<sup>1,2</sup>, and Johannes Neugebauer<sup>1,4</sup>**

<sup>1</sup>*Theoretische Organische Chemie, Organisch-Chemisches Institut and Center for Multiscale Theory and Computation, Westfälische Wilhelms-Universität Münster Corrensstraße 40, 48149 Münster, Germany*

<sup>2</sup>*present address: Physics and Materials Science Research Unit, University of Luxembourg, L-1511 Luxembourg*

<sup>3</sup>*Email: j.unsleber@uni-muenster.de*

<sup>4</sup>*Email: j.neugebauer@uni-muenster.de*

We present key features of our new quantum chemistry program SERENITY. It implements a wide variety of functionalities with a focus on subsystem methodology. The modular code structure in combination with publicly available external tools and particular design concepts ensures extensibility and robustness with a focus on the needs of a subsystem program.

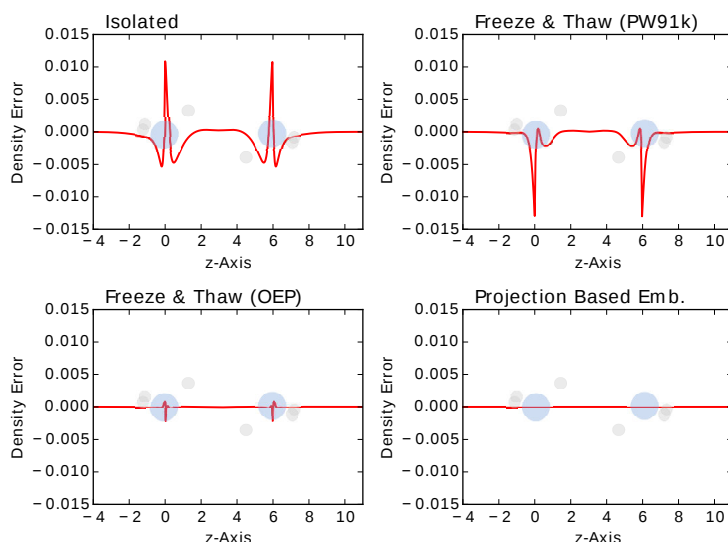


Figure 1: Comparison of different embedding techniques w.r.t. a supersystem calculation in terms of the density error.

Several important features of the program are exemplified with sample calculations using subsystem density functional theory, potential reconstruction techniques, a projection-based embedding approach and combinations thereof. Further features as well as motivation and implementation details are highlighted on the poster.



## Towards laser pulse control of molecular symmetry breaking and restoration

ChunMei Liu<sup>1</sup>, Jörn Manz<sup>1,2</sup>, Jean Christophe Tremblay<sup>1</sup>

<sup>1</sup>*Freie Universität Berlin, Institut für Chemie und Biochemie, 14195 Berlin, Germany*

<sup>2</sup>*Shanxi University, State Key Laboratory of Quantum Optics and Quantum Optics Devices, Institute of Laser Spectroscopy, Taiyuan 030006, China*

Symmetry breaking is a fundamental process in chemistry. Fascinating examples of molecular symmetry breaking by laser pulses have already been demonstrated, both experimentally and theoretically, see Refs. [1, 2, 3, 4]. Here we show that laser pulses can also achieve the opposite effect, symmetry restoration. For this purpose, the laser pulse for symmetry restoration must be designed as the time-reverse of the pulse that broke the symmetry, and the time of time-reversal must coincide with the instant when the molecule with broken symmetry is represented by a real wave function. As a proof-of-principle, quantum dynamics simulations demonstrate restoration of  $D_{6h}$  symmetry of benzene, after laser induced  $D_{6h} \rightarrow C_{2v}$  symmetry breaking[3, 4]. Experimentally, one may allow marginal deviations from the theoretical results. Accordingly, the laser pulse for symmetry restoration has to be applied with 10 as precision. This challenge reminds of analogous requirements for control of the laser pulses' carrier envelope phase (CEP) for various tasks such as high harmonic generation (HHG)[5]. Gratifyingly, the present experimental state-of-the-art allows to control the time delay between two laser pulses with the required resolution.[6]

### ACKNOWLEDGMENTS

Generous financial support by the Deutsche Forschungsgemeinschaft (projects Ma 515/26-1 and Tr 1109/2-1) and China Scholarship Council are gratefully acknowledged.

- [1] N. Elghobashi, L. González, J. Manz, *J. Chem. Phys.* **120**, 8002-8014 (2004).
- [2] A. S. Alnaser, M. Kübel, R. Siemering, B. Bergues, N. G. Kling, K. J. Betsch, Y. Deng, J. Schmidt, Z. A. Alahmed, A. M. Azzer, J. Ullrich, I. Ben-Itzhak, R. Moshhammer, U. Kleineberg, F. Krausz, R. de Vivie-Riedle, M. F. Kling, *Nature Commun.* **5**, 3800-3806 (2014).
- [3] G. Hermann, C. Liu, J. Manz, B. Paulus, J. F. Pérez-Torres, V. Pohl, J. C. Tremblay, *J. Phys. Chem. A* **120**, 5360-5369 (2016).
- [4] D. Jia, J. Manz, B. Paulus, V. Pohl, J. C. Tremblay, Y. Yang, *Chem. Phys.* **482**, 146-159 (2017).
- [5] S. Chelkowski, T. Bredtmann and A. D. Bandrauk, *Phys. Rev. A* **85**, 033404 (2012).
- [6] N. Takei, C. Sommer, C. Genes, G. Pupillo, H. Goto, K. Koyasu, H. Chiba, M. Weidemüller, K. Ohmori, *Nature Commun.* DOI: 10.1038/ncomms13449

## Combining AIMD and Neutron Scattering Data based EPSR Simulations to uncover Water Participation in Catalysis

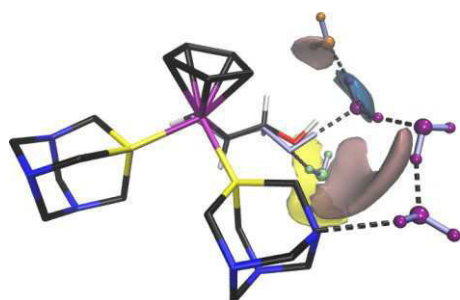
Nicole Holzmann<sup>1</sup>, Silvia Imberti<sup>2</sup>, Franco Scalambra<sup>3</sup>, Antonio Romerosa<sup>3</sup>,  
Leonardo Bernasconi<sup>1</sup>

<sup>1</sup>SCD, STFC Rutherford Appleton Laboratory, Harwell Oxford, Didcot, UK

<sup>2</sup>ISIS, STFC Rutherford Appleton Laboratory, Harwell Oxford, Didcot, UK

<sup>3</sup>Área de Química Inorgánica-CIESOL, Universidad de Almería, Almería, Spain

The advantages of using water as a solvent in catalysis are obvious: it is abundantly available, cheap and easily recyclable. However, the majority of homogeneous catalytic processes mediated by metal complexes take place in organic solvents which is due to the insolubility of many complexes and the easy decomposition of most of the catalytically active metal complexes in water. In order to shed light on the reaction mechanism of catalytic processes in water two things are of key interest: the complex/substrate conformation and the interaction with water. Aqueous solutions pose a challenge for many classical analytic methods. Experimental techniques like NMR or theoretical approaches like DFT can give some indications on complex conformation. By taking into account the



Overlay of AIMD snapshot and EPSR spatial density functions of water

electronic structure, AIMD (*ab initio* molecular dynamics) simulations with explicitly described water are able to give a detailed picture of coordination of single water molecules, their influence on solute conformation and their evolution over time. Small angle neutron scattering is capable of detecting hydrogens and is predestined to examine molecules in water. The EPSR (Empirical Potential Structure Refinement) simulations use data from the neutron scattering measurements to refine structure and determine probabilities of water distribution.

On the example of the water soluble complex  $[\text{RuCp}(\text{H}_2\text{O}-\kappa\text{O})(\text{PTA})_2]^+$  (PTA = 1,3,5-triaza-7-phosphaadamantane) that catalyses the isomerization of allylic alcohols to aldehydes or ketones and that shows increased catalytic efficiency in the presence of more than a stoichiometric amount of water<sup>[1,2]</sup>, we herein present the combination of AIMD and EPSR simulations that can aid identifying catalyst and substrate conformation and water participation in aqueous solutions.

**Acknowledgement:** European Commission FEDER program (CTQ2015-67384-R MINECO), Junta de Andalucía PAI FQM-317, COST Action CM1302 (WG1, WG2).

- [1] M. Serrano-Ruiz, P. Lorenzo-Luis, A. Romerosa, A. Mena-Cruz, *Dalton Trans.* **42**, 7622 (2013).
- [2] F. Scalambra, M. Serrano-Ruiz, A. Romerosa, *Dalton Trans.* **46**, 5864 (2017).

## MD Simulation Analysis on Asynchronous Solute-Solvent Coupling Magnitude in Ring Closing Reaction of Chromene

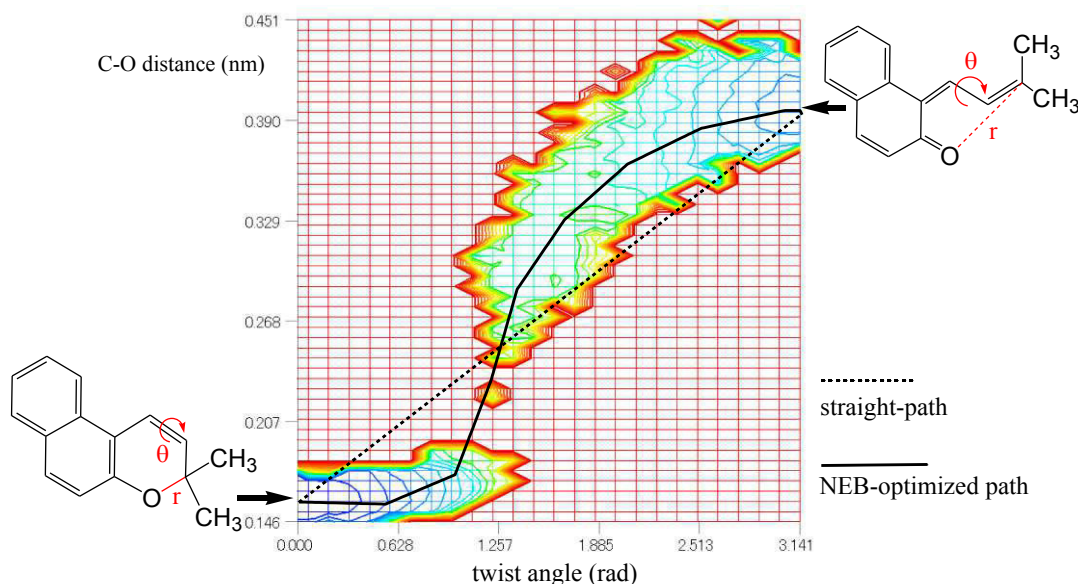
Yasuhiro Shigemitsu<sup>1,2</sup>, Yasushi Ohga<sup>3</sup>

<sup>1</sup>Industrial Technology Center of Nagasaki, Omura 856-0026, Japan

<sup>2</sup>Graduate School of Engineering, Nagasaki University, Nagasaki 852-8521, Japan

<sup>3</sup>Faculty of Science and Engineering, Oita University, Oita 870-1192, Japan

Chemical reaction kinetics in condensed phase normally obey Transition State Theory (TST) under thermal equilibrium of whole system. However, the rate constant behaviour deviate from Arrhenius plot (dynamic solvent effect) when the coupling between solute and solvent become unsynchronous under TST breakdown.



**Fig. 1** Schematic 2D-FES for two CVs ( $\theta$ ,  $r$ ) reaction path

In the present study, the non-TST behavior of reaction rate constants of thermally slow cyclization of chromene is computationally analyzed based on topological characteristics of Free energy surface (FES). FES are constructed by metadynamics sampling along the reaction path optimized Nudged Elastic Band (Fig.1). MD simulations are carried out using REAX-FF [1] which is a special form of force field describable for bond generation/fission. The asynchronous solute-solvent coupling magnitude is estimated by the ratio between  $FES(\theta_{TS}, 0)/FES(\theta_{TS}, r_{TS})$ , which qualitatively correspond to the solvent contribution  $\Delta G$  relative to the whole reaction  $\Delta G$ .

[1] van Duin, Adri C. T.; Dasgupta, Siddharth; Lorant, Francois; Goddard, William A., *J.Phys.Chem.A*, **105**, 9396, (2001).

## Theoretical description of excitations and excitonic couplings of perfluoropentacene

Anna-Katharina Hansmann<sup>1</sup>, Robert Berger<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, 35032 Marburg*

Organic solids consisting of  $\pi$ -conjugated molecules play an important role for the design of different electronic or optoelectronic devices. Perfluoropentacene is a typical example for these organic  $\pi$ -conjugated systems, which are used for instance as organic field-effect transistors.

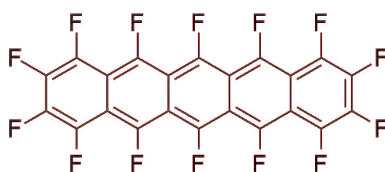


Figure 1: Structural formula of perfluoropentacene

This compound has been chosen as model systems to describe the formation of excitons and the vibrationally assisted transitions between different electronic states. The electronic and vibrational structures are calculated with DFT and CC2 methods, the vibronic transitions are described by Franck-Condon and Herzberg-Teller profiles.

To describe the excitonic coupling in the solid state, an effective model Hamiltonian is used, which is parametrized according to the crystal structure and to the results from the electronic calculations of the molecule.

$$\hat{H}_{\text{eff}} = \hat{H}_{\text{ex}} + \hat{H}_{\text{vib}} + \hat{H}_{\text{ex-vib}}$$

With this, a model description of aggregates is achieved which can be used to compare to experiment and identify the relevant vibronically excited states.

**Lowest electronic states of  
alkali (Li, Na, K, Rb) – alkaline-earth (Ca, Sr) diatomic molecules**

**Johann V. Pototschnig<sup>1</sup>, Ralf Meyer<sup>1</sup>, Andreas W. Hauser<sup>1</sup>, Wolfgang E. Ernst<sup>1</sup>**

<sup>1</sup>*Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria*

Alkali and alkaline-earth atoms are well under control in ultracold physics and are good candidates to form ultracold molecules with a permanent electric and magnetic dipole moment[1]. In contrast to heteronuclear alkali diatomics, which are already under investigation in ultracold physics, allows the combination of an alkali atom with an alkaline-earth atom to produce a molecule with an unpaired electron and due to this a corresponding magnetic moment. This opens up new possibilities to manipulate these molecules and to make use of intermolecular interactions[2]. In the current work the lowest excited states of eight such molecules were determined by a multiconfigurational self-consistent field calculation followed by multireference configuration interaction[3]. This approach yielded reliable potentials in previous studies, where the results were compared to experiments of our group[4, 5, 6]. In order to estimate the methodological uncertainty of the results we also performed coupled cluster and perturbation theory computations. For the four heavier compounds also spin-orbit interaction was considered by two different approaches. The resulting potential energy curves were then used to determine the vibronic states. The Franck-Condon factors in combination with the electronic transition dipole moments were applied to obtain the Einstein A factors between different vibronic states. These results will be presented and trends as well as the influence of uncertainties of the computed properties will be discussed.

- [1] B.Pasquiou, A. Bayerle, S. M. Tzanova, S. Stellmer, J. Szczepkowski, M. Parigger, R. Grimm, and F. Schreck; *Phys. Rev. A*, **88**, 023601 (2013).
- [2] A. Micheli, G. K. Brennen, and P. Zoller; *Nat. Phys.* **2**, 341 (2006).
- [3] J. V. Pototschnig, R. Meyer, A. W. Hauser, and W. E. Ernst; *Phys. Rev. A*, **95**, 022501 (2017).
- [4] G. Krois, J. V. Pototschnig, F. Lackner, and W. E. Ernst; *J. Phys. Chem. A*, **117**, 13719 (2013).
- [5] F. Lackner, G. Krois, T. Buchsteiner, J. V. Pototschnig, and W. E. Ernst; *Phys. Rev. Lett.*, **113**, 153001 (2014).
- [6] J. V. Pototschnig, G. Krois, F. Lackner, and W. E. Ernst; *J. Mol. Spectrosc.*, **310**, 126 (2015).

## Global Search for Periodic Structures of Carbon by Artificial Force Induced Reaction Method

Makito Takagi<sup>1</sup>, Satoshi Maeda<sup>2</sup>

<sup>1</sup> Graduate School of Chemical Sciences and Engineering /Hokkaido University, N10-W8,  
Kita-ku, Sapporo, Japan

<sup>2</sup> Department of Chemistry/Faculty of Science /Hokkaido University, Sapporo, Japan

**[Introduction]** Properties of materials depend not only on their composition but also on their crystal structure. For example, carbon has various allotropes <sup>[1]</sup> such as graphite, diamond, etc. Furthermore, many crystal structures have been predicted theoretically. *M*-carbon and Cco-C<sub>8</sub> (or Z-carbon), etc. are those predicted recently. Prediction of their structures has been a great challenge in computational science. One- or two-dimensional periodic structures such as carbon nanotube and graphene have also been attracted attention as novel materials and catalysts. In our group, an efficient method, artificial force induced reaction (AFIR), <sup>[2]</sup> has been developed for automated exploration of chemical reaction pathways. This method has been applied to various chemical reactions in the gas phase and in the solution phase. In this study, we extended the AFIR method for periodic system by combining this method with periodic boundary conditions (PBCs). This approach is tested for searches of periodic structures of carbon, not only crystal but also one- and two-dimensional structures. <sup>[3]</sup>

**[Method]** All calculations were carried out by utilizing a local developmental version of the GRRM program. Energies, gradients, and lattice stresses were computed by density functional theory (DFT) using the PBE functional and DZP basis sets as implemented in the SIESTA program. Grimme's dispersion is also considered.

**[Results and Discussion]** As a case study, the SC-AFIR was applied to carbon with a very small unit-cell which includes eight carbon atoms (C<sub>8</sub>/unit-cell). The search was initiated from one random structure. Then, we obtained 274 structures of carbon crystals including famous structures such as graphite and diamond. Fig. 1 shows some of local structures. The obtained structures include not only known structures but also a lot of unreported ones. In addition, the searches for one- or two-dimensional periodic structures were also performed. The search found 49 and 122 local structures for the one- and two-dimensional periodic systems, respectively.

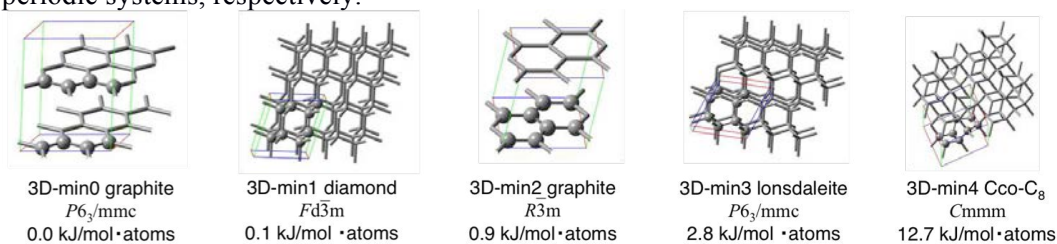


Fig.1 Five most stable structures of the C<sub>8</sub>/unit-cell among 274 structures obtained by the automated search. Name of structure, space group, and relative energy are shown in labels.

[1] V. Georgakilas, *et al.*, *Chem. Rev.* **115**, 4744 (2015). [2] S. Maeda, *et al.*, *Chem. Rec.* **16**, 2232 (2016). [3] M. Takagi, *et al.*, *Phys. Rev. B* in press.

## Decoherence correction and trivial crossing detection in fragment-orbital based surface hopping.

Samuele Giannini<sup>1</sup>, Antoine Carof<sup>1</sup>, Jochen Blumberger<sup>1</sup>.

<sup>1</sup>*Department of Physics and Astronomy, University College London, Gower Street, WC1E 6BT, London, UK.*

Simulations of charge transport in large pi-conjugated systems (e.g. organic semiconductors or biological molecules) are paramount to a better understanding of their carrier mobilities and to improve the performance of low-cost and promising optoelectronic devices. While hopping and wide band theories have proved inappropriate to study this kind of systems in most situations [1, 2], polaronic band theories based on Holstein-Peierl-Hamiltonians have shown to give a better transport description [3]. Going beyond model Hamiltonian approaches, the development of direct charge propagation schemes, such as non-adiabatic molecular dynamics is of great importance. In this respect, Tully's surface hopping approach [4] can aid to deal with these large and complex systems. Within this strategy, the nuclei evolve on a single potential energy surface and nonadiabatic effects are included by allowing hopping from one surface to another according to the fewest switches algorithm. Nevertheless, this method requires the calculation of the Hamiltonian and the nonadiabatic coupling elements at each time step, making the procedure still computationally very demanding.

Our fragment-orbital based surface hopping method (FOB-SH) has been specifically designed to overcome this difficulty. In particular, the ultrafast calculation of Hamiltonian and forces of the system allows us to treat fundamental charge transfer properties in large molecular assemblies without assuming any specific charge transport model [5].

Here, we present the results obtained by applying this strategy to chains of organic molecules. We consider particularly fundamental requirements (e.g. total energy conservation, detailed balance and internal consistency) that the surface hopping algorithm should fulfil. We show how solving well-known limitations of the SH approach for instance the overcoherence of the electronic wavefunction or the trivial crossing problem improves the quality of our simulations. In particular, we investigate different decoherence methods that could be used to reach the internal consistency and also the trivial crossings correction, proposed by Prezhdo *et al.* [6], to deal with finite MD timesteps. We find that damping the wavefunction coefficients at each time step massively improves on internal consistency and the trivial crossing correction gives more accurate Boltzmann population and/or allows for larger time steps.

The results presented in this work will serve as starting point for studying even larger systems (e.g. organic crystal and proteins).

- [1] F. Gajdos, J. Blumberger, *J. Phys. Chem. Lett.*, **4**, 1012 (2013).
- [2] A. Troisi, *Chem. Soc. Rev.*, **40**, 2347 (2011).
- [3] F. Ortmann, K. Hannewald, *Phys. Status Solidi*, **248**, 511 (2011).
- [4] J. Tully, *J. Chem. Phys.*, **07974**, 1061 (1990).
- [5] J. Spencer, J. Blumberger, **064102**, 064102 (2016).
- [6] L. Wang, O. V. Prezhdo, *J. Phys. Chem. Lett.*, **5**, 713 (2014).



## Adsorption and dissociation of water on tungsten trioxide (001) from first principles

Thomas Teusch<sup>1</sup>, Thorsten Klüner<sup>1</sup>

<sup>1</sup>*Institute of Chemistry, Carl von Ossietzky Universität, Carl-von-Ossietzky Str. 9-11, Oldenburg, Germany*

Photocatalytic water splitting is a cutting-edge topic nowadays since there is no environmental friendly and efficient way known for hydrogen production. This reaction can be catalyzed by metal oxides, which are stable, cheap, non-toxic and abundant in nature. Unfortunately, the frequently investigated material titanium dioxide [1] has a too large band gap in order to use the spectrum of visible light efficiently for water splitting. A more promising material in this context is tungsten trioxide, which has on the one hand a more suitable band gap and an appropriate valence band position for oxygen production, but on the other hand an unsuitable conduction band position for hydrogen evolution [2]. At this point, a deeper understanding of the water splitting mechanism is crucial in order to make this reaction more efficient. Calculations with periodic boundary conditions offer a powerful tool regarding the modelling and understanding of adsorption processes and reactions on solid surfaces.

In this work, we present results of the interaction of water in its molecular and its dissociative form on the perfect tungsten trioxide (001) surface. We used hybrid density functional theory as implemented in the CRYSTAL14 [3] program package. These results are useful in order to perform *ab initio* cluster calculations for ground and excited states.

- [1] J. Mitschker, T. Klüner, *Phys. Chem. Chem. Phys.* **17**, 268 (2015).
- [2] F. Wang, C. Di Valentina, G. Pacchioni, *Phys. Chem. C* **116**, 8901-8909 (2012).
- [3] R. Dovesi, R. Orlando, A. Erba, *et al.*, *Int. J. Quantum Chem. A* **114**, 1287-1317 (2014).



## Water adsorption on tantalum(V) nitride (100): favourite adsorption sites and surface behaviour

Thorben Petersen<sup>1</sup>, Thorsten Klüner<sup>1</sup>

<sup>1</sup>*Institute of Chemistry, Carl von Ossietzky University Oldenburg, Carl-von-Ossietzky Str. 9-11, 26129, Oldenburg, Germany*

The efficient splitting of water into its elementary components hydrogen and oxygen represents one of the most studied reactions in nowadays society. A promising approach consists of using an appropriate photocatalyst that harvests the sun light as an energy source to initiate this reaction. Although many oxide semiconductors were already investigated, no feasible catalyst is available yet.[1] However, non-oxide, nitride-based semiconductors gained much attention recently. One candidate is tantalum(V) nitride ( $\text{Ta}_3\text{N}_5$ ) due to its suitable band gap of about 2.1 eV and its band edges.[2] Experimentally, its ability to split water is being improved by controlling its morphology and employ nanostructuring.[3] From a theoretical point of view, the interaction of water with the  $\text{Ta}_3\text{N}_5$  surface represents the key to understand the initial step of the water dissociation reaction and may aid in further improving the design of an efficient Ta-based photocatalyst.

In this contribution, we therefore want to investigate the influence of water adsorption on  $\text{Ta}_3\text{N}_5$  by quantum chemical density functional theory calculations. As a versatile program package to model such adsorbate-surface systems, we use the CRYSTAL14 program code with periodic boundary conditions based on linear combinations of atom centered Gaussian functions.[4] As a first step, we thoroughly analyse the structure and energetics of the (100) surface, which represents the thermodynamically most stable surface.[5] Subsequently, an adequate model system will be utilised for the adsorption of water in its molecular and dissociative form. Our results will be directly comparable to previously published plane-wave based calculations [6] and will constitute the basis for an embedded cluster approach to address the electronically excited state during the water photodissociation process.

- [1] A. Kudo, Y. Miseki, *Chem. Soc. Rev.* **38**, 253 (2009).
- [2] P. Zhang, J. Zhang, J. Gong, *Chem. Soc. Rev.* **43**, 4395 (2014).
- [3] L. Wang, X. Zhuo, N. T. Nguyen, I. Hwang, P. Schmuki, *Adv. Mater.* **28**, 2432 (2016).
- [4] R. Dovesi, R. Orlando, A. Erba, *et al.*, *Int. J. Quantum Chem.* **114**, 1287 (2014).
- [5] E. Watanabe, H. Ushiyama, K. Yamashita, *Chem. Phys. Lett.* **561**, 57 (2013).
- [6] J. Wang, W. Luo, J. Feng, L. Zhang, Z. Li, Z. Zou, *Phys. Chem. Chem. Phys.* **15**, 16054 (2013).

## Towards efficient coupled-cluster theories for periodic systems

**Theodoros Tsatsoulis, Felix Hummel, Andreas Grüneis**

*Max Planck Institute for Solid State Research, Heisenbergstraße 1, D-70569 Stuttgart, Germany*

Over the last few years, quantum-chemical correlation methods have been increasingly often applied to extended systems. In this work we explore canonical coupled-cluster theory within the projector-augmented-wave method using a plane-wave basis as implemented in the VASP code. A combination of Gaussian basis-functions with plane-waves [1], as well as a low-rank factorization of the Coulomb integrals [2] results in an effective quantum-chemical scheme for extended systems. We demonstrate the capabilities of the methods by benchmarking water adsorption on two-dimensional or quasi two-dimensional periodic surfaces [3, 4]. Our findings show that quantum chemical approaches are becoming a robust and reliable tool for solid state electronic structure calculations, providing an additional tool that can further improve widely-used van der Waals density-functionals.

- [1] G. H. Booth, T. Tsatsoulis, G. K. L. Chan, and A. Grüneis, "From plane waves to local Gaussians for the simulation of correlated periodic systems" *The Journal of Chemical Physics*, **145**, 084111 (2016).
- [2] F. Hummel, T. Tsatsoulis, and A. Grüneis, "Low rank factorization of the Coulomb integrals for periodic coupled cluster theory" *The Journal of Chemical Physics*, **146**, 124105 (2017).
- [3] T. Tsatsoulis *et al.* "A comparison between quantum chemistry and quantum Monte Carlo techniques for the adsorption of water on the (001) LiH surface" *The Journal of Chemical Physics*, **146**, 204108 (2017).
- [4] Y. S. Al-Hamdani *et al.* "Properties of the water to boron nitride interaction: from zero to two dimensions with benchmark accuracy" *The Journal of Chemical Physics submitted* (2017).

## Intramolecular electronic flux during adiabatic attosecond charge migration

**Jörn Manz<sup>1,2</sup>, Dennis J. Diestler<sup>1,3</sup>, Gunter Hermann<sup>1</sup>, Kurt Hoffmann<sup>1</sup>,  
Dongming Jia<sup>2</sup>, Beate Paulus<sup>1</sup>, Vincent Pohl<sup>1</sup>, Jean Christophe Tremblay<sup>1</sup>,  
Yonggang Yang<sup>2</sup>**

<sup>1</sup>*Institut für Chemie und Biochemie, Freie Universität Berlin, Berlin, Germany*

<sup>2</sup>*State Key Laboratory of Quantum Optics and Quantum Optics Devices, Institute of Laser Spectroscopy, Shanxi University, Taiyuan 030006, China*

<sup>3</sup>*Department of Agronomy & Horticulture, University of Nebraska-Lincoln, Lincoln, USA*

We develop the quantum theory of the electronic flux that drives the time dependent motions of electrons during charge migration. Applications to model systems reveal the following fundamental aspects (A-J).

$H_2^+$  can be prepared in a superposition state of the electronic ground ( $\sigma_g$ ) and first excited ( $\sigma_u$ ) states such that the charge is localized on one nucleus. From this initial condition, the charge migrates periodically between the nuclei, with the period  $\tau = 550$  as [1]. The model of Eyring, Walter and Kimball allows to derive analytical expressions for time evolutions of the electron density, flux density, axial electron density, and axial flux. Accordingly: (A) the flux is a simple product of the axial electronic yield times a sinusoidal temporal factor; (B) the flux satisfies various symmetry rules; (C) the absolute value of the axial flux is maximal at  $t = \tau/4$ , at the nuclear center of mass where the axial electron density has its local minimum; (D) Charge migration is depleted by decoherence between the bound electronic ground state and dissociative excited state; (E) Charge migration proceeds without electron correlation. [2,3]

Recently, quasi-field-free charge migration in  $HCCI^+$  was investigated [4]. Experimentally, the initial ( $t = 0$ ) state is found to be a superposition state of the electronic ground and first excited state of the cation. We show that: (F) this initial state can be prepared by ultrafast ionization of HCCI [4] or by electronic excitation of  $HCCI^+$ . [5] The excess electronic charge then migrates periodically between the acetylenic and ionic moieties, with period  $\tau = 1.85$  fs; (G) the maximum axial electronic flux occurs between the two moieties where the axial density has its local minimum; (H) the electronic flux is launched already during the laser pulse that prepares the initial state; (I) we can design electric fields to optimize the electronic flux. [6]

Finally, we show (J) how to control the angular electronic flux during charge migration in non-aromatic excited benzene, by means of linearly and circularly polarized laser pulses. [7-9]

Financial support by Deutsche Forschungsgemeinschaft (projects Ma 515/26-1 and Tr1109/2-1) and by the talent program of Shanxi is gratefully acknowledged.

[1] H. Eyring, J. Walter, G.E. Kimball, "Quantum Chemistry", Wiley (New York) 1944, pp. 198-200.

[4] P.M. Kraus, B. Mignolet, D. Baykusheva, A. Rupenyan, L. Horny, E.F. Penka, G. Grassi, O.I. Tolstikhin, J. Schneider, F. Jensen, L.B. Madsen, A.D. Bandrauk, F. Remacle, H.J. Wörner, Science 350 (2015) 790.

[2,3,5-9] see our recent work – will be presented at WATOC 2017

## **In-Silico Homovalent Screening of Hybrid Halide Perovskite Materials for Tandem Solar Cells**

**M. Kar, T. Körzdörfer**

*AG Computational Chemistry, University of Potsdam, Institute of Chemistry, Karl-Liebknecht Straße 24-25, D-14476 Potsdam-Golm*

Solar cells based on hybrid organic-inorganic lead-halide perovskites are among the most promising emerging photovoltaic materials of the past decade. Within only a very short research time span, record efficiencies were achieved with solar cells based on methylammonium lead iodide ( $\text{CH}_3\text{NH}_3\text{PbI}_3$ ). Despite these notable achievements, many of the basic properties of hybrid perovskite materials are not yet fully understood.

The presence of Pb in the currently most efficient perovskite solar cells has raised questions over the possible toxicity of these devices and the extent of their environmental impact. Therefore, a lot of research has been devoted to finding alternative perovskite materials with similar or even better optoelectronic properties. A flipside strategy to improve the efficiency of thin-film solar cells is to build efficient tandem cells by combining materials with specifically tailored band-gaps. The prospect of building thin-film tandem cells made of two or more layers of different hybrid perovskites, however, yet needs to be explored.

The first step towards the development of perovskite-only tandem solar cells is to identify complementary hybrid perovskite materials with specifically tailored band gaps to maximize the efficiency of the tandem cell. The optimal set of optical gaps for a tandem structure made of two different materials is 1.9 eV and 1.0 eV. Since the electronic properties of hybrid perovskites are known to be strongly dependent on the composition and the distortion of the crystal lattice, we start our search by focusing both on the band gap and the perovskite crystal structure calculated from density functional theory (DFT). As a first step, geometrical and electronic structure of the different candidate structures for application in tandem cells are calculated using semilocal (PBE) and hybrid DFT functionals (HSE) with relativistic corrections. To assess the error in the band-gap predicted by the DFT calculations, quasi-particle energy band gaps of some reference structures are calculated using the first principles  $G_0W_0$  approach.

- [1] J. Even, L. Pedesseau, J-M. Jancau and C. Katan, *J.Phys.Chem.Lett.* **2013**, 4, 2999.
- [2] X. Zhao, Nam-Gyu Park, *Photonics* **2015**, 2, 1139.
- [3] T. Körzdörfer and S. Kümmel, *Phys. Rev. B* **2010**, 82, 155206
- [4] M.R. Filip and F. Giustino, *J.Phys.Chem.C* **2016**, 120, 166.

## A Quasi-Diabatization Scheme on the Study of Vibronic Coupling of Chlorophylls Excited States

Petra Shih<sup>1</sup>, Yuan-Chung Cheng<sup>1</sup>

<sup>1</sup>*Department of Chemistry, National Taiwan University, Roosevelt Rd., Taipei, Taiwan*

Radiationless relaxation in molecular excited states plays significant roles in many photophysical and photochemical processes, such as light harvesting in photosynthesis and photoprotection in skin. In particular, the ultrafast dynamics of internal conversion of  $Q_x$  to  $Q_y$  in chlorophylls is crucial to the high efficiency of light harvesting in photosynthesis. In this work, we explored the internal conversion processes of chlorophyll a (Chl a) and bacteriochlorophyll a (BChl a) theoretically by evaluating the vibronic couplings and electronic couplings to construct effective Hamiltonians in diabatic basis describing non-adiabatic phenomena. The first principle study of radiationless relaxation of  $Q_x$  to  $Q_y$  was achieved by combining time dependent density functional theory (TD-DFT) and diabaticization method through enforcement of configuration uniformity [1]. The parameters are obtained using harmonic approximations and TD-DFT calculations, leading to excellent agreement between experimental and simulated absorption and high-resolution fluorescence line narrowing ( $\Delta$ FLN) spectra [2, 3]. Our results successfully predict ultrafast  $Q_x$  to  $Q_y$  relaxation in both chlorophyll systems and indicate that the relatively strongly-coupled modes in high frequency region matching the electronic energy gap facilitate the internal conversion process in the chlorophyll systems. The model we proposed enables detailed dynamical study of the energy relaxation in the chlorophyll systems, allowing us to gain insights into the nature's design of the most important chromophore in photosynthesis. Furthermore, the general methodology shown in this work could be applied to other radiationless relaxation processes, which could find broad applications in the study of photoactive materials used in photovoltaic and photocatalysis.

- [1] K. Ruedenberg and G. J. Atchity, *J. Chem. Phys.* **99**, 3799 (1993).
- [2] M. Rätsep, Z. L. Cai, J.R. Reimers, and A. Freiberg, *J. Chem. Phys.* **134**, 024506 (2011).
- [3] M. Rätsep, J. Linnanto, and A. Freiberg, *J. Chem. Phys.* **130**, 194501 (2009).

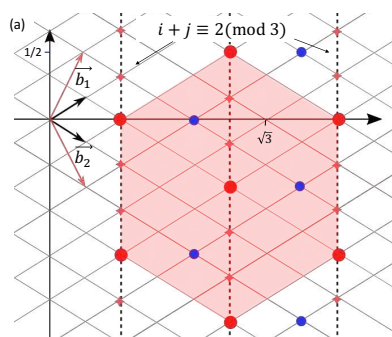
## Evaluation of the Cohesive Energy of a Solid via Lattice Sums

Elke Pahl<sup>1</sup>, Antony Burrow<sup>1</sup>, Peter Schwerdtfeger<sup>1</sup>

<sup>1</sup>Centre for Theoretical Chemistry and Physics, INMS and NZIAS, Massey University, Auckland, New Zealand

The main contribution to the cohesive (binding) energy of a solid comes from the interaction energies between all possible atom pairs in the extended system. Using an extended Lennard Jones functional form,  $\sum_{n>3} c_n x^{-n}$ , to describe the dimer interaction one arrives at an analytical expression for the (two-body) cohesive energy per atom [1]:  $E_{\text{ELJ}}^{\text{coh}} = \frac{1}{2} \sum_{n>3} c_n L_n r_s^{-n}$ . The beauty of this formula is that it only depends on the dimer potential parameters  $c_n$ , the next-nearest neighbour distance  $r_s$  and the so-called Lennard-Jones-Ingham, LJ, coefficients  $L_n$ . Analytical expressions for other solid-state properties like pressure, bulk moduli and zero-point energy follow directly.

The LJ coefficients only depend on the underlying symmetry of the lattice and thus, have only be computed once for every lattice structure, but they present very slowly converging sums. For cubic lattices, several expressions for the LJ have already been derived and techniques for a fast evaluation developed [2]. Here, we will give a visual interpretation of these cubic lattice sums. This visualisation allowed us to find alternative representation for the cubic LJ coefficients and most importantly, a new formula for the hexagonal closed packed structure was found (see figure). This formula allows us to use the same techniques as in the cubic cases. Therefore an efficient and accurate evaluation of the LJ coefficients is now possible.



The B layer (red atoms) of the 'ABAB' hcp structure forms a 2D hexagonal lattice shifted against the A layer (containing the reference atom at the origin). By scaling the basis vectors and mirroring the atoms from the left (blue atoms) one recovers the unshifted lattice again.

- [1] P. SCHWERDTFEGER, N. GASTON, R. P. KRAWCZYK, R. TONNER, AND G. E. MOYANO, Phys. Rev. B **73** (2006) 064112–1–19.
- [2] J. M. BORWEIN, M. JONATHAN, M. L. GLASSER, R. C. MCPHEDRAN, J.G. WAN, AND I. J. ZUCKER, IJ, **150** (2013), Cambridge University Press.

## Molecular dynamics simulation studies of structure and dynamics of poly(acrylic) acid in semidilute concentration regime

Abhishek Kumar Gupta<sup>1</sup>, Upendra Natarajan<sup>2</sup>

<sup>1,2</sup>HSB-152, Macromolecular Modeling and Materials Simulation Laboratory, Dept. of Chemical Engineering, Indian Institute of Technology Madras, Chennai 600036. Email: akgiitm@gmail.com. Ph. +91-44-22574184.

A detailed fully atomistic molecular dynamics (MD) simulation study was carried out with the aid of explicit specification of solvent molecules on poly(acrylic) acid (PAA) in salt free aqueous solution from dilute to semidilute concentration region at different degree of ionization ( $f$ ) values viz.  $f = 0.2, 0.4, 0.7$  and  $1.0$ . The structural properties viz. Radius of gyration ( $R_g$ ), end-to-end distance ( $R$ ), hydrogen bonding (interchain, intrachain and intermolecular), intermolecular structure, bound water ratio, scattering structure factor, interchain distance, interchain contacts and dihedral angle distribution have been elucidated. The dynamic properties viz. hydrogen-bond dynamics and self diffusion coefficient of PAA and counterions have been reported and compared with experimental and model studies. The results have revealed that, conformation size ( $R_g$  and  $R$ ) decreases with increase in polymer volume fraction ( $\phi_p$ ) which is in qualitative agreement with the experimental studies where, ionized PAA particle length decreases with increase in PAA concentration in the semidilute region [1]. Moreover, this behavior is in agreement with the model studies [2] that, demonstrated a decrease in conformational  $R_g$  with polymer concentration. The number of interchain and intrachain H-bonds show an increase with increase in  $\phi_p$ . The self diffusion coefficient of PAA and sodium counterions showed a non-monotonic and monotonic decrease with increase in  $\phi_p$  which, is in good agreement with the bead – spring polyelectrolyte model studies under fully ionized conditions [3]. The details of analysis of properties will be presented.

[1] H. Hoffmann, M. L. T. Liveri, F. P. Cavasino, *J Chem Soc. Faraday Trans.* **93**, 3161 (1997).

[2] U. Micka, C. Holm, K. Kremer, *Langmuir* **15**, 4033 (1999).

[3] R. Chang, A. Yethiraj, *J. Chem. Phys.* **116**, 5284 (2002).

## Quantum chemical investigation of the incorporation of Uranium(V) into Magnetite

R. Polly<sup>1</sup>, B. Schimmelpfennig<sup>1</sup>, I. Pidchenko<sup>1</sup>, T. Vitova<sup>1</sup>, H. Geckeis<sup>1</sup>

<sup>1</sup> *Institut for nuclear waste disposal (INE), Karlsruhe Institute of Technology (KIT), POB 3640, D-76021 Karlsruhe, Germany*

Thorough characterization of the chemical states and redox kinetics of uranium in contact with magnetite are of substantial importance for understanding uranium transport and retention mechanisms in the near and far fields of nuclear waste repositories. Uranium has two main environmentally relevant redox states, highly mobile U(VI) and sparingly soluble U(IV). U(V) is frequently believed to form as an intermediate species in redox processes. It exhibits a so far poorly investigated geochemical behavior, although from a chemical perspective a close analogy with Np(V) is to be expected. Recent experimental studies at KIT-INE applying high-energy resolution X-ray absorption spectroscopy and EXAFS found that uranium(V) incorporated in octahedral magnetite sites remains stable over 226 days under ambient conditions as unambiguously shown for the magnetite nanoparticles containing 1000 ppm uranium [1].

Magnetite has  $\text{Fe}^{3+}$  at octahedral as well as tetrahedral sites and  $\text{Fe}^{2+}$  at octahedral sites.  $\text{Fe}^{3+}$  is a high spin case and the occupation of the five d-orbitals in the ligand field is obvious. This is not so clear anymore for  $\text{Fe}^{2+}$  where two important questions arise: (i) what is the occupation pattern for  $\text{Fe}^{2+}$  and, (ii) is the ground state nondegenerate? These questions were addressed with the multireference complete active space self consistent field (CASSCF) calculations. This is not only of theoretical interest but a major issue because DFT require a nondegenerate ground state. This system was in a first step characterized with CASSCF. Based on these results we further performed plane wave density functional (DFT+U) calculations with periodic boundary conditions on pure magnetite accounting for the strong on-site coulomb repulsion of the 3d electrons by means of the additional U term. We tested this methodology and compared with available structural information and magnetic properties.

In view of the excellent agreement of our theoretical data with available experimental observations for pure magnetite we proceeded to perform calculations of the incorporation of uranium(V) into magnetite. Uranium(V) is a  $5f^1$  system and hence, theoretical, a fairly easy system to be studied with theoretical methods. Still we accompanied these DFT calculations with CASSCF calculations identifying the ground state of uranium(V) in the tetrahedral and octahedral ligand field. For the determination of the changes implied on magnetite upon the incorporation of uranium(V) we employed DFT+U. We probed different incorporation and charge compensation schemes of the incorporation of uranium(V) into magnetite. Overall we found a very good agreement of our theoretical determined structures with the experimental data provided by Pidchenko and Vitova *et al.* [1] and strongly support the characterization of the incorporation site.

[1] I. Pidchenko et al, Environ. Sci. Technol., 2017, 51 (4), pp 2217–2225



# Quantum Chemical Spin Densities for Radical Cations of Photosynthetic Pigment Models

**Denis G. Artiukhin<sup>1</sup>, Christopher J. Stein<sup>2</sup>, Markus Reiher<sup>2</sup>, Johannes Neugebauer<sup>1</sup>**

<sup>1</sup>*Theoretische Organische Chemie, Organisch-Chemisches Institut and Center for Multiscale Theory and Simulation, Westfälische Wilhelms-Universität Münster, Münster, Germany*

<sup>2</sup>Laboratorium für Physikalische Chemie, ETH Zürich, Zürich, Switzerland

The spin-density distribution plays an important role in EPR and NMR measurements. Accurate calculations of this property may shed light on various biophysical processes including photoionization or charge transfer. However, DFT often faces the problem of charge overdelocalization due to self-interaction error and leads to qualitatively wrong spin densities [1].

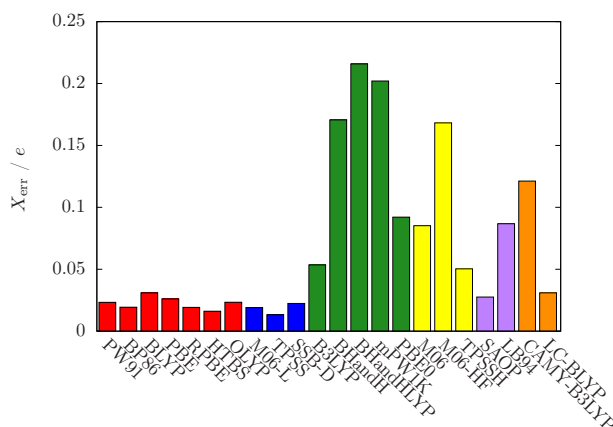


Figure 1: Errors  $X_{\text{err}}$  of DFT spin populations for the  ${}^2A_{1g}$  of the Mg-porphyrin radical cation.

We present multireference quantum chemical spin-density calculations for radical cations of Mg-porphyrin, Mg-chlorine and a truncated chlorophyll *a* model [2]. Because CASSCF spin densities do not converge in certain critical cases w.r.t. the active space size, we suggest to use DMRG [3]. Based on these reference data, we assess the accuracy of different density-functional approximations. Our results provide a starting point for investigations of spin densities of more complex systems such as the hinge model for the primary electron donor in photosystem II [4].

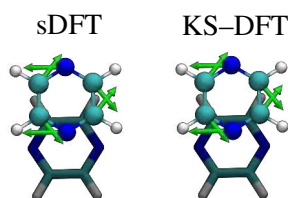
- [1] K. Boguslawski, C. R. Jacob, M. Reiher, *J. Chem. Theory Comput.* **2011**, 7, 2740–2752.
- [2] D. G. Artiukhin, C. J. Stein, M. Reiher, J. Neugebauer, *Photochem. Photobiol.* **2017**, 93, 815–833.
- [3] K. Boguslawski, K. H. Marti, Ö. Legeza, M. Reiher, *J. Chem. Theory Comput.* **2012**, 8, 1970–1982.
- [4] A. Diller, E. Roy, P. Gast, H. J. van Gorkom, H. J. M. de Groot, C. Glaubitz, G. Jeschke, J. Matysik, A. Alia, *PNAS* **2007**, 104, 12767–12771.

## Benchmarking Structures and Vibrational Frequencies from Subsystem DFT

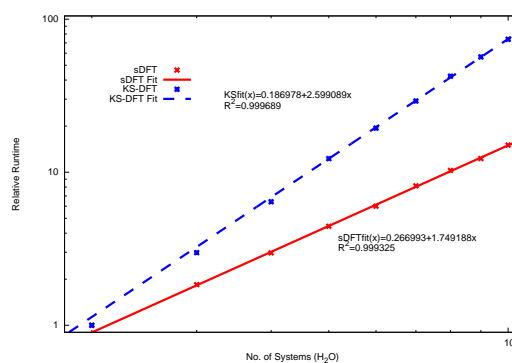
Kevin Klahr<sup>1</sup>, Danny Schlüns<sup>1</sup>, Johannes Neugebauer<sup>1</sup>

<sup>1</sup>*Theoretische Organische Chemie, Organisch-Chemisches Institut and Center for Multiscale Theory and Computation, Westfälische Wilhelms-Universität, Corrensstraße 40, 48149 Münster, Germany*

Describing reaction pathways with computational methods can be a demanding task even for Kohn-Sham density functional theory (KS-DFT), especially if explicit solvation needs to be considered. Subsystem DFT (sDFT), a fragment-based approach to density functional theory, is an efficient alternative to KS-DFT [1–4]. By partitioning the total electron density  $\rho_{\text{tot}}(\mathbf{r})$  into a set of smaller subsystem densities, the ansatz introduces linear scaling with the number of subsystems.



Sample mode from S22 stacked pyrazine dimer structure at 1303.85 cm<sup>-1</sup> (sDFT) / 1306.12 cm<sup>-1</sup> (KS-DFT).



Comparison of relative run times from sDFT and KS-DFT supersystem gradient calculations for H<sub>2</sub>O clusters with increasing system size.

Here, we discuss a benchmark study of our analytical sDFT gradient implementation into our group's quantum chemistry program SERENITY [5]. In addition, a first benchmark of vibrational frequencies based on semi-numerical differentiation is presented.

- [1] G. Senatore, K. R. Subbaswamy, *Phys. Rev. B* **34**, 5754 (1986).
- [2] P. Cortona, *Phys. Rev. B* **44**, 8454 (1991).
- [3] T. A. Wesolowski, A. Warshel, *J. Phys. Chem.* **97**, 8050 (1993).
- [4] C. R. Jacob, J. Neugebauer, *WIREs Comput Mol Sci* **00**, 1-34 (2013).
- [5] T. Dresselhaus, J. P. Unsleber, K. Klahr, D. Schnieders, M. Böckers, D. Barton, J. Neugebauer, manuscript in preparation.

## Optimization of optical properties: Inverse Design of dye-sensitized solar cells

Kai Huwig<sup>1</sup>, Chencheng Fan<sup>1</sup> and Michael Springborg<sup>1,2</sup>

<sup>1</sup>Physical and Theoretical Chemistry, University of Saarland, 66123 Saarbrücken,  
Germany

<sup>2</sup>Tianjin University, Tianjin 300072, PR China

The search for new materials with interesting optical properties is a challenging task. To study all possible systems by pure experimental research is very cost- and time-consuming. A pre-screening of these large pools of systems by theoretical techniques can be one solution to this problem.

Alternatively, in this paper we report an extension of our previous inverse design method<sup>[1]</sup> that automatically optimizes materials regarding their optical properties for solar cell applications. Instead of varying atom types at predefined positions in SiGe clusters as was done in our proof-of-principle study<sup>[1]</sup> we will have a fixed organic backbone and vary the functional groups attached to this core system. In this study we consider benzene as a simple test system. To treat the large number of possible molecules and to identify the best performing ones we make use of genetic/evolutionary algorithms. The optical properties are evaluated via a performance function that can be HOMO-LUMO gap, absorption or the spatial distribution of HOMO and LUMO, etc.

We show that our approach can be applied to organic molecules. We have developed a straightforward scheme for delivering the structural information of our systems via an input file to the source code. This contains information about the organic backbone, its substituent sites, the functional groups, and the symmetry of the core. The organic molecules are build up automatically and afterwards their structures are optimized locally. Subsequently, their optical properties are calculated and only the best ones are kept. These form the new generation within our genetic algorithm. It can be demonstrated that this approach is able to identify a larger number of good candidate structures in a short period of time. Although there are cases where not the best structures are identified during a calculation but “only” the 2<sup>nd</sup> or 3<sup>rd</sup> best, we are convinced that we can provide important information for experimentalists. Our approach provides a foundation for the treatment of large classes of larger organic molecules (e.g. porphyrines, BODIPY) for dye-sensitized solar cells. Not only materials with optimal optical properties can be identified, but our approach can also provide a starting point for other systems and/or properties (e.g. catalysis on crystalline surfaces).



- [1] M. Springborg, S. Kohaut, Y. Dong, K. Huwig, *Comput. Theoret. Chem.* **1107**, 14-22 (2017).

## Benchmarking of Semi-Empirical QM/MM Methods for Proton Transfers between Biomacromolecules and Aqueous Solvent

Henning Henschel<sup>1</sup>, Matti Hanni<sup>1,2,3</sup>, Miika T. Nieminen<sup>1,2,3</sup>

<sup>1</sup>Research Unit of Medical Imaging, Physics and Technology, University of Oulu, P. O. Box 50, FIN-90029 Oulu, Finland

<sup>2</sup>Department of Diagnostic Radiology, Oulu University Hospital, Oulu, Finland

<sup>3</sup>Medical Research Center, Oulu University Hospital and University of Oulu, Oulu, Finland

We are currently developing novel magnetic resonance imaging (MRI) methodologies for the characterisation of cartilage and other musculoskeletal tissues, based on the dispersion of the longitudinal relaxation in the rotating frame ( $T_{1\rho}$ ). One of the mechanisms most likely contributing to the dispersion of  $T_{1\rho}$  dispersion in cartilaginous tissues is the chemical exchange of protons between chondroitin sulfate and water. Our model system for chondroitin sulfate consists of a single disaccharide unit that is repeated in chondroitin-4-sulfate ( $\beta$ -GlcA-(1 $\rightarrow$ 3)- $\beta$ -GalNAc4S), which is capped with methyl groups on both ends (cf. Fig. 1). For the simulation of the dynamics of the several simultaneously possible proton transfer reactions between this compound and the aqueous solvent we are planning to perform semi-empirical QM/MM molecular dynamics simulations. To determine the suitability of a number of different semi-empirical methods for modelling proton transfer reactions between this model compound and water, we have undertaken a series of benchmark calculations. On one hand we probe the methods concerning the accuracy of the model compound's proton binding by calculations of

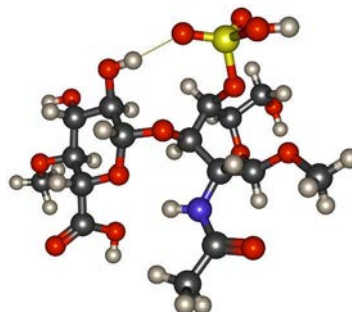


Figure 1: Model compound.

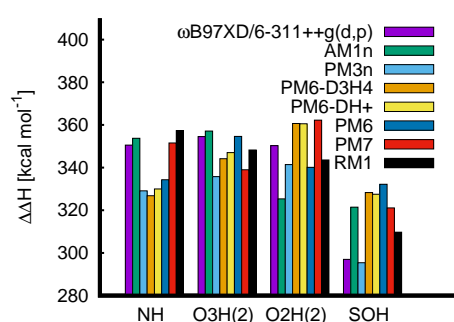


Figure 2: Comparison of gas-phase proton affinities.

the gas-phase proton affinities of the different groups (cf. Fig. 2), and reaction coordinates for proton transfer reaction to isolated water molecules/hydroxide ions, both in comparison to  $\omega$ B97XD/6-311++g(d,p) calculations. On the other hand, we test the suitability of the methods for the dynamics of protons in water by calculations of the 2-D PES of the Zundel ion, and the dynamics of proton transfers in isolated water clusters containing one excess proton, both commensurate to the simulations performed by Wu et al. in their model reparametrisation study.[1]

We thank the Academy of Finland (project 297033) for funding, and CSC-IT Center for Science in Espoo, Finland, for computing time.

[1] X. Wu, W. Thiel, S. Pezeshki, H. Lin, *J. Chem. Theory Comput.* **9**, 2672 (2013).

## Fast estimation of the dynamic electron correlation energy using localized molecular orbitals

Lisa Götte<sup>1</sup>, Robert Franke<sup>1,2</sup>, Volker Staemmler<sup>1</sup>

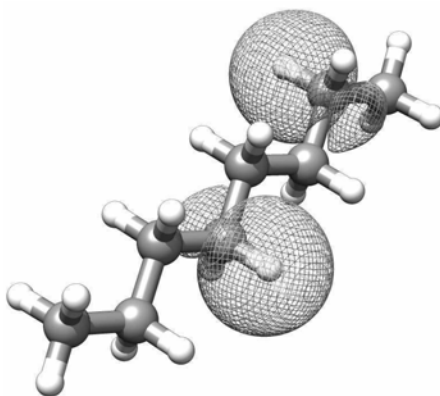
<sup>1</sup>*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Universitätsstraße 150, 44780 Bochum, Germany*

<sup>2</sup>*Evonik Performance Materials GmbH, Paul-Baumann-Straße 1, 45772 Marl, Germany*

The largest source of error in quantum-chemical calculations is the insufficient description of electron correlation. Especially in cases of small energy differences (e.g. isomerization energies, which have a high importance in many industrial research projects) the accurate calculation of electron correlation energies is essential for obtaining predictions with chemical accuracy ( $\pm 5$  kJ/mol). In the last decades, several wavefunction based *ab initio* methods have been developed, which are capable of providing highly accurate results. However, these methods are limited by their high computational costs, which make it very time-consuming or even impossible to carry out calculations for larger systems. At present, for large chemical systems mostly density functional theory (DFT) is the method of choice. As DFT does not allow for improvements in a systematic way and its results are often not sufficiently accurate, large systems can still not be treated satisfyingly.

We propose a novel approach for a fast estimation of electron correlation energies. For this purpose, the total correlation energy of a molecule is decomposed into pair correlation energies of localized molecular orbitals (LMOs). Based on calculations with accurate *ab initio* methods, these pair correlation energies are fitted with respect to the bond length as well as to the spatial extent and the distance between the centers of charge of the LMOs using physically meaningful functions. The total correlation energy of a large system can then be estimated as a sum of the parametrized pair correlation energies of all its LMOs.

Using our approach the total correlation energies for a test set of hydrocarbons could be reproduced within about 1 %. This opens up the possibility to estimate isomerization energies of large hydrocarbons with chemical accuracy.



## Linear response formalism for internally contracted multireference coupled cluster theory to evaluate second order properties

Pradipta Kumar Samanta<sup>1</sup>, Andreas Köhn<sup>1</sup>

<sup>1</sup>*Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, D-70569, Stuttgart, Germany*

Internally contracted multireference coupled cluster (ic-MRCC) methods [1] have been developed and used successfully to calculate the energy of molecular states with pronounced multireference character. One of the variants of ic-MRCC has been extended to study excitation energies [2]. We have also attempted recently to evaluate one-electron first order properties using ic-MRCC which includes both the spin-independent (dipole moments, electric field gradients) and the spin-dependent properties (hyperfine coupling constants).

In this work we proceed towards calculation of second order properties, such as static and dynamic polarizabilities, by developing a linear response formalism for the ic-MRCC theory. The response formalism, developed earlier by Jørgensen *et al.*[3] for the single reference coupled cluster and perturbative methods, has been followed here. We have found that the appearance of unphysical second order poles in the response function is inherent to the ic-MRCC method. Approximations to the original equations to solve the first order parameters and to the expression for the response function have been made to avoid these artifacts. Some of the pilot applications to calculate the polarizabilities have been presented which suggest that the ic-MRCC provides better accuracy for second order properties than other multireference methods.

- [1] A. Banerjee, J. Simons, *Int. J. Quantum Chem.* **19**, 207 (1981); *J. Chem. Phys.* **76**, 4548(1982); U. S. Mahapatra, B. Datta, B. Bandyopadhyay and D. Mukherjee, *J. Chem. Phys.* **30**, 163 (1998); F. A. Evangelista, J. Gauss, *J. Chem. Phys.* **134**, 114102 (2011); M. Hanauer, A. Köhn, *J. Chem. Phys.* **134**, 204111 (2011)
- [2] P. K. Samanta, D. Mukherjee, M. Hanauer and A. Köhn, *J. Chem. Phys.* **140**, 134108 (2014)
- [3] H. Koch and P. Jørgensen, *J. Chem. Phys.* **93**, 3333 (1990); O. Christiansen, P. Jørgensen and C. Hättig, *Int. J. Quantum Chem.* **68**, 1 (1998); F. Pawłowski, J. Olsen and P. Jørgensen, *J. Chem. Phys.* **142**, 114109 (2015)

**Quantitative determinations of photochemistry from first principles:  
Photoluminescence efficiencies of phosphors for OLEDs**

**Daniel Escudero<sup>1</sup>**

<sup>1</sup>*Chimie Et Interdisciplinarité, Synthèse, Analyse, Modélisation (CEISAM), UMR CNRS  
no. 6320, BP 92208, Université de Nantes, 2, Rue de la Houssinière, 44322 Nantes,  
France. E-mail: daniel.escudero@univ-nantes.fr*

Ir(III) complexes are often used as phosphors in phosphorescent organic light-emitting diodes (PhOLEDs). Optimizing their photoluminescence quantum yields (PLQY) at room temperature is key to attain highly performant PhOLEDs.<sup>1</sup> This work demonstrates for the first time that quantitative predictions of their photoluminescence efficiencies can be derived exclusively from electronic structure calculations and the use of kinetic models. More in details, our static approach consists of computing all the competing photodeactivation rates from first principles and then deriving the kinetic master equation. Most of the rates have been herein computed within the framework of the thermal vibration correlation function (TVCF) rate theory<sup>2</sup> in combination with time-dependent density functional theory (TD-DFT) calculations. The thermal processes are modeled with canonical variational transition state theory (CVT). Our preliminary approaches have been proven successful for green-to-blue phosphors.<sup>3</sup> Currently we are developing a general approach valid for all possible Ir(III) complexes, i.e., from red to deep-blue emitters.<sup>4</sup> These approaches are extremely beneficial for the *in silico* prescreening of promising PhOLED emissive materials.

**Acknowledgements:**

Daniel Escudero thanks funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 700961.

**References:**

- 
- [1] D. Escudero, D. Jacquemin, *Dalton Trans.*, **44**, 8346 (2015).
  - [2] Z. Shuai, Q. Peng, *Phys. Rep.*, **537**, 123 (2014).
  - [3] D. Escudero, *Chem. Sci.*, **7**, 1262 (2016).
  - [4] X. Zhang, Q. Peng, D. Jacquemin, Z. Shuai, D. Escudero, *In preparation*.

## Statistical calibration of parametric property models

Jonny Proppe<sup>1</sup>, Markus Reiher<sup>1</sup>

<sup>1</sup>*ETH Zurich, Laboratory of Physical Chemistry, Vladimir-Prelog-Weg 2, CH-8093 Zurich*

One of the major challenges in computational science is to determine the uncertainty of a virtual measurement, that is the prediction of an observable based on calculations. As highly accurate first-principles calculations are in general unfeasible for most physical systems, one usually resorts to parameteric property models of observables, which require calibration by incorporating reference data. The resulting predictions and their uncertainties are sensitive to systematic errors such as inconsistent reference data, parametric model assumptions, or inadequate computational methods [1]. Here, we discuss the calibration of property models in the light of bootstrapping, a sampling method which we apply to assess a linear property model linking the <sup>57</sup>Fe Mössbauer isomer shift to the contact electron density at the iron nucleus [2]. The contact electron density is calculated for a diverse set of molecular iron compounds with twelve density functionals across Jacob's ladder. We provide systematic-error diagnostics (e.g., outlier detection) and reliable, locally resolved uncertainties for isomer-shift predictions. Moreover, we show that both model parameters and prediction uncertainty depend significantly on the composition and number of reference data points. This study presents the first statistically rigorous calibration analysis for theoretical Mössbauer spectroscopy, which is of general applicability and not restricted to isomer-shift predictions.

[1] G. N. Simm, J. Proppe, M. Reiher, *Chimia* **71**, 202 (2017), arXiv:1702.00867.

[2] J. Proppe, M. Reiher, *J. Chem. Theory Comput.*, accepted (2017), arXiv:1703.01685.



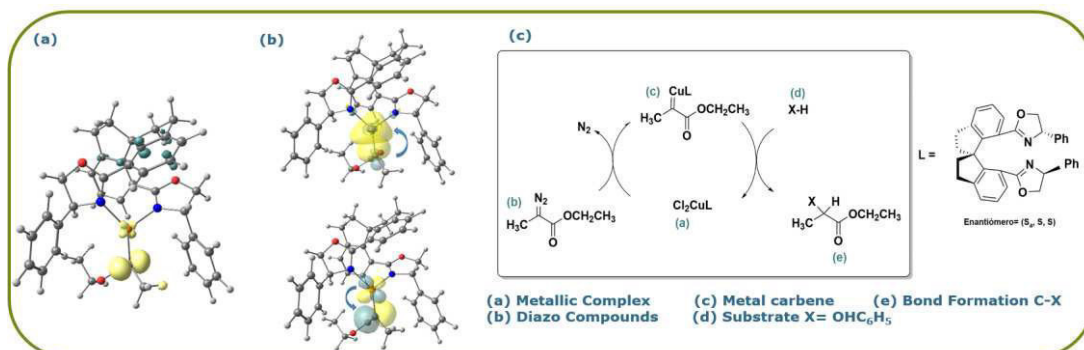
## Reactivity of copper carbenoid toward insertion in O-H bonds. A Density Functional Theory Study

Rocio Durán<sup>1</sup>, Bárbara Herrera<sup>1</sup> and Alejandro Toro-Labbé<sup>1</sup>

<sup>1</sup>Laboratorio de Química Teórica Computacional (QTC), Departamento de Química Física, Facultad de Química, Pontificia Universidad Católica de Chile, Av. Vicuña Mackenna 4860, Santiago, Chile.

One of the major challenges in organic chemistry is the formation of carbon-heteroatom bonds [1], especially in the synthesis of products of industrial interest. A novel solution to this problem is the use of metal carbenoid insertion reactions on O-H bonds. These reactions have attracted considerable interest because they provide a direct and efficient way for the formation of carbon-heteroatom bonds. The use of metal carbenoid is an attractive method, since the O-H activation induced by the metal does not interact directly with it, but rather with the electrophilic carbenoid carbon [2]; additionally the metal complex, initiating the reaction is easily regenerated, so the whole process is recognized as a catalytic reaction.

The main goal of this theoretical study is to propose and evaluate alternative routes (see Figure 1(c)) for the obtention of the mentioned products through a computational analysis. This study is based on the DFT description of the reaction mechanism of the carbenoid insertion reaction, in this particular case, the activation and insertion in O-H bonds effectively, using descriptors such as the reaction force [3] and the reaction electronic flux [4]. In addition, we investigated electronic distribution and the reactivity of carbenoid systems; through global and local reactivity descriptors (see Figure 1 (a)).



**Figure 1:** (a) Dual descriptor for copper carbenoid (b) natural bond orbitals (NBOs) associated with the donor-acceptor interactions Cu-Carbene (c) general reaction mechanism of insertion metal carbenoid in bonds.

**Acknowledgments:** This work was supported by FONDECYT, grant. No. 1170837.

### References

- [1] X.G. Song, Y.Y Ren, S.F. Zhu, and Q.-L. *Adv. Synth. Catal.*, **358**, 15, 366–2370 (2016).
- [2] H. M. L. Davies and R. E. J. Beckwith. *Chem. Rev.* **103**, 8, 2861–2903 (2003).
- [3] B. Herrera and A. Toro-Labbé. *J. Chem. Phys.*, **121**, 15, 096–7102 (2004).
- [4] F. Duarte and A. Toro-Labbé. *J. Phys. Chem. A*, **115**, 14, 3050–3059 (2011).

## Hidden Electrostatic basis of Dynamic Allostery in a PDZ Domain

Amit Kumawat<sup>1</sup>, Suman Chakrabarty<sup>1</sup>

<sup>1</sup>*Physical and Materials Chemistry Division, CSIR-National Chemical Laboratory, India*

Allostery is a phenomenon in which ligand binding at a site is linked to the structural or dynamical changes at a distant site. Although, numerous models have been proposed to understand the molecular mechanism of allostery, a quantitative description of signal propagation still remains elusive. With the newly evolved theories based on thermodynamics and conformational entropy which focuses on slow dynamics and population shifts as crucial determinants of the structural features in information transmission, it will be interesting to gain new insights into allostery, “the second secret of life” at the molecular level.

PDZ domains have been widely used as a model system to understand allosteric transition without structural changes where distal side chain dynamics is modulated upon ligand binding and the origin has been attributed to entropic effects.[1] In this work, we have speculated and explored the energetic basis of the observed “dynamic allostery” in a PDZ3 domain protein using molecular dynamics simulations. Our results suggest that ligand binding information propagates in the form of change in inter-residue interaction energies, especially towards the N-terminal residues and  $\alpha$ 1- $\beta$ 4 region. Interestingly, we find shift in the inter-residue contacts and accompanied side chain orientations as a reason for the large change in interaction energies at a distant region of proteins. Our analyses clearly demonstrate a “population shift” in the hydrogen bonded network and salt bridges upon ligand binding. Interestingly, the internal redistribution and re-wiring of side chain interactions lead to large cancellations resulting in a small change in the overall enthalpy of the protein, thus making it difficult to detect experimentally. This could be the reason for the prevailing focus on “dynamic” or “entropic” effects, whereas the energetics seems to be the more fundamental factor that drives allosteric effects in PDZ3 domain protein.[2]

### References:

- [1] Petit CM, Zhang J, Sapienza PJ, Fuentes EJ, & Lee AL Proc. Natl. Acad. Sci. USA 106(43),18249-18254 (2009)
- [2] A. Kumawat, S. Chakrabarty, Proc. Natl. Acad. Sci. USA, (Accepted), (2017)

## Computer-aided molecular design and modeling of catalysts capable of convert N<sub>2</sub> into ammonia.

Luis Miguel Azofra<sup>1</sup>, Luigi Cavallo<sup>1</sup>

<sup>1</sup>*KAUST Catalysis Center (KCC), King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia*

Ammonia (NH<sub>3</sub>) is increasingly being considered as a real substitute for petroleum as a transportation fuel. The heavy energy-consumption and the considerable, complex plant infrastructure that the classical Haber–Bosch process requires, make the electrochemical synthesis of NH<sub>3</sub> an alternative for a cheap and clean technology of paramount importance from both the industrial and environmental points-of-view.<sup>[1]</sup> Our efforts are mainly focusing on the use of well-resolved DFT calculations with the aim to study the mechanistic aspects of the electrochemical conversion of dinitrogen (N<sub>2</sub>) into NH<sub>3</sub> when occurring on a catalytic surface, not only for the unraveling of the physicochemical events taking place during the reaction mechanism, but also advancing catalytic behaviors on promising materials for the N<sub>2</sub> reduction at mild conditions: N<sub>2</sub> reduction challenges are mainly due to the searching of active materials enabling a spontaneous N<sub>2</sub> fixation<sup>[2]</sup> and decreasing the thermodynamics impediment<sup>[3]</sup> for the limiting step, usually the first proton–electron transfer. We also deal with the estimation of activation barriers (kinetics) that emerge in the form of over-potentials.<sup>[4,5]</sup> In this sense, accurate calculation of over-potentials is a current challenge for DFT, but is also critical for experimentalists to make full use of the calculated results.

[1] C. J. M. van der Ham, M. T. M. Koper, D. G. H. Hetterscheid, *Chem. Soc. Rev.* **43**, 5183 (2014).

[2] L. M. Azofra, N. Li, D. R. MacFarlane, C. Sun, *Energy Environ. Sci.* **9**, 2545 (2016).

[3] J. H. Montoya, C. Tsai, A. Vojvodic, J. K. Nørskov, *ChemSusChem* **8**, 2180 (2015).

[4] L. M. Azofra, C. Sun, L. Cavallo, D. R. MacFarlane, *Chem. Eur. J.* *in press* (2017) DOI: 10.1002/chem.201701113.

[5] X. Nie, M. R. Esopi, M. J. Janik, A. Asthagiri, *Angew. Chem. Int. Ed.* **52**, 2459 (2013).



## **Au Charge and its Role in WGS Reaction on Reduced Gold-Substituted Ce<sub>1-x</sub>O<sub>2</sub>(111) Surfaces**

**Ming-Wen Chang and Wen-Shyan Sheu\***

*Department of Chemistry, Fu-Jen Catholic University, Xinzhuang, New Taipei City 24205,  
Taiwan, R. O. C.*

We investigate the surface structures and the charge on Au for a gold atom adsorbed on the cerium vacancy of the (111) surface of CeO<sub>2</sub> in the presence of oxygen vacancies via density functional theory calculations. The charge of Au can be significantly altered by creating oxygen vacancies on the surface. Detailed analyses show the variation in the Au charge can be attributed to the distribution of the leftover electrons after the oxygen vacancies were created, which, in turn, depends on the vacancy number and locations of the vacancies. Furthermore, we find that the Au<sup>3+</sup> and Au<sup>-</sup> are not catalytically active for the water-gas-shift (WGS) reaction because of a high energy barrier of +1.54 eV required to dissociate water and that of +1.40 eV to produce H<sub>2</sub> and CO<sub>2</sub>, respectively. However, Au<sup>+</sup> is concluded to play a significant role in the WGS reaction at low temperatures ( $T < \sim 550$  K), because the overall reaction barrier for the WGS reaction via the carboxyl mechanism is reduced to be 0.79 eV  $\sim$  0.98 eV in the case of the Au being in a modest oxidation state of +1.

## The Fluctuating Charge Model for improving Force Field electrostatics

Pier Paolo Poier<sup>1</sup>, Frank Jensen<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus, Denmark*

Many different force fields exist which differ in the functional form of energy contributions, the number of cross terms included or the reference data used for fitting the parameters. The majority of commonly used force fields model the electrostatic contribution by fixed atomic charges centered on atoms.

One way of modelling geometry dependent charges is the Fluctuating Charge (FQ) model[1] where the main idea is to expand the electrostatic energy with respect to atomic charges up to second order, with the keys quantities being atomic electronegativities and hardness. Such a model has been used in reactive force fields where bond breaking/forming is described since it allows charge transfer[2], however, current FQ models are incapable of correctly describing covalent bond dissociations[3][4][5].

The geometry dependence of charges is usually introduced in the out-of-diagonal elements of the hardness matrix, often represented by Coulomb terms. This is reasonable for large interatomic distances but atomic wavefunctions have a significant overlap at short distances and a purely Coulombic behavior here seems inappropriate. The correct functional form of out-of-diagonal elements for the hardness matrix represents an open question as well as a consistent geometry dependence of atomic charges.

The out-of-plane dipole moment derivatives (APTs) for planar system allow a unique set of atomic charges that are able to reproduce both molecular charge and dipole moment[6] and these quantities can be calculated for different molecular geometries.

We present analyses of atomic polar tensors and FQ models aimed at reproducing ab initio calculated APTs.

- [1] A. K. Rappe; W. A. Goddard, *Journal of Physical Chemistry* **95**, 3358 (1991).
- [2] A. C. T. Van Duin; S. Dasgupta; F. Lorant; W.A. Goddard, *Journal of Physical Chemistry A* **105**, 9396 (2001).
- [3] J. H. Chen; T. J. Martinez, *Chemical Physics Letters* **438**, 315 (2007).
- [4] J. H. Chen; T. J. Martinez, *Chemical Physics Letters* **463**, 288 (2008).
- [5] D. Mathieu, *Journal of Physical Chemistry* **127**, 224103 (2007).
- [6] U. Dinur, *Journal of Computational Chemistry* **12**, 469 (1991).

## Insight into molecular reactivity and reaction mechanisms from reactive molecular dynamics simulations

Sebastian Brickel<sup>1</sup>, Markus Meuwly<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland*

Following reactions over time is of key importance for analysing and understanding the mechanisms that govern chemical processes. Utilising the reactive molecular dynamics implementation MS-ARMD (Multi-Surface Adiabatic Reactive Molecular Dynamics[1]) allows to study adiabatic reactions related to, i.e. atmospheric chemistry, organic synthesis, and biochemistry. MS-ARMD allows to simulate statistically significant number of trajectories which allows for extensive studies on a system. Furthermore it can be used to calculating converged reaction rates. Example systems that show the versatility and efficiency of MS-ARMD are OH-stretching overtone induced photodissociation of  $\text{HSO}_3\text{F}$ [2] and the Claisen rearrangement reaction of allyl-vinyl-ether (AVE) and chorismate in gas and condensed phase[3].

Extensive simulation of OH-stretching overtone induced photodissociation of  $\text{HSO}_3\text{X}$  ( $\text{X} = \text{F}$ ,  $\text{Cl}$ [4]) in the ns-time scale reveals dynamical effect on the dissociation reaction that differ for the two systems.  $\text{HSO}_3\text{F}$  shows a lack of dissociation in comparison to the previously studied system  $\text{HSO}_3\text{Cl}$ . Detailed analysis implies that coupling of the OH-local mode to bending and torsional degrees of freedom is of importance for the elimination reaction.

Claisen rearrangement is an important [3,3]-sigmatropic rearrangement. In aqueous solution and in the enzyme chorismate mutase (CM) Claisen rearrangement is catalysed by the stabilisation of the cyclic transition state (TS). Utilizing a well parametrised force field of AVE the experimental barrier height[6] of chorismate in CM was reproduced. Analysing the TS conformation shows difference between AVE, AVE-dicarboxylate and chorismate.

- [1] T. Nagy, J. Y. Reyes and M. Meuwly, *J. Chem. Theory Comput.*, **10**, 1366 (2014).
- [2] S. Brickel, M. Meuwly, *J Phys Chem A*, *submitted*.
- [3] S. Brickel, M. Meuwly, *in preparation*.
- [4] J. Y. Reyes, S. Brickel, O. T. Unke and M. Meuwly, *Phys. Chem. Chem. Phys.*, **18**, 6780 (2016).
- [5] F. Claeysens *et al.*, *Org. Biomol. Chem.*, **9**, 1578 (2011).
- [6] P. Kast, M. Asif-Ullah and D. Hilvert, *Tetrahedron Lett.*, **37**, 2691 (1996).

## Polypyridyl iron(II) complexes as promising photoredox catalysts. Theoretical calculation of excited state redox potentials

**Enrique M. Arpa<sup>1</sup>, Diego J. Cárdenas<sup>\*2,3</sup>, Inés Corral<sup>\*1,3</sup>**

<sup>1</sup>Dpto. Química, Facultad de Ciencias. Universidad Autónoma de Madrid.

<sup>2</sup>Dpto. Química Orgánica, Facultad de Ciencias. Universidad Autónoma de Madrid.

<sup>3</sup>Institute of Advanced Chemical Sciences (IAdChem). Universidad Autónoma de Madrid.

C/ Francisco Tomás y Valiente 7. 28049 Cantoblanco (España)

enrique.arpa@uam.es

Photoredox catalysis has emerged as a very powerful tool in synthetic organic chemistry, giving access to a unique reactivity impossible to achieve in the ground state. As a matter of fact, Ir and Ru complexes have proved their worth as photoredox catalysts by activating otherwise inert substrates like aryl halides and N-protected amino acids [1].

However, their toxicity has triggered the search of alternative “green catalysts”, capable of performing such transformations while being eco-friendly. In this context, Fe and Ni complexes have been successfully tested as Pd replacements for cross-coupling reactions; moreover, Ni has been recently applied as a photoredox catalyst [2].

In this work, we assess the potential use of Fe(II) polypyridyl complexes as substitutes for Ir / Ru derivatives in photoredox catalysis by considering the calculated excited state redox potentials for several of these Fe(II) complexes, following the methodology described in ref. [3] in the framework of DFT and TD-DFT. Functional screening shows that a modified version of B3LYP [4] provides the best fit for both vertical excitations and oxidation potentials compared to experimental data. The combination of these results with the calculated reduction potential of several synthetically relevant organic substrates represents encouraging results for the plausible activation of these latter by Fe(II) complexes.

[1] a) C. K. Prier et al., *Chem. Rev.* **113**, 5322 (2013). b) I. Ghosh et al., *Acc. Chem. Res.* **49**, 1566 (2016).

[2] a) M. Guisán-Ceinos et al., *Chem. Sci.* **4**, 1098 (2013). b) Z. Zuo et al., *Science* **345**, 437 (2014).

[3] T. B. Demissie et al., *Organometallics* **34**, 4218 (2015).

[4] a) M. Reiher et al., *Theor. Chem. Acc.* **107**, 48 (2001). b) M. Pápai et al., *J. Chem. Theory Comput.* **9**, 509 (2013).



## Fast and Accurate Geometry Optimization of Lanthanoid Complexes with an extended Tight Binding Method

Markus Bursch<sup>1</sup>, Stefan Grimme<sup>1</sup>

<sup>1</sup>*Mulliken Center for Theoretical Chemistry, Institute for Physical and Theoretical Chemistry, University of Bonn, Beringstraße 4, 53115 Bonn, Germany*

The computational handling of large lanthanoid complex structures is fundamental for theoretical and mechanistic studies in various fields of applied science like lanthanoid-based metal-organic frameworks or homogenous catalysis to only name a few. The recently developed GFN-xTB[1] (G: geometries; F: frequencies; N: non-covalent interactions) tight binding based electronic structure approach was applied for geometry optimization of 78 lanthanoid complexes (La ( $Z = 57$ ) – Lu ( $Z = 71$ )). The results were evaluated with reference to high quality X-ray molecular structures obtained from the Cambridge Structural Database (CSD) and DFT-D3 calculated reference structures for Pm ( $Z = 61$ ). The structural heavy atom root-mean-square deviation (RMSD) and the mean coordination number change of the lanthanoid atoms for GFN-xTB, Sparkle/PM6[2] and HF-3c[3] are compared. It is shown that GFN-xTB yields reasonable structures and performs well in terms of overall computational speed compared to other low cost state of the art methods. The high quality reproduction of large lanthanoid complex structures corroborates the wide applicability of the GFN-xTB approach and its high value as very effective low cost method.

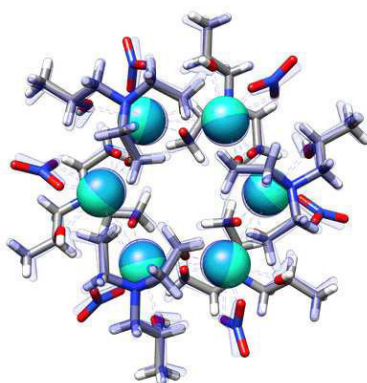


Figure 1: Overlay of GFN-xTB optimized and experimental (X-ray) structure for a prototypical lanthanoid complex

- [1] S. Grimme, C. Bannwarth, P. Shushkov, *J. Chem. Theory Comput.* **13**, 1989 (2017).
- [2] A. M. Simas, R. O. Freire, *J. Chem. Theory Comput.* **6**, 2019 (2010).
- [3] R. Sure, S. Grimme, *J. Comput. Chem.* **34**, 1672 (2013).

## Automated Exploration of Complex Chemical Reaction Networks

Gregor N. Simm<sup>1</sup>, Markus Reiher<sup>1</sup>

<sup>1</sup>*ETH Zürich, Laboratory of Physical Chemistry,  
Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland.*

To be able to accurately predict the product distribution of chemical reactions, a complete reaction network consisting of all relevant intermediates and elementary reactions is necessary. The complexity of such a network may grow rapidly, in particular, if reactive species are involved that might cause a myriad of side reactions. Therefore, only the expected, dominant reaction paths of a chemical reaction network (e.g., a catalytic cycle) are usually explored in practice. In addition, conformational diversity, which is essential for the understanding of catalytic processes, is rarely taken into account. Without a robust protocol, automation, and appropriate data handling, a truly predictive theoretical investigation is tedious and possibly unfeasible.

We present a computational protocol and its implementation that constructs such networks in an automated manner [1, 2]. For each intermediate, conformers are generated and selected based on structural similarity and energy criteria. Pairs of conformers are placed in a *virtual flask* and reactive complexes are formed between them by applying heuristic rules derived from conceptual electronic-structure theory. With a constrained geometry optimization employing quantum-chemical methods, activation barriers are overcome and new intermediates are formed. This procedure is followed by a transition state search.

We demonstrate not only the infrastructure necessary for handling such large amounts of data but also a graphical user-interface for visualization and manipulation of the reaction network. With this framework, a comprehensive picture of the chemical process can be obtained and further studies (e.g., kinetic analyses) can be performed [3]. We demonstrate our approach at the example of the formose reaction [4], an autocatalytic oligomerization reaction of formaldehyde.

- [1] M. Bergeler, G. N. Simm, J. Proppe, M. Reiher, *J. Chem. Theory Comput.* **11**, 5712 (2015).
- [2] G. N. Simm, M. Reiher, *in preparation*.
- [3] J. Proppe, T. Husch, G. N. Simm, M. Reiher, *Faraday Discuss.* **195**, 497 (2016).
- [4] A. Butlerow, *Justus Liebigs Ann. Chem.* **120**, 295 (1861).

## H<sub>2</sub> dissociation and surface oxygen vacancy formation on (111)-CeO<sub>2</sub> surface: a periodic DFT approach

Matz Olivier<sup>1</sup>, Calatayud Monica<sup>1</sup>

<sup>1</sup>Laboratoire de Chimie Théorique, Sorbonne Universités, UPMC Université Paris 6, CNRS, UMR 7616, CC-137 – 4 Place Jussieu, 75005, Paris, France

Most of the applications of ceria are linked to its redox properties associated to the easy formation of oxygen vacancies and so the simple change in oxidation states of cerium: Ce<sup>IV</sup> ↔ Ce<sup>III</sup>. Moreover, ceria is important in heterogeneous catalysis, especially in the alkyne semi-hydrogenation where it has been shown to be able to split H<sub>2</sub> in the absence of noble metal [1]. Interestingly, the hydrogenation of ceria is found to take place through a hydride specie that plays a key role [1,2,3].

In the present study, we investigate the detailed mechanism for the formation of surface oxygen vacancy via H<sub>2</sub> dissociation following by H<sub>2</sub>O desorption on (111)-CeO<sub>2</sub> using PBE+U method and periodic approach as implemented in VASP software.

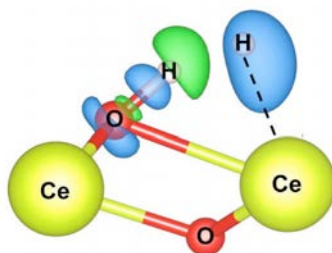


Figure 1. Charge density difference illustrating the ion pair H<sup>δ+</sup> – H<sup>δ-</sup> formation: blue and green isosurfaces display an electronic density gain and depletion, respectively.

It was found that molecular hydrogen adsorbs very weakly to the surface. Then, the strong ionic nature between cerium and oxygen in ceria induces the polarization of the H – H bond and favor an heterolytic dissociation of H<sub>2</sub> with the formation of an ion pair H<sup>δ+</sup> – H<sup>δ-</sup> [2]. However, the product of the heterolytic dissociation being metastable [2,3], the hydride can easily move on to a hydroxyl group to form water molecule. Finally, water desorption leads to the formation of one surface oxygen vacancy along with the reduction of two cerium. Several hydrogen species – like hydride, radical hydrogen and proton – are involved during the different steps of the reaction.

- [1] J. Vecchiotti; M. A. Baltanás; C. Gervais; S. E. Collins; G. Blanco; O. Matz; M. Calatayud; A. Bonivardi, *J. Catal.* **345**, 258 (2017).
- [2] M. García-Melchor; N. López, *J. Phys. Chem. C* **118**, 10921 (2014).
- [3] D. Fernández-Torre; J. Carrasco; M. V. Ganduglia-Pirovano; R. Pérez, *J. Chem. Phys.* **141**, 014703 (2014).

## Reaction rate constants from system-specific, black-box force fields parametrized by quantum chemical data

Julien Steffen<sup>1</sup>, Bernd Hartke<sup>1</sup>

<sup>1</sup>*Institute of Physical Chemistry, University of Kiel, Max-Eyth-Str. 2, 24118 D-Kiel, Germany*

In this work we present a method for automated construction of system-specific force fields used to describe given elementary reaction steps [1]. Based on the quantum-mechanically derived force field (QMDF) [2] and its empirical valence bond extension EVB-QMDF [3], the optimized force fields are able to represent a reliable potential energy surface for any given reaction step in an essentially black-box manner. To generate and parametrize such a force field just a limited and pre-defined set of reference data near the reaction path is needed. Depending on the chosen reaction, different EVB coupling terms might be used to optimize the force fields performance. Built on this data, the new force field establishes an accurate approximation of the reference potential energy surface, on and off the reaction path. This intermediate representation can be used to generate reaction rate data using ring polymer molecular dynamics (RPMD) [4], with far better accuracy and reliability than with traditional approaches based on transition state theory (TST) or its variational extensions (VTST), even if those include sophisticated tunneling corrections. However, the additional expense at the reference level remains very modest. We demonstrate the ability of our approach for three arbitrarily chosen example reactions.

- [1] J. Steffen, B. Hartke, *J. Chem. Phys.* **147**, 161701 (2017).
- [2] S. Grimme *J. Chem. Theory Comput.*, **10**, 4497-4514 (2014).
- [3] B. Hartke, S. Grimme, *Phys. Chem. Chem. Phys.* **17**, 16715-16718 (2015).
- [4] Y. V. Suleimanov, J. W. Allen, W. H. Green, *Comp. Phys. Comm.* **184**, 833 (2013).

## $\pi$ -Conjugated Macrocycles with High Radical Character

**María Eugenia Sandoval-Salinas<sup>1,2</sup>, Tullimilli Y. Gopalakrishna<sup>3</sup>, Liu  
Chunchen<sup>3</sup>, Jishan Wu<sup>3</sup>, David Casanova<sup>2</sup>**

<sup>1</sup>*Departament de Ciència de Materials i Química Física, Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, Martí i Franquès 1-11, Barcelona 08028, Spain*

<sup>2</sup>*Kimika Fakultatea, Euskal Herriko Unibersitatea (UPV/EHU), Donostia International Physics Center (DIPC), Paseo Manuel de Lardiazabal 4, Donostia 20018, Spain*

<sup>3</sup>*Department of Chemistry, National University of Singapore, 3 Science Drive 3, 117543 Singapore*

Nowadays, there are many examples of molecules with an open-shell singlet diradicaloid ground state but organic molecules with higher polyradical character (e.g., tetraradical, hexaradical, ...) are quite rare, to say the least. Recently, two organic stable macrocycles with large polyradical characters were synthesized and characterized, exhibiting singlet ground states that can be regarded as a tetraradicaloid and an hexaradicaloid, respectively [1].

In this work, we present the computational study of the ground state electronic structure of two new polycyclic molecules (8MC and 10MC) holding very large polyradical nature synthesized by Prof. Wu's group. The study includes the relative stability of structural conformers, the quantification of their polyradicaloid character by means of natural orbital occupancies, the vertical energy gaps between low-lying states of different spin-multiplicities and rationalization of global aromaticities. The computational strategy employed combines density functional theory (DFT), constrain DFT (C-DFT) and restricted active space spin-flip (RAS-SF) [2] calculations. Our results suggest 8MC and 10MC as octaradicaloid and decaradicaloid species, respectively.

[1] Das, S.; Heng, T. S.; Zafra, J. L.; Burrezo, P. M.; Kitano, M.; Ishida, M.; Gopalakrishna, T. Y.; Hu, P.; Osuka, A.; Casado, J.; Ding, J.; Casanova, D. and Wu, J., *J. Am. Chem. Soc.* **138**, 7782 (2016).

[2] Casanova, D., Head-Gordon, M., *Phys. Chem. Chem. Phys.* **11**, 9779 (2009).

## Ligand–Field States of Aqua Complexes Revisited with Multireference Calculations: Importance of Solvation Effects

Mariusz Radoń<sup>1</sup>

<sup>1</sup>*Faculty of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060 Krakow, Poland*

Although aqua complexes  $[M(H_2O)_6]^{n+}$  (where  $M^{n+}$  is a transition metal ion) are among the simplest and experimentally best characterized coordination compounds, it is not trivial at all to reproduce their d–d excitation energies by means of quantum chemical calculations. Recently, there were significant controversies regarding the lowest electronic excitation  ${}^6A_{1g} \rightarrow {}^4T_{1g}$  for  $[Fe^{III}(H_2O)_6]^{3+}$  [1, 2]: Whereas the DFT:B3LYP method seems to reproduce the experimental excitation energy quite well, advanced wave function theory (WFT) methods, such as CASPT2 and CCSD(T), appeared to overestimate it by more than 10 kcal/mol! Similar problems may also be noticed for aqua complexes of other 3d-electron metals. However, our recent paper demonstrated that the discrepancies for  $[Fe^{III}(H_2O)_6]^{3+}$  may be plausibly resolved by accounting for hydrogen–bonding interactions with water molecules present in the second solvation sphere, leading to systematic stabilization of the lower-spin state [3]. This approach is now extended to aqua complexes of all 3d-electron metal ions with electronic configurations from  $d^0$  ( $Ti^{III}$ ) to  $d^9$  ( $Cu^{II}$ ). Multireference methods CASPT2 and NEVPT2 are applied to treat their various ligand-field states for which excitation energies are experimentally available. Reliable models with second solvation sphere and extensive active spaces (accounting for covalency of metal–ligand  $\sigma$ -bonds) are employed. It is demonstrated that once an adequate multireference methodology and a realistic solvation model are used, the computed excitation energies are systematically in a very good agreement with the experimental band positions. Since the experimental data of aqua complexes contain a number of d–d transitions between states of different multiplicities (*i.e.*, spin-forbidden transitions), the results obtained also contribute to calibration of computational methods for the problem of spin-state energetics. The latter is generally recognized as a grand challenge for theory in the field of (bio)inorganic chemistry [4]. In this regard, the present work suggests that accounting for solvation/medium effects in the second coordination sphere may be quite important for a balanced description of relative spin-state energetics.

- [1] Y. Yang, M. A. Ratner, G. C. Schatz, *J. Phys. Chem. C* **118**, 29196 (2014).
- [2] A. Ghosh, P. R. Taylor *Curr. Op. Chem. Biol.* **7**, 113 (2003).
- [3] M. Radoń, K. Gąsowska, J. Szklarzewicz, E. Broclawik *J. Chem. Theory Comput.* **12**, 1592 (2016).
- [4] M. Swart *Int. J. Quantum Chem.* **113**, 2 (2013).

## Benzene probes in molecular dynamics simulations reveal novel binding sites for ligand design

Yaw Sing Tan<sup>1</sup>, Judith Reeks<sup>2</sup>, Christopher Brown<sup>3</sup>, Dawn Thean<sup>3</sup>, Fernando Jose Ferrer Gago<sup>3</sup>, Tsz Ying Yuen<sup>4</sup>, David P. Lane<sup>3</sup>, Martin E. M. Noble<sup>2</sup>, and Chandra S. Verma<sup>1</sup>

<sup>1</sup>*Bioinformatics Institute, Agency for Science, Technology and Research (A\*STAR), 30 Biopolis Street, #07-01 Matrix, Singapore 138671*

<sup>2</sup>*Northern Institute for Cancer Research, Newcastle University, Framlington Place, Newcastle upon Tyne NE2 4HH, U.K.*

<sup>3</sup>*p53 Laboratory, A\*STAR, 8A Biomedical Grove, #06-04/05 Neuros/Immunos, Singapore 138648*

<sup>4</sup>*Institute of Chemical & Engineering Sciences, A\*STAR, 8 Biomedical Grove, #07-01 Neuros, Singapore 138665*

Proteins are intrinsically flexible and frequently undergo conformational changes on ligand binding. This poses a major challenge in the identification and characterisation of ligand binding sites. Several computational pocket detection methods that utilize small-molecule probes in molecular dynamics (MD) simulations have been developed to address this issue. In these simulations, the probes interact dynamically with the protein surface, allowing for ligand-induced conformational changes and revealing the locations of binding sites. The use of hydrophobic probes is of particular interest because it reduces solvent polarity, thus facilitating the opening and enlargement of cryptic hydrophobic pockets that may otherwise remain undetected in simulations of the protein in pure water. Ligand-mapping MD (LMMD) [1-3] is one of two current probe-based MD simulation methods [4] that employ hydrophobic probes for pocket detection. Here, we report the use of benzenes as probe molecules in LMMD simulations to predict the existence of two novel binding sites on the surface of the oncoprotein MDM2. Through biophysical assays and X-ray crystallography, we serendipitously validated one of them as a functional binding site by using peptidic ligands that were specifically designed to target the other putative site. These results highlight the predictive power of LMMD, and suggest that predictions derived from LMMD simulations can serve as a reliable basis for the identification of novel ligand binding sites in structure-based drug design.

[1] Y. S. Tan, P. Sledz, S. Lang, C. J. Stubbs, D. R. Spring, C. Abell, R. B. Best, *Angew. Chem. Int. Ed.* **51**, 10078-10081 (2012).

[2] Y. S. Tan, D. R. Spring, C. Abell, C. S. Verma, *J. Chem. Inf. Model.* **54**, 1821-1827 (2014).

[3] Y. S. Tan, D. R. Spring, C. Abell, C. S. Verma, *J. Chem. Theory Comput.* **11**, 3199-3210 (2015).

[4] O. Guvench, A. D. MacKerell, Jr., *PLoS Comput. Biol.* **5**, e1000435 (2009).

# Molecular Quantum-Dot Cellular Automata Based on Diboryl Radical Anions

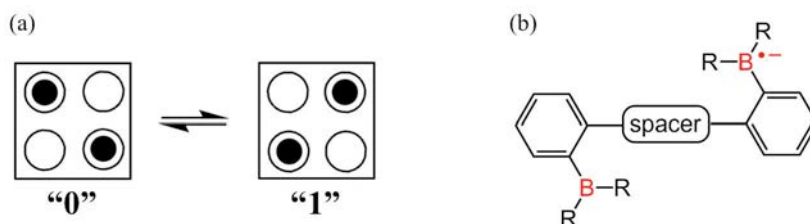
Xingyong Wang<sup>1</sup>, Xiaobo Pan<sup>2</sup>, Haibo Yu<sup>1,3</sup>

<sup>1</sup>*School of Chemistry, University of Wollongong, Northfields Avenue, Wollongong, NSW 2522, Australia*

<sup>2</sup>*College of Chemistry and Chemical Engineering, Lanzhou University, 222 Tianshui South Road, Lanzhou 730000, China*

<sup>3</sup>*Illawarra Health and Medical Research Institute, Wollongong, NSW 2522, Australia*

As a promising alternative to field-effect transistors (FETs), molecular quantum-dot cellular automata (MQCA)<sup>1</sup> has attracted considerable research interests for building the next-generation microelectronic elements. In MQCA, binary information is represented by the charge configuration of a cell with four dots (Fig. 1a). The signal transmission is achieved via Coulomb interaction between neighboring cells with no current flow and extremely low power dissipation<sup>2</sup>. Although a variety of MQCA candidates have been reported, including mixed-valence organometallic complexes, metal cluster carboxylates, zwitterionic boron-allyl complexes, and double-cage fluorinated fullerene anions, it is still a challenge to put them into practical applications due to difficulties in synthesis or surface attachment. Herein we proposed a new candidate system – diboryl radical anion, with the boron radical center as the charge container (Fig. 1b). Such compound has already been isolated and characterized experimentally, demonstrating elegant synthesis and versatile modification in the end groups. Based on this framework, a series of analogous candidates with different substituents and spacers have been investigated and the ones with best performance have been suggested.



**Fig. 1** (a) Schematic illustration of MQCA cells. (b) Molecular skeleton of diboryl radical anion based MQCA candidate.

[1] C. S. Lent, P. D. Tougaw, W. Porod and G. H. Bernstein, *Nanotechnology* **4**, 49 (1993).

[2] C. S. Lent, *Science* **288**, 1597 (2000).



## Computational Insights into the Gas Phase Heterogeneous CO<sub>2</sub> Reduction via Surface Frustrated Lewis Pairs

Kulbir Kaur Ghuman

*International Institute for Carbon Neutral Energy Research, Kyushu University,*

*744 Motooka, Nishi-ku, Fukuoka, 819-0395, Japan*

**Abstract:** The significant challenge faced by our global society, from issues of climate change to question of energy security could be solved if we can find a champion catalyst that can convert atmospheric CO<sub>2</sub> to carbon based fuels. However, designing catalytic nanostructures that can thermochemically or photochemically convert gaseous CO<sub>2</sub> into fuels is a significant challenge which requires a keen understanding of the physical and chemical properties of complex materials and the processes happening on them at atomic and electronic level. In this context, this work will present our recent findings [1-3] that showed that the Frustrated Lewis Pairs (FLPs) created by sterically hindered Lewis acid and Lewis base have the capacity of capturing and reacting with a variety of small molecules, including H<sub>2</sub> and CO<sub>2</sub>, which extends a new strategy for CO<sub>2</sub> reduction. Specifically, I will highlight the insights provided by density functional theory (DFT), time-dependent DFT and metadynamics calculations into the surface chemistry of CO<sub>2</sub> reduction reaction on In<sub>2</sub>O<sub>3-x</sub>(OH)<sub>y</sub> nanoparticles, in the presence and the absence of light and temperature. This work not only resulted in the discovery of a new class of FLP heterogeneous photocatalysts but also provided a path to effectively maximize the activity of surface FLPs in nanocrystalline In<sub>2</sub>O<sub>3-x</sub>OH<sub>y</sub> through isomorphous substitution of In(III) with more electronegative Bi(III) [3], which will also be discussed in this presentation.

- [1] K. K. Ghuman, L. B. Hoch, P. Szymanski, J. Y. Y. Loh, N. P. Kherani, M. A. El-Sayed, G. A. Ozin, C. V. Singh, *J. Am. Chem. Soc.* **138**, 1206 (2016).
  - [2] M. Ghoussoub, S. Yadav, K. K. Ghuman, G. A. Ozin, C. V. Singh, *ACS Catal.* **6**, 7109 (2016).
  - [3] K. K. Ghuman, T. E. Wood, L. B. Hoch, C. A. Mims, G. A. Ozin, C. V. Singh, *Phys. Chem. Chem. Phys.* **17**, 14623 (2015).
  - [4] Y. Dong\*, K. K. Ghuman\*, W. Zhou, J. Y. Y. Loh, A. A. Jelle, J. Jia, P. N. Duchesne, D. Wang, X. Mu, R. Popescu, C. Kübel, M. Ghoussoub, L. M. Reyes, Q. Wang, L. Wang, N. P. Kherani, C. V. Singh, G. A. Ozin, Tailoring Surface FLPs of In<sub>2</sub>O<sub>3-x</sub>(OH)<sub>y</sub> for gas phase Heterogeneous CO<sub>2</sub> Hydrogenation by Isomorphous Substitution of In(III) with Bi(III), *J. Am. Chem. Soc.* (2017) (To be submitted).
- \*First authors

## A scalable explicitly correlated local coupled-cluster method with pair natural orbitals: PNO-LCCSD-F12

Qianli Ma, Max Schwilk, Christoph Köppl, Hans Joachim-Werner

*Institute for Theoretical Chemistry, University of Stuttgart,  
Pfaffenwaldring 55, D-70569 Stuttgart, Germany*

An efficient explicitly correlated local coupled-cluster method PNO-LCCSD-F12 is presented. The method is a part of a new generation of parallel local correlation methods developed in our group [1, 2] using pair natural orbitals (PNOs) to span the virtual space. The PNOs are constructed from projected atomic orbitals (PAOs) and orbital specific virtuals (OSVs). A hierarchy of strong, close, weak, and distant pairs are selected using approximated LMP2 pair energies, and different levels of theory are applied to these pair classes to reduce the computational cost without significant loss of accuracy. The explicit correlation theory is adapted from the cost-effective CCSD-F12 $x$  ( $x = a, b$ ) theory [3, 4]. The cost of the explicitly correlated terms scales linearly with the molecule size asymptotically.

Extensive benchmark results are presented, which demonstrate that the PNO-LCCSD-F12 method yields relative energies within  $\sim 1 \text{ kJ mol}^{-1}$  of the canonical values for a variety of chemical systems. The F12 terms are shown to improve the basis set convergence, and to reduce the domain errors that originate from the truncation of PAOs and PNOs. On a small computer cluster with 100–200 of CPU cores, PNO-LCCSD-F12 calculations of three-dimensional molecules with  $\sim 100$  atoms using the augmented triple- $\zeta$  basis sets can be performed in 1–3 hours of elapsed time. In particular, despite drastic improvements of the accuracy, the explicitly correlated terms typically add only 20–30% of the computational time to a corresponding PNO-LCCSD calculation. The exclusive use of the explicitly correlated variant is therefore strongly recommended.

- [1] H.-J. Werner, G. Knizia, C. Krause, M. Schwilk, M. Dornbach, *J. Chem. Theory Comput.* **2015**, *11*, 484–507.
- [2] Q. Ma, H.-J. Werner, *J. Chem. Theory Comput.* **2015**, *11*, 5291–5304.
- [3] T. B. Adler, G. Knizia, H.-J. Werner, *J. Chem. Phys.* **2007**, *127*, 221106.
- [4] T. B. Adler, H.-J. Werner, *J. Chem. Phys.* **2011**, *135*, 144117.

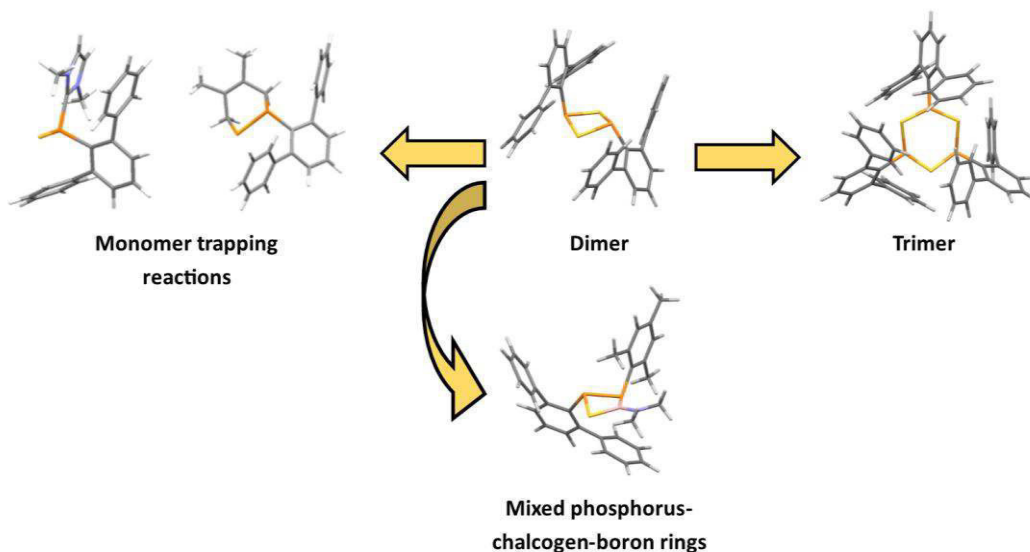
## Phosphinidene Chalcogenides: DFT modeling of monomer trapping, ring expansion and mixed ring systems

Cameron M. E. Graham<sup>1</sup>, Taylor E. Pritchard<sup>1</sup>, Paul D. Boyle<sup>1</sup>, Juuso Valjus<sup>2</sup>,  
Heikki M. Tuononen<sup>2</sup> and Paul J. Ragona<sup>1</sup>

<sup>1</sup>Department of Chemistry and the Centre for Advanced Materials and Biomaterials Research, Western University, 1151 Richmond St., London, Ontario, Canada, N6A 5B7

<sup>2</sup>Department of Chemistry, NanoScience Center, University of Jyväskylä, P.O. Box 35, 40014 University of Jyväskylä (Finland)

The reaction mechanisms of four-membered phosphinidene chalcogenide rings have been solved using density functional theory calculations. These molecules with  $P_2Ch_2$  cores ( $Ch=S,Se$ ) represent the first four-membered organophosphorus-chalcogen rings with phosphorus in the +3 oxidation state. The rings can be broken down using Lewis bases to yield monomeric  $R-P=Ch$ , which can be stabilized by the base or trapped with a diene [1]. The liberation of monomeric  $R-P=Ch$  units enables a base-assisted ring expansion reaction from the four-membered rings into the more stable six-membered  $(RPCh)_3$  rings [2]. The formation of mixed four-membered phosphorus-chalcogen-boron rings with phosphinidene boranes is also modeled.



[1] C. M. E. Graham, T. E. Pritchard, P. D. Boyle, J. Valjus, H. M. Tuononen, P. J. Ragona, *Angew. Chemie Int. Ed.* **2017**, 56, 6236–6240.

[2] C. M. E. Graham, T. E. Pritchard, P. D. Boyle, J. Valjus, H. M. Tuononen, P. J. Ragona, *manuscript in progress*.

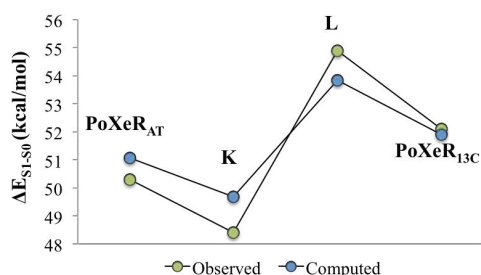
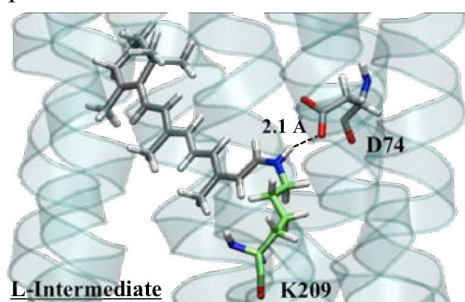
## QM/MM modeling of PoXeR:

### A light-driven inward proton pump with unidirectional rotary motion

**María del Carmen Marín<sup>1</sup>, Hideki Kandori<sup>2</sup>, Francesca Fanelli<sup>3</sup>, Luca De Vico<sup>1</sup> and Massimo Olivucci<sup>1</sup>**

<sup>1</sup>Department of Biotechnology, Chemistry and Pharmacy, University of Siena, Via Aldo Moro 2, Siena, Italy. <sup>2</sup>Department of Frontier Material, Graduate School of engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, Japan. <sup>3</sup>Department of Life Science, University Modena and Reggio Emilia, Via Università 4, Modena, Italy  
mariadelcarmen.ma@student.unisi.it

There are two types of membrane-embedded ion transport machineries in Nature: inward and outward. Two of the rhodopsins contained in the deep-ocean bacterium, *Parvularcula Oceani*, have a light-driven inward (from the outer to the inner side of the cell membrane) ion pump function. The *P. Oceani* inward H<sup>+</sup> pump rhodopsin PoXeR has, surprisingly, similar (51%) amino acid sequence to Anabaena Sensory Rhodopsin (ASR): a sensory rhodopsin which can be transformed into an inward H<sup>+</sup> pump via a single amino acid replacement.



In a previous computational study we have provided evidence that ASR works as a four-stages molecular rotor powered by two photons. Here, we present a parallel study on PoXeR. The results indicate that the same rotary motion is possible in PoXeR, even if powered by a single photon. The same results are also employed to understand how this rotary motion could couple to the inward H<sup>+</sup> transport. After looking at the computed structure of the L intermediate, we propose that a key event in the transport mechanism is the reorientation of the NH bond of the Schiff base towards the counterion (D74) thus facilitating the counterion protonation.

- [1] A. Kawanabe, Y. Furutani, K. H. Jung & H. Kandori, *JACS*. **131**, 16439 (2009).
- [2] A. Strambi, B. Durbeej, N. Ferré & M. Olivucci, *PNAS*. **107**, 21322 (2010).
- [3] K. Inoue, S. Ito, Y. Kato, Y. Nomura, M. Shibata, T. Uchihashi, S. P. Tsunoda & H. Kandori, *Nat. Commun.* **7**, 13415 (2016).

## Reaction Mechanisms of Polycyclic Aromatic Hydrocarbons with Oxygen: Site and Size Effects

Özlem Yönder<sup>1</sup>, Christof Hättig<sup>1</sup>

<sup>1</sup>*Institute for Theoretical Chemistry, Ruhr-University Bochum, D-44780 Bochum, Germany*

Coal-fired power plants produce about 40% of global electricity. Oxy-fuel combustion technology applied to conventional coal-fired power plants can reduce CO<sub>2</sub> and NO<sub>x</sub> emissions by operating under oxygen rich environments rather than those of normal atmospheric air. (To find details of the SFB/TRR 129 Oxyflame project visit the webpage: <http://www.oxyflame.com/>) Even though there is an intensive body of research on this technology, the governing reaction mechanisms are poorly understood and are mostly limited to simplified reaction models.

As an initial attempt to build a detailed reaction model, we aim to understand the reactions during the combustion of char. As a starting point to understand this process, we investigate the reaction mechanisms of polycyclic aromatic hydrocarbons (PAHs) with oxygen atoms. We use density functional theory calculations (DFT), TPSSh hybrid meta-GGA functional and the TZVP basis set. We particularly try to understand the effect of different molecular regions (Figure 1) and sizes of PAHs. Here, we report initial results for the reactions of triplet oxygen (O(<sup>3</sup>P)) with different sites of PAHs.

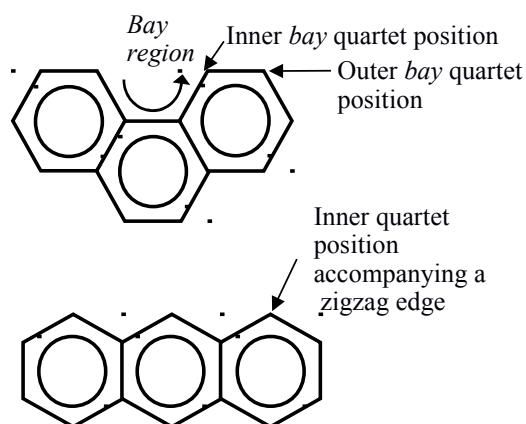


Figure 1: Phenanthrene and anthracene as an example to different molecular regions of PAHs.

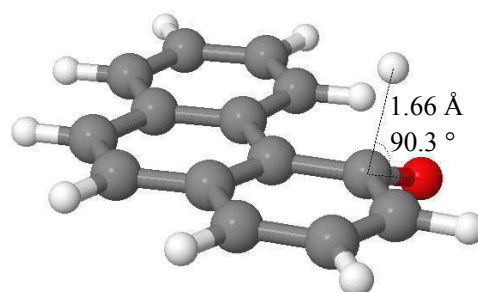


Figure 2: The transition state structure of phenanthrene for the *second step* of the oxygen addition reaction,  $C_{14}H_{10} + O(^3P) \rightarrow \cdot C_{14}H_{10}O \cdot \rightarrow \cdot C_{14}H_9O + H \cdot$ , to the inner bay quartet position.

## Studying the redox properties of DNA with hybrid quantum/classical molecular dynamics simulations

**Polydefkis Diamantis<sup>1</sup>, and Ursula Rothlisberger(\*)<sup>1</sup>**

<sup>1</sup>*Institute of Chemical Sciences and Engineering, EPFL, Rue Forel 2, CH-1015 Lausanne, Switzerland*

While the structure and function of enzymes involved in the recognition and repair of damaged bases in DNA is known, the mechanism through which they coordinate their action to interrogate the entire genome in a physiologically relevant time scale remains elusive. Recently, a scheme based on charge transfer has been proposed [1],[2], according to which DNA lesions are detected based on differences in redox properties compared to natural DNA bases. To investigate whether such a mechanism is possible, native and damaged DNA fragments in physiological conditions are simulated at the mixed quantum/classical level of theory, and their redox properties are computed using a theoretical method that associates them with the distributions of the vertical energy gaps between the two oxidation states [3-5]. Replacement of a guanine (G) by an 8-oxoguanine (8OG) defect leads to an increase of the DNA's oxidation potential by 0.93 V. This difference between G and 8OG is significantly higher than the corresponding value at the single nucleoside level (0.55 V [6]). The same methodology is currently applied to an isoguanine defect, while more lesions are also under consideration.

[1] A. K. Boal, J. C. Genereux, P. A. Sontz, J. A. Gralnick, D. K. Newman, J. K. Barton, *P.N.A.S.* **106**, 15237 (2009).

[2] M. A. Grodick, H. M. Segal, T. J. Zwang, J. K. Barton, *J. Am. Chem. Soc.* **136**, 6470 (2014).

[3] A. Warshel, *J. Phys. Chem.* **86**, 2218 (1982).

[4] G. King, A. Warshel, *J. Phys. Chem.* **93**, 8692 (1990).

[5] P. Diamantis, J. F. Gonthier, I. Tavernelli, U. Rothlisberger, *J. Phys. Chem. B* **118**, 3950 (2014).

[6] S. Steenken, S. V. Jovanovic, M. Bietti, K. Bernhard, *J. Am. Chem. Soc.* **122**, 2373 (2000).

## **Towards Branching Ratio Control in Hot Photoassociation of $\text{Mg}_2$ – Theory, Numerics and Experiment**

**Daniel M. Reich<sup>1</sup>, Wojciech Skomorowski<sup>1,2</sup>, Liat Levin<sup>3</sup>, Leonid Rybak<sup>3</sup>, Ronnie Kosloff<sup>4</sup>, Zohar Amitay<sup>3</sup>, Christiane P. Koch<sup>1</sup>**

<sup>1</sup>*Theoretische Physik, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany*

<sup>2</sup>*Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482, United States*

<sup>3</sup>*The Shirlee Jacobs Femtosecond Laser Research Laboratory, Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel*

<sup>4</sup>*Fritz Haber Research Centre and The Department of Physical Chemistry, Hebrew University, Jerusalem 91904, Israel*

Recently, coherent control of bond making has been successfully demonstrated under thermal conditions [1]. Specifically, in a strong-field multiphoton experiment using femtosecond laser pulses, it was found that the yield of detected magnesium dimer molecules was enhanced for positive chirps pulses and suppressed for negative chirps. Using an *ab initio* model it was demonstrated that control is achieved by purification combined with chirp-dependent Raman transitions. We will discuss the theoretical and numerical aspects that went into our modeling of the experiment and present new results which shed light onto the chirp-dependent dynamics invoked by the laser field. In particular we find that the optimal chirping rate depends on the considered UV emission wavelength, which provides a signature of the photoassociated dimers. This feature points towards the possibility to achieve branching ratio control in photoassociation experiments at room temperature.

- [1] L. Levin, W. Skomorowski, L. Rybak, R. Kosloff, C. P. Koch, and Z. Amitay *Phys. Rev. Lett.* **114**, 233003 (2015).

**Missing states and irregularities in excited states manifold of 2,2'-bithiophene  
– basis set dependence study**

**Marcin Andrzejak<sup>1</sup>, Mercedes Kukulka<sup>1</sup>, Henryk A. Witek<sup>2</sup>**

*<sup>1</sup> Department of Theoretical Chemistry, Faculty of Chemistry,  
Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland*

*<sup>2</sup> Department of Applied Chemistry and Institute of Molecular Science,  
National Chiao Tung University, Hsinchu, Taiwan*

At the example of the 2,2'-bithiophene it is shown that the excitation energy spectra computed using sequences of cc-pVnZ and aug-cc-pVnZ basis sets reveal surprisingly strong dependence of the excited states manifold on the quality of the basis set. The observed computational artefacts include: numerous missing states, wrong order of states, and considerable shifts in the energy spectrum [1]. The presented results suggest that the cc-pVnZ basis sets are completely unsuitable for modelling optical spectra of organic molecules and that the aug-cc-pVnZ basis sets are capable of predicting only the lowest portion of the energy spectrum. A simple and inexpensive remedy for the observed problems is suggested: an additional, molecule-centered, Rydberg basis should be rudimentarily used in quantum chemical calculations aiming at modeling optical spectra of molecules. The main conclusions seem to be general and independent of the chemical identity of the studied system (as demonstrated also for other organic chromophores) and of details of the employed computational methodology.

[1] M. Andrzejak, M. Kukulka, and H. A. Witek, *Mol. Phys.* in press.



## Computational study of the reaction mechanism of the selective catalytic reduction of NO<sub>x</sub> using the copper(II) zeolite catalyst SSZ-13

Julian Rudolph<sup>1</sup>, Christian-Andre Brauer<sup>1</sup>, Christoph R. Jacob<sup>1</sup>

<sup>1</sup>*TU Braunschweig, Institute of Physical and Theoretical Chemistry,  
Gaußstraße 17, 38106 Braunschweig*

The development and improvement of cheap and efficient ways to remove NO<sub>x</sub> from the exhaust gas of Diesel engines remains a major challenge for research in catalysis.

The selective catalytic reduction (SCR) of NO<sub>x</sub> by ammonia over copper-based catalysts is presently the predominant way to remove hazardous NO<sub>x</sub> from exhaust gases. In particular, the chabazite-based catalyst Cu-SSZ-13 has recently attracted strong interest due to its outstanding performance and hydrothermal stability. Although Cu-SSZ-13 has already been commercialized, the reaction mechanism and the structure of the active sites are strongly debated. A prerequisite for improving this known catalytic system is to understand the SCR mechanism over Cu-SSZ-13 [1,2].

Here, we present energetic studies for the SCR reaction based on density-functional theory (DFT) calculations. We choose the simplest possible model of the zeolite catalyst, which is used to explore different possible reaction paths for the reduction half-cycle. At every step of the proposed mechanism, different reaction steps are explored in order to identify or exclude possible intermediates. We also consider different possible charge states of the catalytic center [3].

We find that the SCR reaction on Cu catalysts proceeds via absorption of NH<sub>3</sub>, followed by building a NH<sub>2</sub>NO species which decomposes to nitrogen (N<sub>2</sub>) and water (H<sub>2</sub>O). The proposed mechanism is consistent with spectroscopic data [3].

[1] A. Boubnov, H. W. P. Carvalho, D. E. Doronkin, T. Günter, E. Gallo, A. J. Atkins, Ch. R. Jacob, J.-D. Grunwaldt, *J. Am. Chem. Soc.* **136**, 13006-13015 (2014).

[2] T. Günter, H. W. P. Carvalho, D. E. Doronkin, T. Sheppard, P. Glatzel, A. J. Atkins, J. Rudolph, Ch. R. Jacob, M. Casapu, J.-D. Grunwaldt, *Chem. Commun.* **51**, 9227-9230 (2015).

[3] J. Rudolph, C.-A. Brauer, Ch. R. Jacob, *to be submitted* (2017).

## Fast QM/MM Electronic Coupling Calculations for Charge Transfers in Proteins

Natacha Gillet,<sup>1</sup> Daniel Holub,<sup>1</sup> Marcus Elstner<sup>1</sup>

<sup>1</sup> Theoretical Chemical Biology, Karlsruhe Institute of Technology, Kaiserstr. 12, Karlsruhe, Germany

Long-range biological electron transfer (ET) reactions play an essential role in biological processes such as respiration, photosynthesis and enzymatic reactions. Complex and inhomogeneous ET requires computationally cheap approaches, in order to address the complexity of the medium and thermal fluctuations through many conformations.<sup>1</sup> Driving force and reorganization energies associated with ETs can be determined from QM/MM free energy calculations assuming a sufficient conformational sampling. However, the rate constant is also proportional to the square of the electronic coupling, while this latter decrease exponentially with distance. Biological complex environment helps to maintain a good electronic coupling value using intermediate redox states or tunneling the charge through protein backbone, aromatic residues or solvent.

Determination of the electronic coupling between the electronic states remain however more controversial at the theoretical level allowed by the size of the protein systems (DFT or semi-empirical/MM). To assess the necessary approximations associated with cheaper calculations, benchmarking analyses provide a base from which to investigate and compare the accuracy of the different methods and their respective sources of error.[2–4]

After a description of these benchmark studies, we focus on electronic coupling calculations for different ETs in protein using the FO/DFTB approach developed in our group [5,6]: tunneling in Azurin, comparison between direct and bridged transfer in a photolyase, long range charge transfer in ribonucleotide reductase through backbone, polar and aromatic residues.

[1] J. Blumberger, *Chem. Rev.* **115**, 11191 (2015).

[2] A. Kubas, F. Hoffmann, A. Heck, H. Oberhofer, M. Elstner and J. Blumberger, *J. Chem. Phys.* **140**, 104105 (2014).

[3] A. Kubas, F. Gajdos, A. Heck, H. Oberhofer, M. Elstner and J. Blumberger, *Phys Chem Chem Phys* **17**, 14342 (2015).

[4] N. Gillet, L. Berstis, X. Wu, F. Gajdos, A. Heck, A. de la Lande, J. Blumberger and M. Elstner, *J. Chem. Theory Comput.* **12**, 4793 (2016).

[5] T. Kubař, P. B. Woiczikowski, G. Cuniberti and M. Elstner, *J. Phys. Chem. B* **112**, 7937 (2008).

[6] A. Heck, J. J. Kranz, T. Kubař and M. Elstner, *J. Chem. Theory Comput.* **11**, 5068 (2015)

## Solvent Accessibility and Ligand Binding in Copper Nitrite Reductases

**Kakali Sen<sup>1,2</sup>, Michael A. Hough<sup>1</sup>, Richard W. Strange<sup>1</sup>, Chin W. Yong<sup>2</sup>,  
Thomas W. Keal<sup>2</sup>**

<sup>1</sup> *School of Biological Sciences, University of Essex, Wivenhoe Park, Colchester, Essex,  
CO4 3SQ, UK*

<sup>2</sup> *Scientific Computing Department, STFC Daresbury Laboratory, Warrington, Cheshire,  
WA4 4AD, UK*

Microbial copper-containing nitrite reductases (CuNiRs) are enzymes that catalyze the reduction of  $\text{NO}_2^-$  to  $\text{NO}$ , a key denitrification step in the global nitrogen cycle. This process involves a proton-coupled electron transfer reaction involving the two copper sites, the electron donating T1Cu site and the catalytic T2Cu site. We are investigating the pathways of proton and electron transfer and the reductive mechanism at the T2Cu site using multiscale computer modelling.

Initial classical MD simulations starting from crystal structures of two-and three-domain CuNiRs in their native state give an insight into how the flexible active site residue Asp<sub>CAT</sub> facilitates water and proton accessibility to the active site of  $\text{NO}_2^-$  reduction (T2Cu). The protonation state of Asp<sub>CAT</sub> enhances the mobility of either itself or other active site residues and this movement strongly influences solvent accessibility. With standalone QM and hybrid QM/MM studies on both native and ligand ( $\text{NO}_2^-$  and  $\text{NO}$ ) bound states we identify the conformations of the ligand binding at the T2Cu site. We further establish a correlation between the copper oxidation state and the conformational orientation of ligands bound at the T2Cu site. Our results corroborate closely to our serial crystallography observations of two different binding modes of  $\text{NO}_2^-$  at the T2Cu site to its oxidation state and loss of one water in native state on reduction of Cu at T2Cu site [1,2]. These results lay the foundation for combined QM/MM simulations to understand the underlying mechanistic reasons for the observed behaviors.

[1] S. Horrell, S. V. Antonyuk, R. R. Eady, S. S. Hasnain, M. A. Hough, R. W. Strange, *IUCrJ* **3**, 271 (2016)

[2] K. Sen, S. Horrell, D. Kelilli, C. W. Yong, T. W. Keal, H. Atakisi, D. W. Moreau, R. E. Thorne, M. A. Hough, R. W. Strange, *IUCrJ* **4**, (2017) [in press].  
<https://doi.org/10.1107/S2052252517007527>

**MetScore: Site of Metabolism Prediction beyond CYP P450 enzymes**

**Andreas H. Göller<sup>1</sup>, Arndt R. Finkelmann<sup>2</sup>, Daria Goldmann<sup>3</sup>, Gisbert Schneider<sup>2</sup>**

*1 Drug Discovery, Bayer Pharma Div., Bayer AG, 42096 Wuppertal, Germany.*

*2 Dept. of Chemistry and Applied Biosciences, ETH Zurich, Switzerland*

*3 Toxicology Research, Crop Science Div., Bayer AG, 06906 Sophia Antipolis, France.*

The complexity and diversity of chemical transformations involved in drug metabolism impose a hurdle on computational models for Site of Metabolism (SoM) prediction [1]. Ligand-based machine learning models are general and potentially useful tools for SoM prediction. Contrary to typical QSAR problems where one can use molecular descriptors, reactivity is atom-centered and needs atom descriptors that capture the reactivity-determining features, especially the anisotropy of the electron distribution.

Earlier, we developed multiple novel atom reactivity descriptors that characterize the steric and electronic environment, approximated by the mass or partial charge distribution in the atom's proximity. The charge distribution is based on charge schemes (NPA, CM5 DFTB+ charges) that have (a) a low method- and basis dependence and (b) a low dependence on conformation and therefore allow for a one-conformer approach [2].

High effort was put into the extraction, verification and cleaning of the training data, reducing the raw amount of more than 120,000 metabolic transformations from three different sources of published data to about 12,000 transformations for phase I and 6,000 transformations for phase II metabolism.

Random Forest machine learning with DFTB+ charge-based and steric atom descriptors as well as selected molecular descriptors yield two classification models for phase I [3] and phase II, respectively, with Matthews correlation coefficients of 0.63 and 0.75.

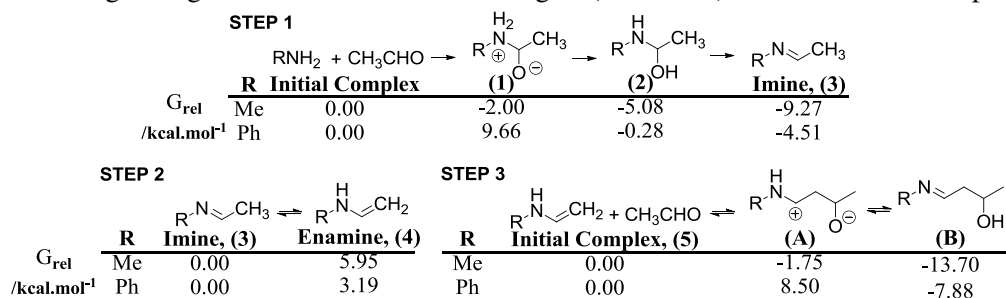
Even more important from the perspective of a medicinal chemist in need to stabilize his compound versus metabolism, the precision, *i.e.* the ratio of experimentally verified predicted SoMs, increased from 0.3 for our predecessor model CypScore to 0.6 for MetScore for a Bayer-internal benchmark data set as well as for a literature data set not included in training.

- [1] J. Kirchmair, A.H. Göller, D. Lang, J. Kunze, B. Testa, I.D. Wilson, R.C. Glen, G. Schneider: *Nat. Rev.*, **14**, 387 (2015).
- [2] A.R. Finkelmann, A.H. Göller, G. Schneider: *Chem. Commun.*, **52**, 681 (2016).
- [3] A.R. Finkelmann, A.H. Göller, G. Schneider: *ChemMedChem*, **12**, 505 (2017).
- [4] M. Hennemann, A. Friedl, M. Lobell, J. Keldenich, A. Hillisch, T. Clark, A.H. Göller: *ChemMedChem*, **4**, 657 (2009).

## DFT investigation for a new Route of the Prins-Reaction

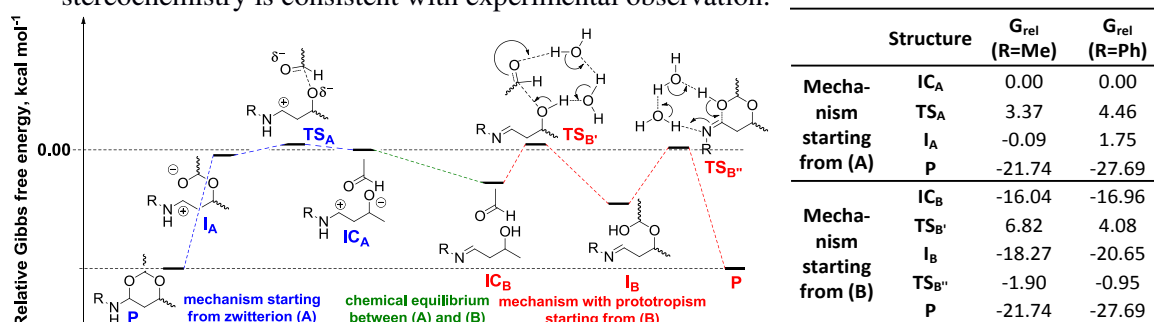
Rodolfo G. Fiorot<sup>1</sup>, G. Rambabu<sup>2</sup>, Y. B. Kiran<sup>2</sup>, José W. de M. Carneiro<sup>1</sup><sup>1</sup> Instituto de Química, Universidade Federal Fluminense, Outeiro de São João Batista, s/n, 24020-150 Niteroi, RJ, Brazil<sup>2</sup> Sree Vidyanikethan Engineering College, A. Rangampet, Tirupati, India

1,3-Dioxanes are important building blocks in organic synthesis, being found in natural products and bioactive compounds[1]. Motivated by a green protocol using no catalyst in aqueous medium[2], we investigated the mechanism for the unexpected formation of 2-amino-1,3-dioxanes from phenyl- (Ph) or methyl- (Me) amine and acetaldehyde, in a Prins-like mechanism as the main step. Structures were optimized with the  $\omega$ B97X-D/6-311++G(d,p) combination of functional and basis set. Implicit and explicit solvation effects (water) were included using the IEFPCM solvation method or the supermolecule model. Figure 1 gives relative Gibbs free-energies (kcal mol<sup>-1</sup>) for the three first steps.



**Figure 1.** Relative Gibbs Free Energies (kcal mol<sup>-1</sup>) for the initial steps.

The reaction steps represented above, which precede the Prins-like cyclization, occur with low relative energies for both amines. In the first step, explicit microsolvation is required to allow formation of the imine in aqueous medium [3]. In **step 3**, two isomers can be obtained: a zwitterion (A) and a molecule with no charge separation (B). Thus, two possibilities arise. In both of them stepwise pathways were found. Explicit water molecules are necessary to stabilize charges in the intermediates. Starting from A, the relevant transition state is **TS<sub>A</sub>**. Cyclization occurs with low activation energy, since it connects atoms with opposite charges. Starting from B, the mechanism involves prototropisms with transition state **TS<sub>B'</sub>**, forming intermediate **I<sub>B</sub>** which can cyclize through **TS<sub>B''</sub>**, leading to the product **P**. Although **IC<sub>B</sub>** is more stable than **IC<sub>A</sub>**, the transition states connecting the products have essentially same energy, therefore both pathways can be followed. Microsolvation is required in the mechanism involving prototropism. The final computed stereochemistry is consistent with experimental observation.



**Figure 2.** Mechanistic possibilities of the Prins-like step to afford 1,3-dioxane.

**Acknowledgements:** UFF, PPGQ-UFF, IQ-UFF, IFRJ.

[1] G. Marucci, A. et al. *Med. Chem. Res.* **14**, 274 (2005); [2] G. Rambabu, et al. *Res. Chem. Intermed.*, **41**, 8441 (2015); [3] C. Solís-Calero, et al. *Theor. Chem. Acc.*, **131**, 1263 (2012).

## Developing Inhibitors of the Enzyme “TRMT2A” for the Treatment of PolyQ Diseases

M.A. Margreiter<sup>1, 2</sup>, A. Voigt<sup>3</sup>, J.B. Schulz<sup>3, 4, 6</sup>, N.J. Shah<sup>4, 7</sup>, G. Rossetti<sup>1, 2, 3, 5</sup>

<sup>1</sup>*Institute of Advanced Simulations (IAS-5)*

<sup>2</sup>*Institute of Neuroscience and Medicine (INM-9)*

<sup>3</sup>*Department of Neurology, RWTH University Aachen, Aachen, Germany.*

<sup>4</sup>*JARA-Institute Molecular Neuroscience and Neuroimaging, Forschungszentrum Jülich GmbH and RWTH Aachen University, 52074, Aachen, Germany.*

<sup>5</sup>*JSC: Division Computational Science - Simulation Laboratory Biology - Jülich Supercomputing Centre (JSC)*

<sup>6</sup>*Institute of Neuroscience and Medicine (INM-11)*

<sup>7</sup>*Institute of Neuroscience and Medicine (INM-4)*

Polyglutamine (PolyQ) diseases are a heterogenic group of neurodegenerative disorders including Huntington’s disease (HD), for which no cure is available at this time. [1] Their common feature is an expanded CAG repeat in the coding region of the gene, which results in an extended Q tract in the protein, which leads to the formation of toxic aggregates.

Recently, experimental evidence produced by Dr. Voigt, in Prof. Schulz’s group, showed that inhibiting tRNA methyltransferase 2 homolog A (TRMT2A) function might cause an error-prone translation, leading to an increased number of non-Q insertions in the otherwise uninterrupted polyQ stretch. These interruptions decrease the probability of polyQ stretches to form toxic aggregates. Upon silencing the TRMT2A gene, decreased PolyQ aggregation was observed in yeast, flies and HEK293T cells.

TRMT2A features a catalytic domain (CD) and an RNA recognition motif (RRM). Successful inhibition of one of the two is thought to hamper TRMT2A function. We built a ligand-based pharmacophore model across known tRNA methyltransferase inhibitors against the CD. This was combined with structural models of the domain to allow educated guesses about spatial requirements of the binding pocket and protein-ligand interaction hotspots. The resulting molecules of this first ligand-based *in silico* screening successfully inhibit polyQ aggregation in HEK293 cells. In parallel, we are analysing the structural and dynamic properties of the RRM (crystalized by Dr. Niessing’s lab) by molecular dynamics simulations and bioinformatics tools. Possible druggable binding pockets have been identified, and structure-based virtual screening has been performed. Ligands are currently under test in Dr. Voigt’s lab. *Ex vivo* and *in vivo* magnetic resonance imaging on healthy and HD mouse brains will be performed in Prof. Shah’s lab.

1. Fan, H.-C. *et al.*, *Cell Transplantation* **23**, 441–458(18) (2014).

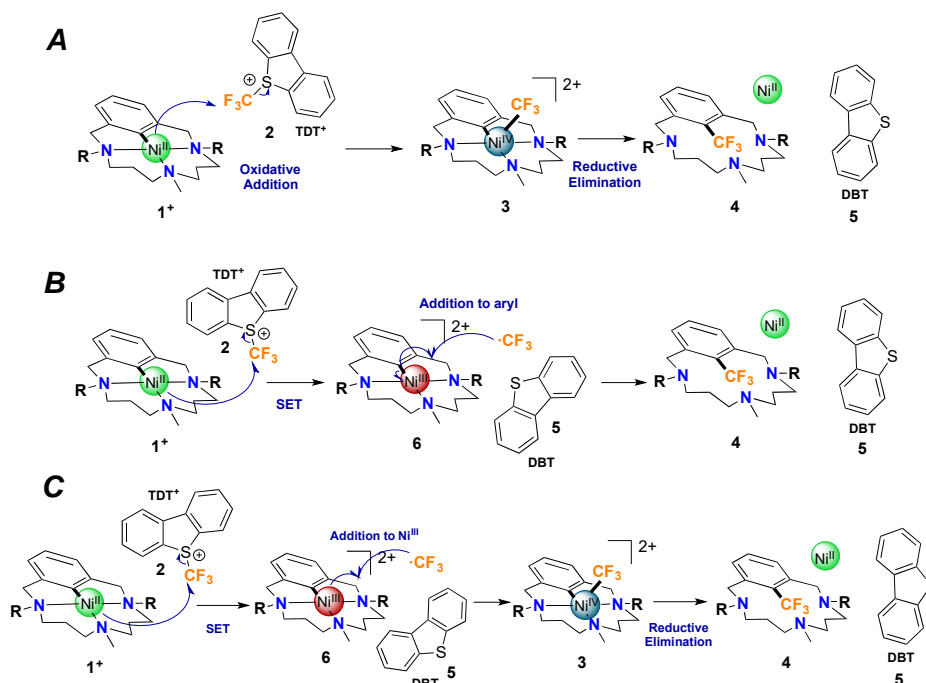
2. Irbäck, A. & Mohanty, S., *J Comput Chem* **27**, 1548–55 (2006).

## Mechanistic insights into trifluoromethylation of a planar aryl-Ni<sup>II</sup> complex involving Ni<sup>III</sup>/CF<sub>3</sub>• and Ni<sup>IV</sup>-CF<sub>3</sub> intermediate species

**Josep M. Luis, Steven Roldán-Gómez, Mireia Rovira, Xavi Ribas<sup>1</sup>**

<sup>1</sup> *Institut de Química Computacional i Catàlisi (IQCC) and Departament de Química, Universitat de Girona, Facultat Ciències, E17071 Girona (Catalonia), Spain*

The mechanism of the Nickel mediated trifluoromethylation of a model macrocyclic ligand (L<sub>1</sub>) has been studied by means of DFT. The reaction of [L<sub>1</sub>-Ni<sup>II</sup>](OTf) with CF<sub>3</sub><sup>+</sup> sources afforded L<sub>n</sub>-CF<sub>3</sub> products in quantitative yield. A combined experimental and theoretical mechanistic study provides new insights into the operative mechanism for this transformation. Three proposed mechanism A, B and C (see figure) were proposed. Computational analysis indicate the occurrence of an initial Single Electron Transfer (SET) to 5-(trifluoromethyl)dibenzothio-phenium triflate (TDTT) furnishing a transient L<sub>1</sub>-Ni<sup>III</sup>/CF<sub>3</sub>• adduct, which rapidly recombines to form a [L<sub>1</sub>-Ni<sup>IV</sup>-CF<sub>3</sub>](X)<sub>2</sub> intermediate species. A final facile reductive elimination affords L<sub>1</sub>-CF<sub>3</sub>. To the best of our knowledge, this is the first example of well-defined square-planar model platforms allowing stepwise information all the way through the redox chemistry of nickel, from Ni<sup>0</sup> to Ni<sup>IV</sup>, thus gaining insight into the geometry-dependent reactivity of multiple oxidation states and facilitating the development of new Ni-based trifluoromethylation methodologies.





## New aspects of the reactivity of rhenium tricarbonyl complexes towards activated alkynes through DFT calculations

M. Isabel Menéndez, Daniel Álvarez, Ramón López

<sup>1</sup>*Departamento de Química Física y Analítica, Universidad de Oviedo,  
C/ Julián Clavería 8, 33006 Oviedo, Spain*

The reactivity of rhenium(I) complexes of type  $[\text{ReX}(\text{CO})_3(\text{bipy})]$  ( $\text{X} = \text{OMe}$  (methoxo),  $\text{OH}$  (hydroxo),  $\text{NHpTol}$  (*para*-tolylamido),  $\text{PPh}_2$  (diphenylphosphanido);  $\text{bipy} = 2,2'$ -bipyridine) towards activated alkynes has been studied experimentally [1] and, in some cases, theoretically. [2] All reactions start with an initial attack of the nucleophilic ligand  $\text{X}$  to one of the acetylenic carbon atoms. In the alkoxo complex a vinyl carbanion forms and inserts into the  $\text{Re-OMe}$  bond, whereas in the hydroxo and amido complexes the just added alkyne bonds to a  $\text{CO}$  ligand in *cis* disposition forming a metallacycle that becomes highly stabilized by the transposition of a proton from the nucleophilic ligand to the attacked  $\text{CO}$ . Phosphanido complexes open the way to a new kind of product coming from the addition of the vinyl carbanion to the bidentate ligand, in spite of the inertness attributed to this kind of ligands. Neither experimental nor theoretical works have been reported for the reaction of  $[\text{Re}(\text{NRR}')(\text{CO})_3(\text{bipy})]$  complexes with activated alkynes such as methyl propiolate (HMAD,  $\text{HC}\equiv\text{CCO}_2\text{Me}$ ), so in this poster we present a theoretical study of the mechanism of this reaction and predict the expected product. On top of this, interesting issues come from the comparison of this information with that obtained for the analogous reaction with  $[\text{Re}(\text{PPh}_2)(\text{CO})_3(\text{bipy})]$ .

[1] a) E. Hevia, J. Pérez, L. Riera, V. Riera, *Organometallics* **21**, 1750 (2002). b) E. Hevia, J. Pérez, V. Riera, *Organometallics* **22**, 257 (2003). c) L. Cuesta, D.C. Gerbino, E. Hevia, D. Morales, M.E. Navarro-Clemente, J. Pérez, L. Riera, V. Riera, D. Miguel, I. del Río, S. García-Granda, *Chem. Eur. J.* **10**, 1765 (2004), d) A. Gabrielsson, M. Busby, P. Matousek, M. Towrie, E. Hevia, L. Cuesta, J. Pérez, S. Zális, A. Vlcek, Jr *Inorg. Chem.* **45**, 9789 (2006).

[2] D. Álvarez, R. Mera-Adasme, L. Riera, G.I. Cárdenas-Jirón, J. Pérez, J. Díaz, M.I. Menéndez, R. López, *Inorg. Chem.* DOI: 10.1021/acs.inorgchem.7b00767, Publication Date (Web): May 18, (2017).

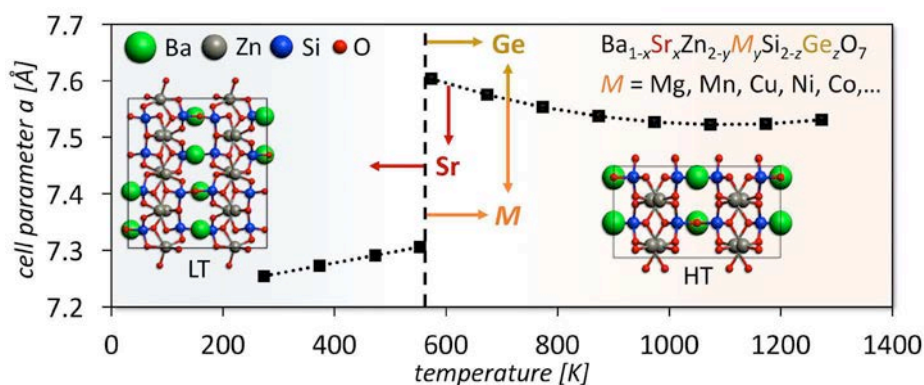


## *In silico* design of zero thermal expansion materials

Andreas Erlebach and Marek Sierka

*Otto Schott Institute of Materials Research, Friedrich Schiller University, Jena, Germany*

Materials showing no expansion with changing temperature have numerous applications ranging from commonplace ceramic hobs to astronomy. Among these materials are glass ceramics containing crystal phases with negative thermal expansion in one crystallographic direction, *e.g.*, the high temperature (HT) phase of  $\text{Ba}_{1-x}\text{Sr}_x\text{Zn}_{2-y}\text{M}_y\text{Si}_{2-z}\text{Ge}_z\text{O}_7$  ( $M=\text{Mg, Mn, Cu, Ni, etc.}$ ) solid solutions [1, 2]. Such a wide range of possible chemical compositions allows the targeted design of the structure and materials properties (*cf.* Figure), but makes the experimental characterization to a very demanding task. This work employs simulations at the DFT level for determination of the atomic structure, phase stability, mechanical properties and thermal expansion of  $\text{Ba}_{1-x}\text{Sr}_x\text{Zn}_{2-y}\text{M}_y\text{Si}_2\text{O}_7$  solid solutions. Structure optimizations yield not only a good agreement between calculated and experimentally observed cell parameters, but also a correlation of relative energies of the HT phase and the measured phase transition temperatures allowing a rapid, qualitative prediction of the phase stability with varying chemical composition. Furthermore, *ab initio* molecular dynamics simulations at constant pressure were used for calculation of the thermal expansion showing a remarkable agreement with experiments. Together with the predicted elastic constants, this provides vital information for optimization of the microstructure and fabrication of these zero thermal expansion glass ceramics.



**Figure** Change of structure and phase stability of the low (LT) and high temperature (HT) phase of  $\text{BaZn}_2\text{Si}_2\text{O}_7$  (black curve) caused by variation of the chemical composition.

- [1] C. Thieme, T. Waurischk, S. Heitmann, C. Rüssel, *Inorg. Chem.* **55**, 4476-4484 (2016).
- [2] C. Thieme, C. Rüssel, *Materials* **9**, 631 (2016).

## Structure Over Energy: An Alternative Approach for Low-Cost Methods in Crystal Structure Prediction

Luc M. LeBlanc<sup>1</sup>, Alberto Otero-de-la-Roza<sup>2</sup>, Erin R. Johnson<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Dalhousie University, 6274 Coburg Road, Halifax, Canada*

<sup>2</sup>*Department of Chemistry, University of British Columbia, Okanagan, 3247 University Way, Kelowna, Canada*

*In silico* prediction of crystal structures (CSP) strictly from a molecular diagram is a challenging task. The difficulties, in part, lie in developing electronic structure methods that are accurate enough to capture small energy differences, while remaining computationally inexpensive. While the various low-cost approximate methods proposed in the literature [1, 2] provide a framework to tackle the issue, the levels of accuracy achieved for computed energy differences between structures are unsatisfactory; it can be argued that their accuracy is insufficient to rank polymorphs or candidate crystal structures in the context of CSP. We propose an alternative approach: using low-cost methods as a means of yielding geometries that are transferred to single-point energy calculations with higher-level methods. Provided the low-cost method gives reliable geometries, this removes the need to correct for any errors due to, e.g., localized basis sets. The same accuracies for lattice energies as if one had used the high-level method alone are then obtained. Applications to organic molecular solids [3] and to preferential crystallization of chiral molecules [4] will be presented.

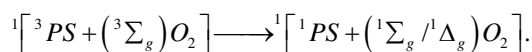
- [1] J. G. Brandenburg, M. Hochheim, T. Bredow, S. Grimme, *J. Phys. Chem. Lett.* **5**, 4275 (2014).
- [2] D. J. Carter, A. L. Rohl, *J. Chem. Theory. Comput.* **10**, 3423 (2014).
- [3] S. R. Whittleton, A. Otero-de-la-Roza, E. R. Johnson, *J. Chem. Theory Comput.* **13**, 441 (2017).
- [4] A. Otero-de-la-Roza, B. H. Cao, I. K. Price, J. E. Hein, E. R. Johnson, *Angew. Chem. Int. Ed.* **53**, 7879 (2014).

## A Kinetic Model for Singlet Oxygen Photosensitization

Shuming Bai<sup>1</sup>, Mario Barbatti<sup>1</sup>

<sup>1</sup>Aix Marseille Univ, CNRS, ICR, Marseille, France (shuming.bai@univ-amu.fr)

Thio-modified nucleobase derivatives have been often investigated as potential phototherapeutic agents, in which the generated singlet oxygen is the reactive oxygen species.<sup>1,2</sup> Using multireference quantum chemical methods, we have explained the unique phenomena during their photoexcitation and intersystem crossing process to T<sub>1</sub> state.<sup>3</sup> On the basis of the double  $\pi\pi^*$  minimum topography of T<sub>1</sub>, a two-step mechanistic model is proposed to explain the triplet intrinsic decay dynamics to S<sub>0</sub> in thionucleobases, which is accompanying and competitive process with the singlet oxygen production.<sup>4</sup> Based on these works, we focus on the last step of singlet oxygen generation, the photosensitization of PS-O<sub>2</sub> complex, where the photosensitizer PS is a thionucleobase:



To investigate this weakly-coupled intermolecular energy-transfer process directly from quantum chemical calculations, we have built a kinetic model for computation of the reaction rates. Based on a divide-to-conquer principle, the model splits the system into sets of orthogonal coordinates, to compute diabatic couplings, activation energies, and reorganization energies at minimum computation costs. It offers an effective way to evaluate the reaction probability along different incidence/orientation directions between the monomers of the PS-O<sub>2</sub> complex, thus, connecting reaction kinetics and quantum chemical calculations.

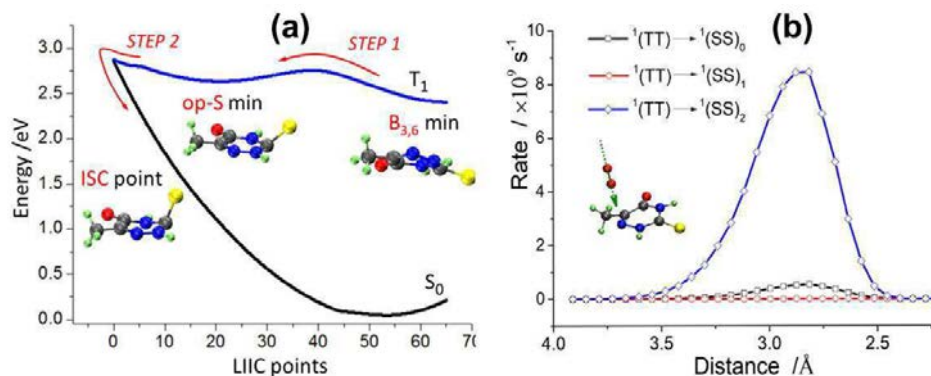


Figure 1. (a) Two-step model for triplet decay dynamics of thionucleobase; (b) The singlet oxygen photosensitization rates along one direction from the kinetic model.

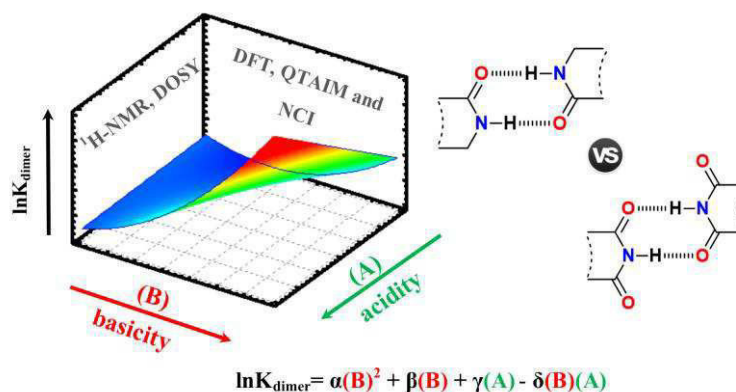
- [1] M. Pollum, et al, *J. Am. Chem. Soc.*, **136**, 17930 (2014).
- [2] H. Kuramochi, et al, *J. Phys. Chem. B*, **114**, 8782 (2010).
- [3] S. Bai and M. Barbatti, *J. Phys. Chem. A*, **120**, 6342 (2016).
- [4] S. Bai and M. Barbatti, *Phys. Chem. Chem. Phys.*, **19**, 12674 (2017).
- [5] S. Bai and M. Barbatti, *in preparation* (2017).

## The role of acceptor-donor capacity in amide and imide dimerization. A theoretical–experimental study

Wilmer E. Vallejo<sup>1</sup>, Eddy I. Jiménez<sup>2</sup>, Eduardo Romero-Montalvo<sup>1</sup>, Marcos Hernandez-Rodríguez<sup>2</sup> and Tomás Rocha-Rinza<sup>1</sup>

<sup>1</sup>Department of Physical Chemistry and <sup>2</sup>Department Organic Chemistry, Institute of Chemistry, National Autonomous University of Mexico, Circuito Exterior, Ciudad Universitaria, Mexico City.

Amides dimerize more strongly than imides in spite of the larger acidity of the latter functional group. This unexpected result had been explained regarding repulsions involving the spectator carbonyls in imides [1]. However, we did not find any indication of this repulsion by electron density topology analysis. Intrigued by this result, we studied the self-association of amides and imides through NMR experiments and theoretical calculations to give a rationale of this phenomenon based on electronic effects. We found that there is a good relationship among self-association constant, acidity of the N-H and the basicity of the carbonyl group, which conforms to a second-order polynomial model. This model describes an appropriate balance between the acceptor and donor capacity, which in turn explains the experimental results. The findings not only explain the studied phenomenon but also provide a predictive model which can be used to examine more complicated hydrogen bonded systems involving these functional groups in areas such as molecular recognition, synthesis of supramolecular materials, crystal engineering, organocatalysis and sensor design.



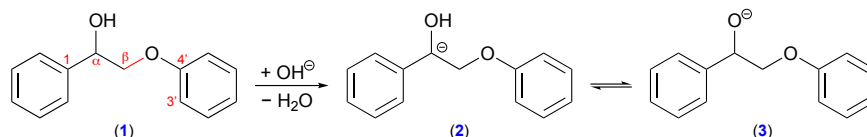
[1] K.-S. Jeong, et al., *J. Am. Chem. Soc.* **112**, 3215 (1990).

## Molecular Dynamics Study of Lignin Degradation under High Pressure and Temperature

Timm Lankau, Chin Hui Yu\*

Department of Chemistry, National Tsing Hua University, 101 KuangFu Road Sec.2,  
HsinChu 30013, Taiwan

The base catalysed depolymerisation (BCD) of lignin [1] into small molecules as an alternative feedstock becomes increasingly important in the search for sustainable chemical feedstocks. A recent computational study [2] of the hydrolysis of 2-phenoxy-1-phenylethanol (1) as model for the  $\beta\text{O}4'$  linkage in lignin showed that the cleavage of the  $\beta\text{O}4'$  link can either arise from the carbanion (2) or the alkoxide (3).



Both anions yield the desired products, but the reaction path starting from the alkoxide (3) passes through intermediate oxiranes which can partake in the formation of undesired byproducts. While the different pathways are clearly separated from each other at low temperatures, QM/MM molecular dynamics simulations of (2) and (3) in aqueous solution indicate that this difference vanishes at high temperatures and low solvent densities mimicking the reactors used for the BCD experiments in the laboratory. Hence, any attempt to increase the selectivity of the lignin hydrolysis has to include a reduction of the reaction temperature.

[1] V. M. Roberts, V. Stein, T. Reiner, A. Lemonidou, X. Li, J. A. Lercher, *Chem. Eur. J.* **17**, 5939 (2011).

[2] T. Lankau, C. H. Yu, *Green Chem.* **18**, 1590 (2016).

## Excited state gradients in polarizable QM/MM models: an induced dipole formulation

Maximilian F.S.J. Menger<sup>1,2</sup>, Stefano Caprasecca<sup>1</sup>, Benedetta Mennucci<sup>1</sup>

<sup>1</sup>*Dipartimento di Chimica e Chimica Industriale, University of Pisa, Via Giuseppe Moruzzi 13, 56124 Pisa, Italy.*

<sup>2</sup>*Institut für Theoretische Chemie, Faculty of Chemistry, Währinger Str. 17, A-1090 Wien, Austria.*

Charge and structural properties of electronically excited states in embedded systems are strongly affected by the environment. Multiscale approaches where different levels of theory are combined in a single calculation, have shown to properly describe such effects combining accuracy with computational efficiency.

Here we present an extension of a fully polarizable QM/MM scheme to analytic excited state gradients following a Lagrangian approach [1, 2]. Time-dependent density functional theory is used as the QM method of choice, whereas the classical environment is treated in terms of a polarizable force-field, where the polarization is included through induced dipoles [3]. The method is applied to study of formation and relaxation of the bright excited state of an organic dye (DAPI) intercalated in a DNA pocket. The results indicate the non negligible effect of polarization between the DAPI and DNA pocket, in determining the fluorescence properties of the embedded dye [4].

**Acknowledgments:** MM gratefully acknowledges financial support from the European Union's Horizon 2020 research and innovation program under the Marie Curie Skłodowska-Curie grant agreement No.642294.

- [1] F. Furche, R. Ahlrichs, *J. Chem. Phys.* **117** 2002; Erratum *J. Chem. Phys.* **121**, 2004.
- [2] G. Scalmani *et al.* *J. Chem. Phys.* **124**, 2006.
- [3] S. Caprasecca *et al.* *J. Chem. Theory Comput.* **10**, 2014.
- [4] M. Menger, S. Caprasecca, B. Mennucci *submitted* 2017.

## Computational insights into induction period of ethylene polymerization by the $\text{CrO}_x/\text{SiO}_2$ (Phillips) catalyst

**Maciej Gierada, Jarosław Handzlik**

*Faculty of Chemical Engineering and Technology, Cracow University of Technology,  
ul. Warszawska 24, 31-155 Kraków, Poland; e-mail: mgierada@chemia.pk.edu.pl*

The ( $\text{CrO}_x/\text{SiO}_2$ ) Phillips catalyst is one of the most commonly used chemical system to perform ethylene polymerization that currently accounts for about 40-50% of world's annual total production of high-density polyethylene [1]. However, a chemical nature of this catalyst is not well known. In particular, one of the biggest questions concerns the so-called induction period, i.e., the initial stage of the reaction when its rate is very low. We still do not know how do the initial oxidized Cr(VI) species transform into Cr(II) and Cr(III) and what is the reason for the observed induction period. Here, based on DFT investigations, we aim to solve these issues.

The cluster models of the system studied were developed employing two different amorphous silica structures: (i) derived from  $\beta$ -cristobalite framework [2] and (ii) from previous periodic simulations [3-5]. Geometry optimization were performed using the PBE0 functional combined with the def2-SVP basis sets. Dispersion interactions were included in the single point energy calculations at the PBE0-D3/def2-TZVPP level of theory. In some of the reaction pathways studied, spin-crossing occurs and we calculated minimum energy crossing points (MECPs) between two potential energy surfaces, following the methodology developed by Harvey and co-workers.

We have found that the most kinetically favored reduction pathway involves the reaction between ethylene and both oxo ligands of the major dioxo Cr(VI) surface species. Consequently, the Cr(II) site should be formed together with two formaldehyde molecules. The calculated energy barrier for reduction is comparable with that for initiation [6]. We also propose that surface defects might be involved into one-electron Cr(II) to Cr(III) transformation [6].

**Acknowledgments:** This work was supported by the National Science Centre, Poland, Project No. 2015/19/N/ST4/00007, and by the PL-Grid Infrastructure.

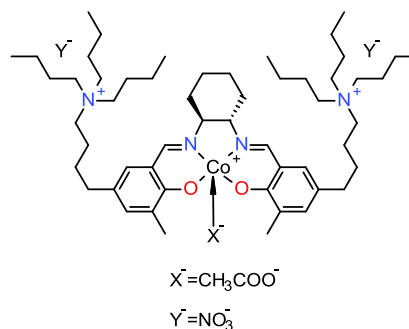
- [1] M. P. McDaniel, *Adv. Catal.* **123** (2010).
- [2] A. F. Wright, A. J. Leadbetter, *Philos. Mag.* **31**, 1391 (1975).
- [3] F. Tielens, C. Gervais, J. F. Lambert, F. Mauri, D. Costa, *Chem. Mater.* **20**, 3336 (2008).
- [4] J. Handzlik, R. Grybos, F. Tielens, *J. Chem. Phys. C*, **117**, 8138 (2013).
- [5] M. Gierada, P. Michorczyk, F. Tielens, J. Handzlik, *J. Catal.* **340**, 122 (2016).
- [6] M. Gierada, J. Handzlik, *J. Catal.* (2017),  
<http://dx.doi.org/10.1016/j.jcat.2017.05.025>.

## Theoretical studies on the cobalt(III)-based catalysts for CO<sub>2</sub>/epoxide copolymerization

Karol Dyduch, Monika Srebro-Hooper, Artur Michalak

*Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University,  
R. Ingardena 3, 30-060 Krakow, Poland*

Over the last few years several highly active and selective catalytic systems towards transformation of CO<sub>2</sub> into biodegradable polycarbonates have been reported [1]. One of the most promising catalyst generation is based on cobalt(III)-salen-type scaffolds and includes so-called binary and bifunctional catalytic systems [2]. The former consist of electrophilic part (electroneutral organometallic octahedral Co(III) complex with tetradentate salen-type ligand) and nucleophilic part (quaternary ammonium salt) acting as a co-catalyst; both playing a significant role during formation and growth of a polymer chain [2]. In the latter (see the figure), electrophilic and nucleophilic parts are combined into a single chemical entity, resulting in much higher catalytic activity of bifunctional vs. binary systems. Based on experimental premises from studies on simple Co(III)-salen complexes, the ability to adopt distinctive geometrical isomers is listed among factors that affect the catalytic activity of these compounds [3,4]. However, there is still no information which of possible isomer is preferred in a case of bifunctional catalysts and whether such preference is affected by structure and arrangement of cationic chains. The main goal of presented theoretical studies is to provide insight into stability of geometrical isomers for bifunctional catalytic systems. To ensure a proper sampling of the conformational space of such complexes the computational protocol employing extensive conformational search at the level of semiempirical method for preliminary selection of conformers followed by DFT optimizations and energy refinement was proposed. Preliminary analysis of possible intermediates in the catalytic CO<sub>2</sub>/epoxide copolymerization cycle for simplified catalyst models will also be presented.



- [1] G. W. Coates, D. R. Moore, *Angew. Chem. Int. Ed.* **43**, 6618 (2004).
- [2] X.-B. Lu, W.-M. Ren, G.-P. Wu, *Acc. Chem. Res.* **45**, 1721 (2012).
- [3] P. D. Knight, P. Scott, *Coord. Chem. Rev.* **242**, 125 (2003).
- [4] A. Cyriac, J. Y. Jeon, J. K. Varghese, J. H. Park, S. Y. Choi, Y. K. Chung, B. Y. Lee, *Dalton Trans.* **41**, 1444 (2012).



## An Algorithm to Locate Optimal Bond Breaking Points on Potential Energy Surfaces for Mechanochemical Reactions

**Josep Maria Bofill<sup>1</sup>, Jordi Ribas-Ariño<sup>2</sup>, Sergio Pablo García<sup>2</sup>, Wolfgang Quapp<sup>3</sup>**

<sup>1</sup>*Departament de Química Inorgànica i Orgànica and IQTCUB, Universitat de Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain. E-mail: jmbofill@ub.edu*

<sup>2</sup>*Departament de Ciència de Materials i Química Física and IQTCUB, Universitat de Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain. E-mail: j.ribas@ub.edu*

<sup>3</sup>*Mathematisches Institut, Universität Leipzig, Augustus-Platz PF 100920, D-04009 Leipzig, Germany. E-mail: quapp@uni-leipzig.de*

Mechanochemistry is an emerging research field that focuses on the promotion of chemical reactions by means of mechanical forces.[1] It is well established that the force-induced structural changes of minima and saddle points can be described by a Newton Trajectory (NT) on the original or stress-free potential energy surface (PES).[2] Given a reactive molecular system and a well-fitting pulling direction, there is a sufficiently large value of the force for which the minimum configuration of the reactant and the saddle point configuration of a transition state collapse at one point on the corresponding NT. This point is called barrier breakdown point or bond breaking point (BBP).[3] The Hessian matrix at the BBP has a zero eigenvalue and the corresponding gradient indicates which force (both in magnitude and direction) should be applied to the system to mechanically induce the reaction in a barrierless process. Within the manifold of BBPs, there exist optimal BBPs [3] which indicate what is the optimal pulling direction and what is the minimal magnitude of the force to be applied for a given mechanochemical transformation. At the optimal BBPs, the gradient coincides with the eigenvector of the Hessian matrix with null eigenvalue. Since these special points are very important in the context of mechanochemistry and catalysis, it is crucial to develop efficient algorithms for their location. Here, we shall present a Gauss-Newton algorithm that is based on the minimization of a positively defined function (the so called  $\sigma$ -function). The behavior and efficiency of the new algorithm will be shown for 2D test functions and for a real chemical example.

[1] J.Ribas-Arino and D. Marx, *Chem.Rev.* **112**, 5412 (2012); T. Stauch and A. Dreuw, *Chem. Rev.* **116**, 14137 (2016).

[2] J.M. Bofill and W. Quapp, *J. Chem. Phys.* **134**, 074101 (2011).

[3] J.M. Bofill and W. Quapp, *Theor. Chem. Acc.* **135**, 113 (2016).

## A Stochastic approach to thermal density functional theory

**Yael Cytter<sup>1</sup>, Daniel Neuhauser<sup>2</sup>, Eran Rabani<sup>3</sup>, Roi Baer<sup>1</sup>**

<sup>1</sup>*Fritz Haber Center for Molecular Dynamics, Institute of Chemistry, Hebrew University of Jerusalem, Israel*

<sup>2</sup>*Department of Chemistry and Biochemistry, University of California, USA*

<sup>3</sup>*Department of Chemistry, University of California and Lawrence Berkeley National Laboratory, USA*

Warm dense matter (WDM) is a phase characterized by temperatures of the order of 10,000 K and high nuclei densities. WDM is of high interest in many fields of physics, chemistry, planetary sciences and even industry: from giant gas planets, the earth's core, laser-heated solids and surfaces, and up to ignition of inertial confinement fusion capsules. Nowadays, using intense lasers, WDM properties can be investigated in the laboratory, thus requiring attention to theoretical research for interpretation and understanding of the results. In terms of tools for theoretical description it is considered a complex regime, being the intermediate between condensed matter physics (i.e., quantum description) and plasma physics (classic thermodynamics). WDM is often described theoretically using finite-temperature Kohn-Sham (KS) density functional theory (DFT) calculations with reasonably good agreement to experiments. These calculations in finite (non-zero) temperatures are, however, extremely expensive due to the large number of fractionally occupied KS orbitals involved in them. In fact, the computational cost exhibits exponential scaling with temperature. Orbital-free DFT is often considered a solution to this problem as it uses non-interacting kinetic energy approximations that depends directly on the electronic density, thus avoiding the use of KS orbitals. This approximation, however, has been known to be less accurate than the KS single particle wave function approach.

Stochastic methods, developed recently [1] appear to be a fitting approach to this scaling problem, since it is somewhat of an orbital free KS method. It uses the states occupation operator to calculate the energy, but skips the step of finding the orbitals and finds the electronic density by taking the trace of it using random orbitals. We introduce stochastic calculations of the canonical free energy. We further demonstrate our ability to calculate the zero pressure lattice constant (first order derivative) and the bulk modulus (second order derivative) of bulk silicon in different temperatures, despite the noise associated with the calculations. I will discuss the calculations' convergence as a function of temperature and system size as well as the computational effort that is required for it.

- [1] R. Baer, D. Neuhauser, E. Rabani, *Phys. Rev. Lett.* **111**, 106402 (2013)

# Comparing non-empirical DFT tuning procedures as a starting point for $G_0W_0$

J. Bois<sup>1</sup>, T. Körzdörfer<sup>1</sup>

<sup>1</sup>AG Computational Chemistry, Institute of Chemistry, University of Potsdam, Karl-Liebknecht-Strasse 24-25, Potsdam, Germany

The ability to accurately predict the ionization potential (IP) of organic molecules and polymers is imperative for progress in theoretical calculations of organic electronic materials. Many body perturbation theory within the  $GW$  approximation is a method widely used for the calculation of IPs, both self-consistently (known as  $ScGW$ ) and as a single step correction on top of a DFT calculation (known as  $G_0W_0$ ). It has been shown that, in combination with the right DFT starting point,  $G_0W_0$  calculations can give extremely accurate IPs for a wide range of systems at a fraction of the cost of  $ScGW$ . The choice of the functional used in the underlying DFT calculation is, however, non-trivial, as a strong starting point dependence of  $G_0W_0$  can be observed.

To obtain a reliable IP from  $G_0W_0$ , using an exchange-correlation functional as a starting point that already describes the IP relatively well is imperative. Such an accurate description of a systems IP by DFT can be achieved by non-empirical tuning procedures, which vary the amount of exact exchange in a hybrid functional, resulting in a system specific functional. While in general non-empirical tuning methods have been shown to give improved results for a range of problems over standard DFT functionals, they can suffer from a lack of size consistency. Unfortunately, size consistency is a crucial characteristic for the investigation of organic polymers following the oligomer approach, where polymer properties are extrapolated from the property trends of increasingly long oligomer chains.[1]

We have investigated three unique tuning procedures, both with and without size consistency, as a starting point for  $G_0W_0$  to predict the IPs of a series of polyacetylene oligomers. The DFT  $\Delta$ SCF IPs showed a strong dependence on the fraction of exact exchange present in the functional and hence on the size consistency of the tuning procedure, with the most reliable results given by the most size consistent method. In contrast, the HOMO eigenvalue IPs obtained after the  $G_0W_0$  correction seemed not to depend on size consistency, as the  $G_0W_0$  correction step was able to counteract the trends with increasing oligomer length. It was shown that although IP tuning lacks size consistency, making it problematic for many calculations on  $\pi$ -conjugated polymers, it is a good starting point for  $G_0W_0$  calculations of IPs and provides results in excellent agreement with CCSD(T) reference data.[2]

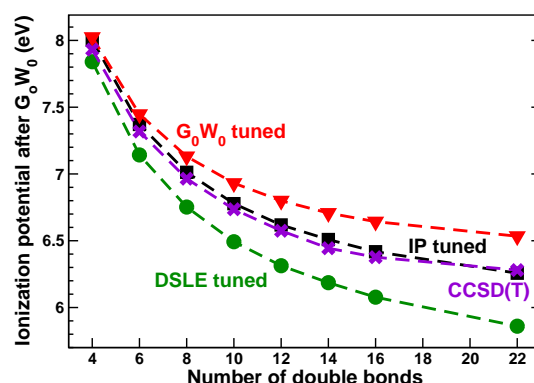


Figure 1: Evolution of ionization potential with polyacetylene chainlength for different  $G_0W_0$  starting points.

[1] J. Bois, T. Körzdörfer, *J. Chem. Theory Comput.* **12**, 1872-1882 (2016).

[2] J. Bois, T. Körzdörfer, submitted, arXiv:1706.00196 (2017).

## Comparing anharmonic *ab initio* methods: Determining IR spectra of $\text{N}_2\text{O}_5 + \text{X}^-$ ( $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$ )

Laura M. McCaslin<sup>1</sup>, R. Benny Gerber<sup>1, 2</sup>

<sup>1</sup>*Department of Physical Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

<sup>2</sup>*Department of Chemistry, University of California-Irvine, Irvine, California 92697, United States of America*

$\text{N}_2\text{O}_5$  participates in many complex and essential reactions in the regulation of atmospheric ozone, formation of secondary organic aerosols, and deposition of acid precipitation on the Earth's surface. Specifically, multiphase reactions of atmospheric  $\text{N}_2\text{O}_5$  at the ocean surface have gained much scientific interest due to the high density of accessible reaction pathways at ambient temperatures. While many mechanisms for these heterogeneous reactions have been proposed, laboratory experiments and theoretical analysis are necessary to confirm these hypotheses. Our work analyzes the IR spectra of the model system  $\text{N}_2\text{O}_5 + \text{X}^-$  ( $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$ ) reacting in water. Due to the weakly-bound character of these systems, harmonic analysis alone cannot be expected to accurately predict experimental frequencies and intensities. In this work we present the IR spectra of  $\text{N}_2\text{O}_5 + \text{X}^-$  computed using two anharmonic methods: vibrational self-consistent field theory (VSCF) and spectra determined from classical Born-Oppenheimer molecular dynamics (BOMD). We find that at the  $\omega\text{B97X-D/aug-cc-pVDZ}$  level, anharmonic frequency shifts are much smaller than the differences between calculated harmonic and experimental frequencies, indicating the system's strong dependence on chosen potential. Significant anharmonic blue shifts in the asymmetric  $\text{NO}_2$  and  $\text{NO}_3$  stretches are found in these calculations, which point to the potential "hardening" effect of the halide. Intensities calculated by each method are compared and discussed showing that VSCF-computed relative intensities compare significantly more favorably to experimental results than those calculated from BOMD trajectories, indicating significant quantum effects (i.e. interference) not well-described by classical BOMD. Despite the two theories' starkly different theoretical underpinnings, we find that for these systems, anharmonic frequency shifts calculated from VSCF and BOMD trajectories are qualitatively similar, though VSCF remains far superior in generating relative intensities due to its quantum foundation.

## Accurate Embedding based on Potential Reconstruction: Top-Down vs. Bottom-Up

David Schnieders<sup>1,2</sup>, Johannes Neugebauer<sup>1,2</sup>

<sup>1</sup>*Organisch-Chemisches Institut, WWU Münster, Corrensstraße 40, 48149 Münster, Germany*

<sup>2</sup>*Center for Multiscale Theory and Computation, Corrensstraße 40, 48149 Münster, Germany*

Approximate QM/QM embedding methods based on Frozen-Density Embedding theory suffer from rather poor approximations to the non-additive kinetic energy and the corresponding potential in applications to strongly interacting systems [1]. Several accurate embedding approaches related to Frozen-Density Embedding using potential reconstruction techniques have been proposed in the literature [2, 3, 4, 5]. It could be shown that this allows to generate potentials that accurately reproduce Kohn–Sham DFT densities [3, 4]. Within our quantum chemistry code SERENITY, we implemented a variety of reconstruction techniques. We distinguish between the “top-down” reconstruction approach [4], requiring an initial supersystem calculation, and the “bottom-up” reconstruction approach [3, 6], which iteratively generates supersystem densities as a sum of subsystem densities. Both are available in this implementation. Here, we compare the advantages and disadvantages of these approaches as well as their dependence on initial guesses/fragmentations and explore possible simplifications suitable for larger systems.

- [1] Fux, S.; Kiewisch, K.; Jacob, C. R.; Neugebauer, J.; Reiher, M. *Chem. Phys. Lett.* **461**, 353 (2008).
- [2] Roncero, O.; de Lara-Castells, M. P.; Villarreal, P.; Flores, F.; Ortega, J.; Paniagua, M.; Aguado, A. *J. Chem. Phys.* **129**, 184104 (2008).
- [3] Goodpaster, J. D.; Ananth, N.; Manby, F. R.; Miller III, T. F. *Chem. Phys. Lett.* **133**, 084103 (2010).
- [4] Fux, S.; Jacob, C. R.; Neugebauer, J.; Visscher, L.; Reiher, M. *J. Chem. Phys.* **132**, 164101 (2010).
- [5] Huang, C.; Carter, E. A. *J. Chem. Phys.* **134**, 154110 (2011).
- [6] Unsleber, J. P.; Neugebauer, J.; Jacob, C. R. *Phys. Chem. Chem. Phys.* **18**, 21001 (2016).

## The Global Reaction Route Map DB and QM-based Conformational Search

Hiroko Satoh<sup>1,2</sup>, Tomohiro Oda<sup>3</sup>, Kumiyo Nakakoji<sup>4</sup>, Takeaki Uno<sup>5</sup>,  
Satoru Iwata<sup>6</sup>, Koichi Ohno<sup>7</sup>

<sup>1</sup> Research Organization of Information and Systems (ROIS), Minatoku, Tokyo, Japan

<sup>2</sup> Department of Chemistry, University of Zurich, Winterthurerstr. 190, Zurich, Switzerland

<sup>3</sup> Software Research Associates Inc., Toshimaku, Tokyo, Japan

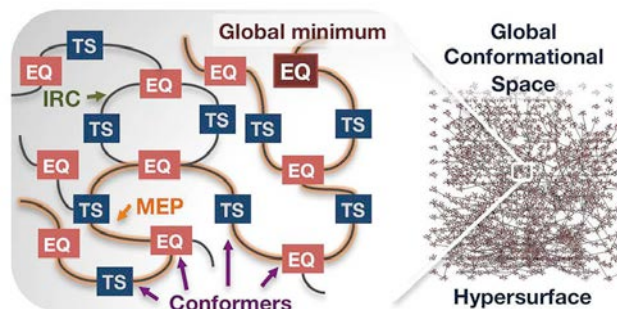
<sup>4</sup> C-PIER, Kyoto University, Sakyo, Kyoto, Japan

<sup>5</sup> National Institute of Informatics (NII), Chiyodaku, Tokyo, Japan

<sup>6</sup> Department of Mathematical Informatics, University of Tokyo, Bunkyo, Tokyo, Japan

<sup>7</sup> Department of Chemistry, Tohoku University, Aoba, Sendai, Japan

Our QM-based data centric chemistry project is based on *Global Reaction Route Mappings* (GRRM) for molecular and reaction discovery.<sup>1</sup> The approach globally explores potential energy surfaces (PES) of various chemical formulae in different QM levels to obtain reaction route maps (r-maps). We have developed a tool to collect data about r-maps (r-map DB) and an interactive analytical software system for the r-map DB, called RMapView (<https://github.com/ReactionMap/RMapView>). Each of the r-map is composed of equilibrium (EQ) and dissociation channel (DC) structures connected by IRC reaction routes via transition state (TS) structures obtained by the PES-search using the *Scaled Hypersphere Search of the Anharmonic Downward Distortion Following* method (SHS-ADDF)<sup>2</sup>. In the QM-based data centric chemistry project, we have applied the SHS-ADDF and RMapView to automatic deduction of conformational transition networks.<sup>3</sup> This search uses large ADDF, which makes it possible to trace only low TS barriers while restraining bond lengths and structures with high free energy. We have obtained conformational landscapes of D-glucose conformers with this method. We present the overview of our project, the development of the r-map DB and RMapView, and the application to the QM-based conformational search.



- [1] H. Satoh, T. Oda, K. Nakakoji, T. Uno, S. Iwata, K. Ohno, *J. Comput. Chem., Jpn.* **14**, 77 (2015).
- [2] K. Ohno, S. Maeda, *Chem. Phys. Lett.* **384**, 277 (2004).
- [3] H. Satoh, T. Oda, K. Nakakoji, T. Uno, H. Tanaka, S. Iwata, K. Ohno, *J. Chem. Theory Comput.* **12**, 5293 (2016).

## Large-Scale First-Principles GW+Bethe-Salpeter Simulations Targeting 200 Atom Systems

Yoshifumi Noguchi and Osamu Sugino

*Institute for Solid State Physics, The University of Tokyo,  
5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, JAPAN*

First-principles GW+Bethe-Salepter method is a well-established method, based on many-body perturbation theory that goes beyond the framework of density functional theory (DFT). This method is capable of simulating the optical properties of not only isolated systems such as molecules and clusters but also extended systems such as crystals. The applications of this method have increased over the recent years. However, greater computational expense compared with conventional DFT, strongly restricted the tractable system size. We addressed this problem in the past several years by employing large-scale parallel computations. Our original program employs an all-electron mixed basis approach, in which a one-particle wave function was expressed as a linear combination of numerical atomic orbitals (AOs) and plane waves (PWs), is now capable of handling thousands of CPU cores without significantly reducing the parallel efficiency. Moreover, we can complete the GW+Bethe-Salpeter calculations for the molecules composed of up to N=200 atoms without necessitating any reduction in the computational accuracy.

In this demonstrative study, we applied our method to some carbon-based molecules such as a defective warped nanographene (= 110 atoms) [1], cycloparaphenylene (= 30-160 atoms) [2], and carbon nanocages (= 108-198 atoms) [3]. The theoretical accuracy of our method was evaluated and agree quite well with the available experimental UV-vis absorption spectra. In addition, we propose the exciton wave function-based analysis method [4] to quantify each type of exciton. We discuss a novel perspective arising from our method, which elucidates the detailed optical properties of the above molecules in terms of overlap strength between electron and hole wave function, exciton size, electron-hole separation distance, electron (hole) delocalization, exciton binding energy, and exciton maps.

- [1] Y. Noguchi and O. Sugino, J. Chem. Phys., **142**, 064313 (2015).
- [2] Y. Noguchi and O. Sugino, J. Chem. Phys., **146**, 144304 (2017).
- [3] D. Hirose, Y. Noguchi and O. Sugino, in preparation.
- [4] D. Hirose, Y. Noguchi, and O. Sugino, J. Chem. Phys., **146**, 044303 (2017).

## Implementation of divide-and-conquer density-functional tight-binding method for large-scale quantum mechanical molecular dynamics simulations

Yoshifumi Nishimura<sup>1</sup>, Hiromi Nakai<sup>1-4</sup>

<sup>1</sup>*Research Institute for Science and Engineering, Waseda University,  
3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan*

<sup>2</sup>*Department of Chemistry and Biochemistry, Waseda University,  
3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan*

<sup>3</sup>*CREST, Japan Science and Technology Agency,  
4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan*

<sup>4</sup>*ESICB, Kyoto University, Kyotodaigaku-Katsura, Kyoto 615-8520, Japan*

We have recently reported an implementation of divide-and-conquer density-functional tight-binding molecular dynamics (DC-DFTB-MD) method for achieving quantum mechanical simulations of large systems [1]. The advantage of the present approach is three-fold in terms of computational efficiency: (a) linear-scaling computational cost with respect to system size by fragmentation of the entire system, (b) small computational pre-factor due to parameterized electronic structure calculation, and (c) development of massively parallelized program which makes it possible to perform energy and gradient calculations of millions of atoms on a supercomputer consisting of numerous nodes with multiple cores. The ubiquitously occurring chemical bond formation and cleavage can be treated in an automatic manner by dividing the system into several grid boxes at each time step. The multipole- and interpolation-based evaluation of charge-charge interaction enables an acceleration of periodic calculations with arbitrary accuracy. Sampling free energy profile is easily accessible in combination with metadynamics technique [2]. As we have demonstrated for proton transfer in aqueous solution models containing thousands of atoms [3–5], the DC-DFTB-MD simulation can track mechanisms involving chemical reactions and evaluate dynamical properties in reasonable agreement with experiment. In this presentation, theoretical aspects and numerical results on performance of DC-DFTB calculations will be discussed.

- [1] H. Nishizawa, Y. Nishimura, M. Kobayashi, S. Irle, H. Nakai, *J. Comput. Chem.* **37**, 1983 (2016).
- [2] A. Barducci, M. Bonomi, M. Parrinello, *WIREs Comput. Mol. Sci.* **1**, 826 (2011).
- [3] H. Nakai, A. W. Sakti, Y. Nishimura, *J. Phys. Chem. B* **120**, 217 (2016).
- [4] A. W. Sakti, Y. Nishimura, H. Nakai, *J. Phys. Chem. B* **121**, 1362 (2017).
- [5] A. W. Sakti, Y. Nishimura, H. Sato, H. Nakai, *Bull. Chem. Soc. Jpn.*, submitted.



## Electronic Structure Properties of $[n]$ Cyclacenes Investigated by Semi-Empirical and Wave Function Methods

Stefano Battaglia<sup>1,2</sup>, Noelia Faginas-Lago<sup>2</sup>, Dirk Andrae<sup>3</sup>, Stefano Evangelisti<sup>1</sup>,  
Thierry Leininger<sup>1</sup>

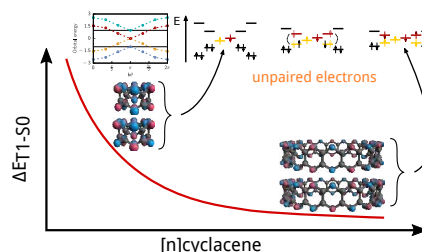
<sup>1</sup>Laboratoire de Chimie et Physique Quantiques, IRSAMC, Université de Toulouse, CNRS, UPS, 118 Route de Narbonne, 31062 Toulouse Cedex, France

<sup>2</sup>Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, Vie Elce di Sotto 8, 06123 Perugia, Italy

<sup>3</sup>Physikalische und Theoretische Chemie, Institut für Chemie und Biochemie, Freie Universität Berlin, Takustraße 3, 14195 Berlin, Germany

The first *ab-initio* calculations on  $[n]$ cyclacenes appeared almost 20 years ago[1, 2] and these systems are still under active investigation today because of their complicated electronic structure and their potential applications[3, 4]. Similarly to their linear counterparts, the polyacenes, theoretical investigations have been proven difficult from a methodological perspective, which resulted in contradicting results. In this contribution, different properties such as the total position spread tensor, the singlet-triplet energy gap and the radical character of the ground state are presented as a function of the system size at different levels of theory. An active space selection method suggested by the semi-empirical results is presented and used for the subsequent high-level multireference wave function calculations. Dynamic electron correlation effects are taken into account by perturbation theory.

The results obtained show a decreasing singlet-triplet gap and an increasing radical character with increasing size of the system in agreement with the most recent study based on TAO-DFT[3]. This work complements and enlarges the knowledge on this type of systems and confirms by wave function theory the behavior of the studied properties when the size of the cyclacenes is increased.



[1] H. S. Choi, K. S. Kim, *Angew. Chemie - Int. Ed.* **38**, 2256 (1999).

[2] K. N. Houk, P. S. Lee, M. Nendel, *J. Org. Chem.* **66**, 5517 (2001).

[3] C.-S. Wu, P.-Y. Lee, J.-D. Chai, *Nat. Sci. Rep.* **6**, 37249 (2016).

[4] S. Battaglia, N. Faginas-Lago, D. Andrae, S. Evangelisti, T. Leininger, *J. Phys. Chem. A* **121**, 3746 (2017).

## Nonadiabatic simulations of carbon monoxide photodissociation in H64Q neuroglobin

J. Rydzewski<sup>1</sup>, W. Nowak<sup>1</sup>

<sup>1</sup>*Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland*

Carbon monoxide (CO) is a leading cause of poisoning deaths worldwide, with no available antidotal therapy. Building upon a new potential treatment paradigm for CO poisoning based on longtime binding of CO by an engineered (H64Q) neuroglobin (Ngb) [1], we study temporal, structural and energetic determinants of the photodissociation and geminate recombination of CO in Ngb by means of molecular dynamics simulations. A model for the ground and the excited diabatic states is constructed based on available experimental data. The hopping between the diabatic surfaces is treated using the Landau-Zener theory [2]. In our computational scheme, the relaxation of the photon energy into the protein matrix is also considered in a simulation that match a complete experimental setup. Simulations are conducted for the native form of Ngb and for the mutant, H64Q. We collected 1-microsecond of aggregate simulation time, allowing us to observe many photodissociation and geminate recombination events. Our investigation suggests that the mutation of the distal histidine to glutamine in Ngb has an impact on the concurrent binding to the heme. Moreover, our results show that cavities of the native form and the Ngb mutant are differently populated by the photodissociated CO. This study may bring the structural, temporal and energetic basis for the mechanisms of the near-irreversible binding of CO to the engineered Ngb, providing a better understanding to the new treatment for CO poisoning. The proposed methodology is general and thus may serve as a starting point for development of new methods suitable for simulating ligand diffusion in proteins beyond the Born–Oppenheimer approximation.

JR acknowledges funding (grant 2015/19/N/ST3/02171) from National Science Centre, Poland. The results used in this study were obtained using Interdisciplinary Centre for Modern Technologies computational facilities, NCU.

- [1] I. Azarov, L. Wang, J. J. Rose, Q. Xu, X. N. Huang, A. Belanger, Y. Wang, L. Guo, C. Liu, K. B. Ucer, C. F. McTiernan, C. P. O'Donnell, S. Shiva, J. Tejero, D. B. Kim-Shapiro and M. T. Gladwin, *Sci. Transl. Med.* **8**, 368 (2016).
- [2] G. Cottone, G. Lattanzi, G. Ciccotti and R. Elber, *J. Phys. Chem. B* **116**, 10 (2012).

## **Difference of electron chirality between enantiomers as a possible solution to homochirality in Nature**

**Masato Senami<sup>1</sup> and Keito Ito<sup>1</sup>**

*<sup>1</sup>Department of Micro Engineering, Kyoto University, Nishikyo, 615-8540 Kyoto, Japan*

The electron is known to have its chirality determined by the directions of spin and momentum. It has been found that total electron chirality in chiral molecules is different between enantiomers. Here the total electron chirality is defined as the integration of electron chirality over a molecule. In this work, we propose that this difference of the total electron chirality may explain the origin of the (biological) homochirality, which means that amino acids produced biologically are dominantly L-chiral, while those produced in laboratories are racemic.

It is widely believed that the generation of the homochirality is deeply related to the weak interaction of the standard model of particle physics, which violates the parity symmetry. The weak interaction works only for left-handed electrons, while right-handed electrons do not have any gauge charge for the weak interaction. Hence, if the numbers of the left-handed electron in molecules are different, reaction rates of molecules for weak interaction are different. In general, the left-handed electron has usually the same number as the right-handed one due to the electron mass, which is known as the interaction with Higgs field in the vacuum. Thus, for most molecules, the reaction rate for the weak interaction is the same for molecules of the same structure.

In our work, we report that in chiral molecules have different total chirality between enantiomers, that is, the number of the left-handed electron is different between enantiomers of the same molecule. This difference has been known for only H<sub>2</sub>Te<sub>2</sub> [1]. We report that this difference is general property for chiral molecules. Therefore, we suggest that this difference of the total electron chirality may be the origin of the (biological) homochirality. Different total chirality means different reaction rate for the weak interaction. The different reaction rate probably induces different numbers between D- and L-chiral amino acids in the early universe.

In this work, we report that chiral molecules have different total chirality of electron for such as H<sub>2</sub>X<sub>2</sub> (X=O, S, Se, Te) and alanine. H<sub>2</sub>X<sub>2</sub> is one of the simplest structure chiral molecule. Hence this molecule is suitable for the study of the relation between molecular parity violation and the electron chirality.

[1] R. Bast et al., *Phys. Chem. Chem. Phys.* **13**, 864 (2011).

## Heme vs. Siroheme Models of the Sulfite Reductase Active Site

Adrian Brânzanic<sup>1</sup>, Ulf Ryde<sup>2</sup>, Radu Silaghi-Dumitrescu<sup>1</sup>

<sup>1</sup> *Department of Chemistry, Babeş-Bolyai University, str.Arany Janos 11., Cluj-Napoca, Romania*

<sup>2</sup> *Department of Theoretical Chemistry, Lund University, Lund, Sweden*

A test set of models that describe bioinorganic centers was employed to benchmark the performance of several density functional methods for the accurate description of overall spin states of these centers. The set comprises four models derived from biological active sites that possess different ground state multiplicities (high-spin, low-spin and intermediate-spin state), as depicted in Figure 1.

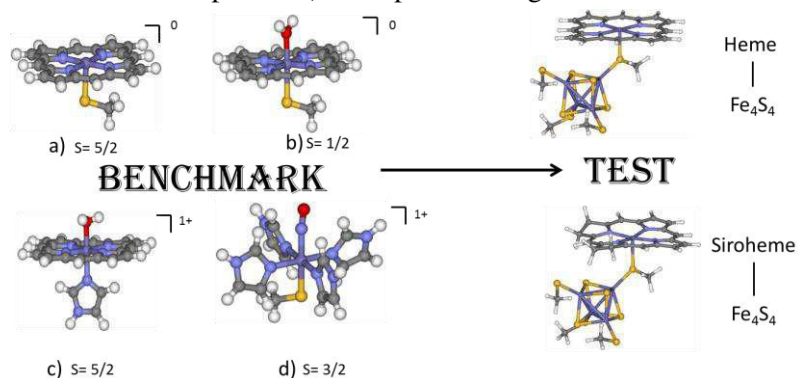


Fig.1. Left: Bioinorganic models derived from the active sites of the following proteins: ferric cytochrome P450 with a vacant distal position (a) and aqua-bound (b), ferric haemoglobin (c) and ferrous-nitrosyl superoxide reductase (d). Right: heme- $[\text{Fe}_4\text{S}_4]$  and siroheme- $[\text{Fe}_4\text{S}_4]$  systems

In general, when conducting quantum chemical calculation on open-shell systems using the framework of density functional theory, it is observed that hybrid functionals tend to overestimate the stability of high-spin states, while pure functionals over stabilize low-spin states. Thus, finding a functional that performs acceptable in all spin state situations encountered in bioinorganic molecules is not a trivial task. In this study, we engage in such a quest, by choosing a set of functionals that use a different amount of exact Hartree–Fock exchange in their evaluation of the exchange integrals.

Further theoretical investigations are carried out with the best performing functionals on bioinorganic models derived from the active site of sulfite reductase in which differences in terms of energetics, bonding, spin coupling are emphasized between the biologically occurring siroheme- $[\text{Fe}_4\text{S}_4]$  system and the fictive heme- $[\text{Fe}_4\text{S}_4]$  system in order to get more insights on nature's preferences for the former system.

## **Improved GBSA force field with modified CMAP and non-bonded interactions**

Haiping Zhang<sup>1</sup>, Lanyuan Lu<sup>1</sup>

<sup>1</sup> *School of Biological Sciences, Nanyang Technological University, 60 Nanyang Drive, Singapore, 637551*

### **Abstract**

Compared with conventional force fields with explicit water molecules, implicit solvent models can significantly accelerate the computational efficiency by reducing the total degrees of freedom in simulation. However, current GBSA-based force fields are usually less accurate than the explicit solvent counterparts and still require improvement. In this work, we improved the GB-Neck2 combined with ff14SBonlysc force field, which is one of the most accurate implicit solvent models in literature. We implemented a CMAP potential energy term to adjust the secondary structure propensity for each type of residues. Moreover, non-bonded parameters regarding side chains containing aromatic rings were modified to better mimic the pi-pi interaction. The simulation results show improvement on secondary structure propensity as well as tertiary structure accuracy.

A test set of 19 small peptides with known native PDB structures and with diversified secondary structures was constructed to test the accuracy of our force field. For 84.2% (16 in 19) cases, the experimental native structures were correctly produced from extended starting structures by replica-exchange simulations, using a RMSD criterion of 0.45 nm. This result is significantly superior to that using the original force field with the success ratio 47.3 % (9 in 19 cases). Additionally, some small proteins were selected to investigate the force field's performance on larger systems, and better results from our modified parameters were also observed for those cases. Furthermore, the free energy surfaces from the protein simulations illustrate that our force field produces global free energy minima in the vicinities of native structures, while a broad range of conformations can still be sufficiently sampled in the simulations. In conclusion, we developed a new GBSA-based atomistic force field with improved secondary and tertiary structure results. Our force field can efficiently sample the conformational space of peptides and small to median sized proteins.

## Photochemistry of Acrylic Acid: Semiempirical and Ab Initio Molecular Dynamics vs. Experiment

Dorit Shemesh<sup>1</sup> and R. Benny Gerber<sup>1,2</sup>

<sup>1</sup>*Institute of Chemistry and The Fritz Haber Research Center, The Hebrew University, Jerusalem 91904, Israel*

<sup>2</sup>*Department of Chemistry, University of California, Irvine, CA 92697, USA*

The photochemistry of acrylic acid is of considerable atmospheric importance. However, the mechanisms and the timescales of the reactions involved are unknown. In this work, the photochemistry of acrylic acid is investigated theoretically by molecular dynamics simulations on the second excited state  $\pi\pi^*$  using the semiempirical OM2/MRCI method and the ADC(2) method. Over a hundred trajectories were computed for both methods. Results are compared to experimental finding of Okumura [1]. The objectives of this research are twofold: 1) The simulations enable the interpretation of the experiments in terms of molecular mechanisms, yields and timescales of the processes involved. 2) Comparison between the ADC(2) method and the semiempirical OM2/MRCI gives insight into the performance of both methods.

A rich variety of reaction channels are predicted for the single potential energy surface employed using the OM2/MRCI method. Products predicted by the calculations are in accord with experiments. Insights are obtained into the mechanisms of the various channels. Timescales and yields are provided for some of the channels.

ADC(2) simulations predict fewer pathways than the semiempirical OM2/MRCI method. Insights are gained from comparing both methods. The differences in the reaction pathways is attributed to different heights of barriers in the two methods.

The results encourage further simulations of this kind as a tool for interpreting photochemical dynamics of carboxylic acids.

[1] A.J. Fleisher, B.J. Bjork, T.Q. Bui, K.C. Cossel, M. Okumura, J.Ye, *J. Phys. Chem. Lett.*, **5**, 2241 (2014).

## Combined Quantum Chemical Calculations and QSPR on Olefin Polymerization using *ansa*-Zirconocene for Designing New Catalysts

Manussada Ratanasak<sup>a</sup>, Vudhichai Parasuk<sup>a,\*</sup>

<sup>a</sup> Computational Chemistry Unit Cell, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

\*Corresponding author. Tel: +6622187603; Fax: +6622187603;  
E-mail address: [vudhichai.p@chula.ac.th](mailto:vudhichai.p@chula.ac.th)

### ABSTRACT

The Density Functional Theory (DFT) study on homopolymerization of ethene (ET), propene (PP), 1-butene (BT), 1-hexene (HX), and styrene (ST) by a *Rac* [Zr{1-Me<sub>2</sub>Si(3-Pr-( $\eta^5$ -C<sub>9</sub>H<sub>5</sub>))(3-H-( $\eta^5$ -C<sub>9</sub>H<sub>5</sub>))}ClCH<sub>3</sub><sup>+</sup>] *ansa*-zirconocene catalyst were investigated. The study unveils the following: (i) PP, BT, HX, PS monomers prefer 1,2-insertion over 2,1-insertion and the 1,2-*si* is the most probable insertion path, (ii) *ansa*-zirconocene is regio- and stereoselective catalyst for PP, BT, HX, PS polymerization, (iii) with *ansa*-zirconocene calculated %isotactic for PP, BT, HX, and ST monomers are 94.9, 92.2, 96.4, and 89.50, respectively. In addition, new *ansa*-zirconocene catalysts for ethylene polymerization have been suggested by QSPR model. The model suggests that potent *ansa*-zirconocene catalysts should have more number of propyl groups on indenyl ligands and less positive charge on Zr atom. This information will provide guides for the development of zirconocene catalysts for ethylene polymerization.

**Keywords:** *ansa*-zirconocene, polyolefin, metallocene, QSPR, homopolymerization

## Theoretical Analysis on Ion Conduction in Superconcentrated Electrolyte Solution for Na-ion Battery

Masaki Okoshi<sup>1,2</sup>, Chien-Pin Chou<sup>3</sup>, Hiromi Nakai<sup>1-4</sup>

<sup>1</sup>*Department of Chemistry and Biochemistry, Waseda University, Tokyo, Japan*

<sup>2</sup>*Elements Strategy Initiative for Catalysts & Batteries, Kyoto University, Kyoto, Japan*

<sup>3</sup>*Research Institute for Science and Engineering, Waseda University, Tokyo, Japan*

<sup>4</sup>*CREST, Japan Science and Technology Agency, Saitama, Japan*

Na-ion batteries (SIBs) attract growing attentions as the alternative to Li-ion batteries (LIBs) with shrinking resources of lithium. Electrolyte solutions, one of the main components of secondary battery, have a crucial impact on the performances of batteries. Among the electrolyte solutions, the superconcentrated solutions receive intense interests as a novel class of electrolyte for the specific favorable characteristics, such as high electrochemical (oxidative/reductive) stabilities, low volatilities, and so forth [1].

Since superconcentrated solutions generally show high viscosities, the carrier ion conductivity is a crucial problem. The ion diffusion mechanism is one of the remaining fundamental issues for superconcentrated electrolyte solutions with small number of free solvents, in which conventional vehicular-type diffusion mechanism cannot take place.

The present study analyzed the diffusion properties of electrolytes for SIB by using the divide-and-conquer density-functional tight-binding molecular dynamics (DC-DFTB-MD) simulations. Dimethoxy ethane (DME) and Na-FSA (FSA; bis-fluorosulfonyl amide anion ( $\text{NSO}_2\text{F})_2^-$ ) were employed as solvent and salt, respectively. Simulation boxes were setup for dilute and superconcentrated systems with 5% (3454 atoms), 10% (3388 atoms) and 40% (2924 atoms) of salt concentrations, under the three-dimensional periodic boundary condition. Production runs were performed for 20 ps under NVE ensemble following 10 ps of equilibration runs under NVT ensemble ( $T = 298.15$  K).

Averaged coordination number of Na ion was ca. six for all systems. The numbers of free DME decreased from 77 – 83% to 11% with increasing concentration. Diffusion coefficient of DME decreased to ca. 1/4 in superconcentrated system ( $6.8 \times 10^{-10}$  m<sup>2</sup>/sec) compared to dilute system ( $24.9 - 25.8 \times 10^{-10}$  m<sup>2</sup>/sec), while that for Na ion decreased by about a half (5%/10%/40% = 8.4/7.2/3.2 ( $10^{-10}$  m<sup>2</sup>/sec)). Ligand exchange reactions were newly found as an alternative conduction path of Na ion. The time-correlation analyses of ligand-exchange reactions showed ca. 1.5 – 2.0 times frequent reaction rates in the superconcentrated solution than the dilute solutions.

[1] Y. Yamada, A. Yamada, *J. Electrochem. Soc.* **162**, A2406 (2015).

[2] H. Nishizawa, Y. Nishimura, M. Kobayashi, S. Irle, H. Nakai, *J. Comput. Chem.* **37**, 1983 (2016).

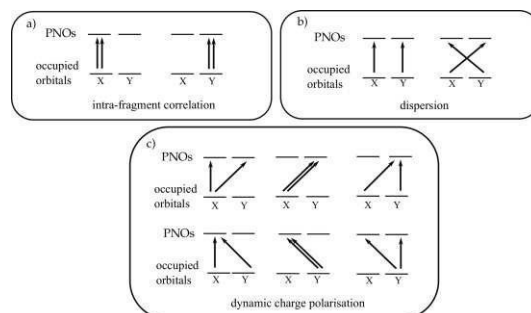


## Decomposition of intermolecular interaction energies in the DLPNO-CCSD(T) framework. Theory and applications in homogenous catalysis.

Giovanni Bistoni<sup>1</sup>, Alexander A. Auer<sup>1</sup>, Frank Neese<sup>1</sup>

<sup>1</sup>*Department Of Molecular Theory And Spectroscopy/ Max Planck Institute for Chemical Energy Conversion, Stiftstr. 34-36, 45470 Mülheim an der Ruhr, Germany*

The domain-based local pair natural orbital CCSD(T) (DLPNO-CCSD(T)) method [1] allows for single point coupled cluster energy calculations to be performed on systems with hundreds of atoms. In order to facilitate the interpretation of DLPNO-CCSD(T) results, we recently proposed a Local Energy Decomposition (LED) scheme for the interaction energy between two fragments. [2, 3] This approach exploits the locality of the occupied and virtual orbitals in the DLPNO-CCSD(T) framework for decomposing both the HF and the correlation energy into physical meaningful contributions (see Figure 1).



**Figure 1:** Double excitations constituting the: a) intra-fragment, b) dispersion, and c) charge transfer components of the correlation energy (X and Y are molecular fragments).

In this work, this approach is used for characterizing a wide range of covalent and non-covalent interactions of importance in various fields of homogenous catalysis, including: (i) the interaction of Lewis acids and bases in classical Lewis adducts and Frustrated Lewis pairs for the activation of molecular hydrogen in solution; [3] (ii) the interactions contributing to the stability of the lowest energy diastereomeric transition state of the chirality-determining step of organocatalytic asymmetric transformations.

[1] C. Riplinger, P. Pinsky, U. Becker, E. F. Valeev, F. Neese, *J. Chem. Phys.* **144**, 024109 (2016).

[2] W. B. Schneider, G. Bistoni, M. Sparta, M. Saitow, C. Riplinger, A. A. Auer, F. Neese, *J. Chem. Theory Comput.* **12**, 4778 (2016).

[3] G. Bistoni, A. A. Auer, F. Neese, *Chem. Eur. J.* **23**, 865 (2017).

## Interpreting the hydrolysis/transglycosylation partition in a $\beta$ -glucosidase using constant pH molecular dynamics

Inacrist Geronimo<sup>1</sup>, Christina M. Payne<sup>2</sup>, and Mats Sandgren<sup>1</sup>

<sup>1</sup>*Department of Molecular Sciences, Swedish University of Agricultural Sciences, Almas allé 5, Uppsala, Sweden*

<sup>2</sup>*Department of Chemical and Materials Engineering, University of Kentucky, F. Paul Anderson Tower, Lexington, Kentucky, U. S. A.*

$\beta$ -glucosidases play an important role in cellulose degradation by relieving endoglucanase and cellobiohydrolase product inhibition through hydrolysis of cellobiose to glucose. Among those used in commercial enzyme cocktails is Cel3A from *Hypocrea jecorina* (HjCel3A), which was found to enhance the conversion of various cellulosic substrates by nearly 10% [1]. However, the catalytic activity of HjCel3A and other  $\beta$ -glucosidases is significantly reduced at high cellobiose or glucose concentration due to transglycosylation, a competing pathway to hydrolysis, wherein another sugar, instead of water, is transferred to the glycosyl-enzyme intermediate. Previous studies, such as that by Turunen et al. [2], suggest that the partition between the two reactions depends on the  $pK_a$  of the acid/base residue and/or nucleophile. The impact of the  $pK_a$  of ionizable residues on the pH-activity profile and hydrolysis/transglycosylation partition of HjCel3A is investigated using constant pH molecular dynamics. In this method, ionizable residues are switched between the protonated and deprotonated states through the introduction of a titration coordinate,  $\lambda$ , which continuously changes between 0 (protonated) and 1 (deprotonated) [3].  $pK_a$  changes during the catalytic reaction are monitored and factors that modulate this property, including hydrogen bonding, charge coupling with other residues, and solvent accessibility, are identified. The findings of this study could serve as guide to protein engineering of  $\beta$ -glucosidase variants with improved hydrolytic activity.

### References

- [1] S. Karkehabadi, K. E. Helmich, T. Kaper, H. Hansson, N.-E. Mikkelsen, M. Gudmundsson, K. Piens, M. Fajdala, G. Banerjee, J. S. Scott-Craig, J. D. Walton, G. N. Phillips, M. Sandgren, *J. Biol. Chem.* **289**, 31624 (2014).
- [2] S. Anbarasan, T. Timoharju, J. Barthomeuf, O. Pastinen, J. Rouvinen, M. Leisola, O. Turunen, *J. Mol. Catal. B: Enzym.* **118**, 62 (2015).
- [3] J. A. Wallace, J. K. Shen, *J. Chem. Theory Comput.* **7**, 2617 (2011).

## Calculation by QM of UV spectra of short-lived intermediates of $\text{OsCl}_6^{2-}$ in aqueous solutions.

**Marina V. Rogozina<sup>1,2</sup>, Roman G. Fedunov<sup>2</sup>**

<sup>1</sup> Voevodsky Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, 3 Institutskaya Str., 630090, Novosibirsk, Russia

<sup>2</sup> Volgograd State University, 100 University Avenue, 400062, Volgograd, Russia

Ultrafast dynamics of transition metal complexes is an active area of research in chemical physics [1]. Plyusnin's scientific group have reviewed the efforts in studying the primary photophysical and photochemical processes in hexahalide complexes of tetravalent ions of platinum group metals [2].

We have recently performed experiments on ultrafast spectroscopy of  $\text{Os}^{\text{IV}}\text{Cl}_6^{2-}$  in aqueous solutions [3]. The main result of [4] was the registration of the intermediate (further – key intermediate, KI) with the maximum in the region of 450-470 nm and plateau in the region of 550-650 nm. The characteristic lifetime of the KI is about 20 ps.

In accordance with the method of identification of KI in [3], two possible preliminary mechanisms of the reaction of photoaquation of  $\text{Os}^{\text{IV}}\text{Cl}_6^{2-}$  were proposed. According to the first mechanism KI is the lowest electronic excited state of  $\text{Os}^{\text{IV}}\text{Cl}_6^{2-}$ . According to the second mechanism KI is the ionic pair  ${}^3\text{Os}^{\text{IV}}\text{Cl}_5^- \dots \text{Cl}^-$ .

To determine which mechanism [3] is preferable, quantum-chemical calculations of the geometric and electronic structure of  $\text{Os}^{\text{IV}}\text{Cl}_6^{2-}$  were performed. The calculation was carried out using a program package FireFly 8.1 [4], electronic spectra were computed at the framework of XMCQDPT [4] the electronic excitation energies were computed with 8 active orbitals and 10 active electrons. Effect of solvent (water) was taken into account at the framework of the PCM. The report presents the results of calculations of the geometric and electronic structure and also UV spectra of  ${}^3\text{Os}^{\text{IV}}\text{Cl}_6^{2-}$  and  ${}^3\text{Os}^{\text{IV}}\text{Cl}_5^-$ .

The calculated spectra for  $\text{Os}^{\text{IV}}\text{Cl}_6^{2-}$  and  $\text{Os}^{\text{IV}}\text{Cl}_5^-$  in the triplet and quintet states are in good agreement with the experimentally observed spectra [3]. While for singlet states the calculated spectral bands start in the far short-wavelength region, that differs significantly from the observed band maxima in the experiment [3]. The results indicate the possibility of the reaction of photoaquation of  $\text{Os}^{\text{IV}}\text{Cl}_6^{2-}$  through a sequence of stages:  ${}^3\text{Os}^{\text{IV}}\text{Cl}_6^{2-}$  (LMCT)  $\rightarrow {}^5\text{Os}^{\text{IV}}\text{Cl}_6^{2-} \rightarrow {}^5\text{Os}^{\text{IV}}\text{Cl}_5^- \rightarrow {}^3\text{Os}^{\text{IV}}\text{Cl}_5^-$  (KI)  $\rightarrow {}^3\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})^-$ . This sequence of stages is similar to second mechanism proposed in [3]. Thus,  $\text{Os}^{\text{IV}}\text{Cl}_5^-$  in the triplet state is a key intermediate of the reaction of photoaquation of  $\text{Os}^{\text{IV}}\text{Cl}_6^{2-}$ .

[1] J.K. McCusker, Femtosecond, *Acc. Chem. Res.* **36**, 876-887 (2003).

[2] E.M. Glebov, I.P. Pozdnyakov, V.F. Plyusnin, I. Khmelinskii, *J. Photochem. Photobiol. C: Photochem. Rev.*, **24**, 1-15 (2015).

[3] E.M. Glebov, I.P. Pozdnyakov, S.G. Matveeva, A.A. Melnikov, S.V. Chekalin, M.V. Rogozina, V.V. Yudanov, V.P. Grivin, V.F. Plyusnin, *Photochem. Photobiol. Sci.*, **16**, 220-227 (2017).

[4] (a) A.A. Granovsky, *J. Chem. Phys.* **134**, 214113 (1-14) (2011);

(b) Firefly Project homepage: <http://classic.chem.msu.su/gran/firefly/index.html>.

## Activation Strain Model to understand oxidative addition of Carbon-Carbon Bonds to Gold(I) complexes

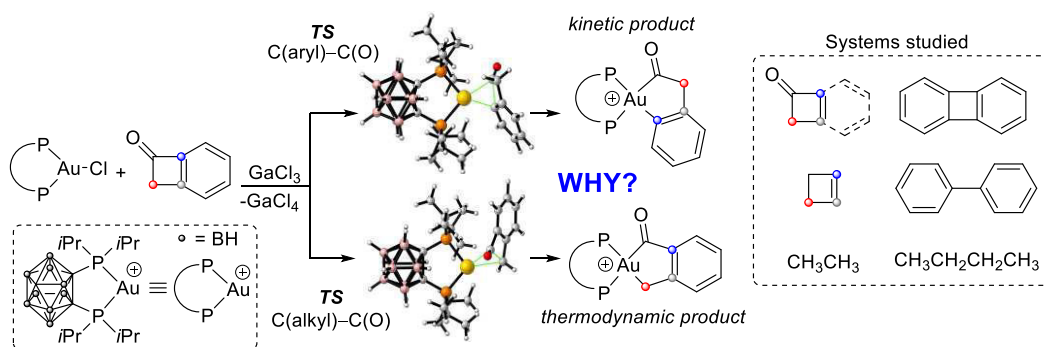
**E. D. Sosa Carrizo,<sup>1</sup> A. Amgoune,<sup>2</sup> D. Bourissou,<sup>2</sup> K. Miqueu.<sup>1</sup>**

<sup>1</sup>IPREM UMR CNRS 5254, Université de Pau et des Pays de l'Adour. Hélioparc 2 avenue P. Angot 64053 Pau Cedex 09 (France). E-mail: [eric-daiann.sosa-carrizo@univ-pau.fr](mailto:eric-daiann.sosa-carrizo@univ-pau.fr);

<sup>2</sup>LHFA UMR CNRS 5069, Equipe LBPB, Université Paul Sabatier, Toulouse Cedex 09 (France).

The C–C bond cleavage by transition metal complexes is one of the most challenging reactions in organometallic chemistry.[1] Only few efficient complexes, based on late transition metals of group 9 and 10 (Rh and Pt) have been described to date. Recently, A. Amgoune, D. Bourissou and co-workers characterized cationic organogold(III) complexes resulting from oxidative addition of strained C–C bonds to diphosphino-carborane gold(I) complexes (DPCbAu<sup>+</sup>). Especially, these bent gold complexes insert into four-membered rings of benzocyclobutenone (see Figure) and cleave selectively either the C(aryl)–C(O) or the C(alkyl)–C(O) as a result of kinetic/ thermodynamic control.[2]

This poster will report the use of the recently introduced activation strain model (ASM) [3] to understand the activation of these non-polar  $\sigma$ -bonds at gold center gold. This approach recently allowed us to understand other process like  $\beta$ -elimination reactions at Ni, Pd and Pt centers.[4] Here, a deeper understanding of the oxidative addition of different C–C bond to Au(I) will be presented. The energy profiles have been calculated at the DFT level of theory. The physical factors that control the energy barriers of this process and the origin of this unusual selectivity will be explained in detail thanks to ASM approach.



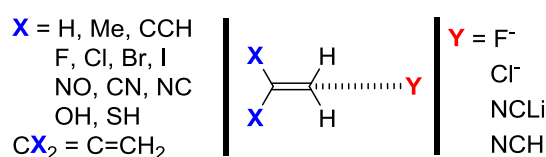
- [1] L. Soullart, N. Cramer, *Chem. Soc. Rev.*, **115**, 9410 (2015).
- [2] M. Joost, L. Estévez, K. Miqueu, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.*, **54**, 5236 (2015).
- [3] I. Fernández, F. M. Bickelhaupt, *Chem. Soc. Rev.*, **43**, 4953 (2014).
- [4] E. D. Sosa Carrizo, I. Fernández, F. M. Bickelhaupt, *Chem. Eur. J.*, **21**, 14362 (2015).

## Sigma-Hole Carbon-Bonding Interactions in Carbon-Carbon Double Bonds: An Unnoticed Contact.

David Quiñonero<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of the Balearic Islands, Crta. Valldemossa km 7.5,  
Palma de Mallorca, Spain*

Apart from the hydrogen bond there are also other types of noncovalent interactions in which the H bridging atom is replaced by a member of group IV, V, VI, VII or VIII, usually denoted as tetrel,<sup>1</sup> pnictogen, chalcogen, halogen and aerogen bonds, respectively. These interactions share an important feature: an electron-rich region of a system interacts with an electron deficient region of another system, corresponding to a region of surface electrostatic potential. These electrostatic potential regions can be regarded as  $\sigma$ - and  $\pi$ -holes and are due to the anisotropy of the atom's charge distribution resulting from the formation of covalent bonds.<sup>2</sup> The  $\sigma$ - and  $\pi$ -holes are regions of lower electron density which are along the extension of a covalent bond to an atom for the former, and perpendicular to a portion of a molecular framework for the latter. Particularly  $\sigma$ -hole complexes with group IV atoms mostly focus on the heavier tetrel atoms,<sup>1</sup> leaving carbon-bonding (CB) much less studied. Also  $\pi$ -hole CB has only been studied for several systems, namely,  $X_2C=O$  ( $X=H, F, Cl$ ),<sup>2</sup>  $F_2C=X$  ( $X=S, Se, Te$ ) and  $XCN$  ( $X= F, Cl, Br, I$ ).<sup>3</sup> Despite having a  $\sigma$ -bond, the  $C=C$  group remains unexplored in terms of its potential for establishing  $\sigma$ -hole CB interactions. Due to the abundance of methylene groups in both organic chemistry and biochemistry, here we study the feasibility of noncovalent CB for a series of alkenes as donors and both neutral and anionic systems as acceptors (Chart 1). This is the first time that  $\sigma$ -hole interactions are reported between an  $sp^2$ -hybridized carbon atom of a Lewis acid and a Lewis base.<sup>4</sup>



**Chart 1.** Complexes under study.

- [1] A. Bauzá, T. J. Mooibroek and A. Frontera, *Angew. Chem. Int. Ed.* **52**, 12317 (2013).
- [2] J. S. Murray, P. Lane, T. Clark, K. E. Riley, P. Politzer, *J. Mol. Model.* **18**, 541 (2012).
- [3] V. de P. N. Nziko, S. Scheiner, *Phys. Chem. Chem. Phys.* **18**, 3581 (2016).
- [4] D. Quiñonero, *Phys. Chem. Chem. Phys.* DOI: 10.1039/C7CP01780D (2017).

## § Atom Types Introduction and RMSD-based Selection for Drug Metabolites Collision Cross Section Calculation Using MOBCAL

**D. A. Ivashchenko<sup>1</sup>, A. Magalhaes<sup>1</sup>, N. M. F. S. A. Cerqueira<sup>1</sup>, I. Corral<sup>2</sup>,  
A. Roberts<sup>3</sup>, A. Webb<sup>3</sup>, C. Beaumont<sup>3</sup>, J. Munoz-Muriedas<sup>4</sup>**

<sup>1</sup> UCIBIO/REQUIMTE, Faculty of Sciences, University of Porto, 4169-007, Portugal.

<sup>2</sup> Departamento de Química, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain.

<sup>3</sup> Global Spectroscopy, GlaxoSmithKline, Ware, SG12 0DP, UK.

<sup>4</sup> Computational Toxicology, GlaxoSmithKline, Ware, SG12 0DP, UK.

Ion Mobility Mass Spectrometry (IM/MS) is a technique that allows separation of isomeric species based on differences in their collision cross sections (CCSs) in the gas-phase, thus providing specific information on the potential structure of a compound [1]. In combination with Molecular Modelling, it is considered as a potential tool for small molecule identification by measuring their gas-phase CCSs and comparing them to theoretically derived CCS databases. A protocol for theoretical determination of CCS has been introduced in [2] and its improvement is at the core of this project.

In the initial stage of the project we have developed a script – an extensive automation of the protocol, which allows all the routine and necessary steps of the algorithm to be performed automatically. It minimises human intervention and saves valuable time. Further research aims to investigate deeper possible sources responsible for the differences between the theoretical and experimental CCS values.

In the present work, new atomic parameters employed in the CCS determination software (MOBCAL [3]) have been introduced: the protocol has been modified to be able to distinguish between different atom types and to assign appropriate parameters. Another modification includes an additional step in the protocol that calculates RMSDs of the found conformations and performs filtering based on the level of similarity among structures. Extensive tests of the protocol with the introduced changes are to be made in order to assess the performance of the new script. Additionally, the calculation of the partial charges used by MOBCAL to calculate the ion-induced part of the potential is to be included in the protocol. Further research includes the study of the possible effect of the dipole moment on the CCS of a metabolite and the assessment of the possible use of QSAR in the protocol.

[1] I. Campuzano et al., *Anal. Chem.* **84**, pp 1026–1033, (2012).

[2] E. Reading et al., *Anal. Chem.* **88** (4), pp 2273–2280, (2016).

[3] A.A. Shvartsburg, M.F. Jarrold., *Chem. Phys. Lett.* **86-91**, 261, (1996).

## Uncommon molecular insertion complexes:

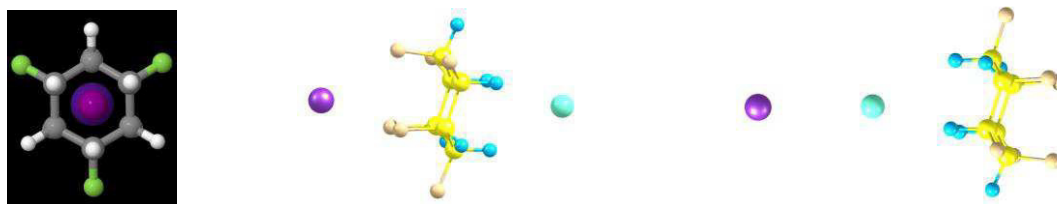
### Non-dipoles and dipoles inside of dipoles

F. Y. Naumkin, B. Cochrane

*Faculty of Science, UOIT, Oshawa, ON, L1H 7K4, Canada*

Highly polar molecular systems are in demand as means of enabling many important practical applications based on light-matter interactions. Novel insertion complexes of non- and polar molecules noncovalently trapped between alkali-halide (MX) counter-ions are studied and compared [1,2], revealing useful insights. For specific selected compositions, the M-molecule-X systems are predicted to exhibit from a metastability (being higher in energy) to a stability relative to molecule + MX by up to 1 eV. Moreover, the polar-molecule insertion complexes can be even more bound than their common dipole-dipole MX-molecule isomers, thus being thermodynamically stable highly polar species, with dipoles of around 20 D. The features of interest include the nonobvious contributions of the molecule polarity to the system stability and dipole moment, the cooperative non-additivity of pair interactions, molecule reshaping and linking by framing ion-pairs.

In addition, due to the neutralization of the M-X charge-transfer in the excited triplet state, these complexes represent unique spin-controlled dipole-switch molecular systems with a large dipole reversibly turned off or even inverted by the spin state, hence potentially allowing various spintronic and optoelectronic applications. The IR spectra are predicted to sensitively indicate the formation of both the M-molecule-X and MX-molecule isomers, with intensities increasing by up to an order of magnitude in the complexes, thus facilitating their reliable detection and differentiation in experiments. In particular, the above indicates possible ways of adding polarity (via attached ion-pairs) to nonpolar molecules and thus of their efficient experimental detection and characterization. The increased attraction could also promote molecular self-assembly, chemical reactions.



- [1] F. Naumkin, *J. Phys. Chem. A* **XXX**, xxx (2017), DOI: 10.1021/acs.jpca.7b02576.
- [2] B. Cochrane, F. Naumkin, *Chem. Phys. Lett.* **643**, 137 (2016).



## Tri-coordinated oxygen at the surface of graphene oxide (GO)

Tapas Kar\* and Steve Scheiner

*Department of Chemistry and Biochemistry, Utah State University, 0300 Old Main Hills,  
Logan, UT 84322-0300, USA*

### Abstract

In recent years, graphene (Gr) has attracted significant attention due to its exceptional electronic, optical, mechanical and chemical properties, which have found potential applications in many fields. Different oxygen-containing functional groups (such as carboxyl, carbonyl, hydroxyl, epoxy, peroxy, lactols) are present in graphene oxide (GO) and reduced GO (RGO), formed during the oxidative preparation of graphitic oxide from graphite and reduction processes, respectively. Structures of GO and RGO are still not fully understood and continuation of studies may reveal fruitful new information to define all of the structural details of these fascinating materials. Understanding of such structures will be essential to control and tune properties in developing application-oriented products.

Determinations of the structures of atomic oxygen-doped graphene are guided by basic concepts of organic chemistry. So far, researchers thought of ether, epoxy and lactols arrangements for such GO/RGO structures. However, a completely new structural arrangement of oxygenated Gr structure is possible where an oxygen atom is linked to three carbons at the junctions of hexagons of the carbon network.

Such tri-coordinated oxygen is known in organic chemistry as open ( $\text{OR}_3^+$ ,  $\text{R} = \text{H}$ ,  $\text{CH}_3$  etc) and cyclic oxonium ions. An oxonium ion is a species containing an oxygen atom that has an octet of valence electrons but bears a formal charge of +1. Stable alkyloxonium salts exist and play significant roles in chemistry, such as ion-neutral complexes, and play a role in medicinal chemistry. Thus, chemistry of GrO may have significant implications mediated by tri-coordinated oxygen.

Density functional theory (DFT) is employed to determine structure and properties of tri-coordinated oxygen at the surface of graphene sheet, where a single carbon atom is substituted by an oxygen atom. IR, NMR and XPS spectra obtained from DFT calculations are used for structural characterization and compared with experimental spectra.

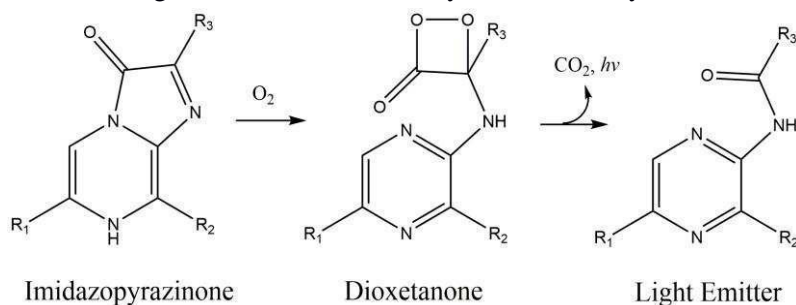


## Mechanistic Insight into Imidazopyrazinone Bioluminescence by TD-DFT Calculations.

L. Pinto da Silva<sup>1\*</sup>, R.F.J. Pereira<sup>1</sup>, C.M. Magalhães<sup>1</sup>, J.C.G. Esteves da Silva<sup>1</sup>

<sup>1</sup>Chemistry Research Unit of University of Porto (CIQUP), R. Campo Alegre 687, 4169-007 Portugal. \*luis.silva@fc.up.pt.

Bioluminescence (light emission from a biochemical reaction) has gained use in bioimaging, bioanalysis and biomedicine [1]. While bioluminescence can be found in 700 *genera*, most species use substrates containing an imidazopyrazinone scaffold [1,2]. These compounds undergo oxygenation to form a dioxetanone intermediate, which thermolysis allows for chemiexcitation (Scheme 1) [1]. While the thermolysis reaction of dioxetanone is a key step, its known instability has prevented its experimental characterization [1,3,4]. We studied the thermolysis of different imidazopyrazinone dioxetanones by performing TD-DFT calculations with the  $\omega$ B97XD functional [3,4]. Both anionic and neutral dioxetanones decompose via a stepwise-biradical mechanism. However, the biradical is formed either by electron transfer (anionic species) or by homolytic bond cleavage (neutral species). Efficient chemiexcitation is explained by a long PES region where the ground and excited states are degenerated, which can only be accessed by neutral dioxetanone.



**Scheme 1** - Bioluminescent reaction of imidazopyrazinone.

Acknowledgment to projects PTDC/QEQ-QFI/0289/2014, NORTE-01-00145-FEDER-000028 and POCI-01-0145-FEDER-006980.

[1] C.M. Magalhães, J.C.G. Esteves da Silva, L. Pinto da Silva, *ChemPhysChem* **17**, 2286 (2016).

[2] E.A. Widder, *Science* **328**, 704 (2010).

[3] L. Pinto da Silva, C.M. Magalhães, J.C.G. Esteves da Silva, *ChemistrySelect* **1**, 3343 (2016).

[4] L. Pinto da Silva, C.M. Magalhães, D.M.A. Crista, J.C.G. Esteves da Silva, *Photochem. Photobiol. Sci.* (2017) DOI: 10.1039/c7pp00012j.

## Perturbative Monte Carlo Simulations - a Hybrid QM/MM Approach

Jonas Feldt<sup>1</sup>, Ricardo A. Mata<sup>1</sup>

<sup>1</sup>*Institute of Physical Chemistry, University of Goettingen, Tammannstr. 6, Göttingen, Germany*

Processes in condensed phase are strongly influenced by environmental effects. Simulations with Molecular Mechanics (MM) are well established but for many effects a description of the electronic structure through Quantum Mechanics (QM) is necessary. One is faced with the questions of how to consider environment effects in the QM calculation.

Hybrid QM/MM approaches are routinely used in the recent years. However, several challenges restrict the scope of this approach for simulations. Molecular Dynamics (MD) coupled with QM/MM requires expensive electronic structure calculations to compute the energy and gradient at every step. Hundreds of picoseconds simulations are required to exhaustively sample the phase space. Although by far most of the degrees of freedom are in the environment many QM calculations have to be carried out. This limits the simulated time scales as well as the size of the QM part or the accuracy of the QM method.

We propose to use perturbation theory to decouple the dependency of the QM and MM part based on work of Truong and Stefanovich[1]. It allows us to independently sample the configurational space of QM and MM part with Metropolis Monte Carlo (MC) simulations. Compared to MD, no gradient evaluations are necessary and the larger number of energy evaluations is more than outweighed by the negligible computational costs of perturbative steps. Only a limited number of full QM calculations has to be carried out during a simulation to ensure the accuracy of the perturbation approach. Furthermore, we brought forward a hybrid implementation utilizing GPUs which cuts down the computational costs by an order of magnitude[2].

The influence of the approximations and technical parameters on the results have been thoroughly investigated. Benchmark studies have been carried out by looking at the solvent structure, the description of thermodynamics and reactivity in solution and properties as well as electronic spectra of the solute.

[1] T. N. Truong, E. V. Stefanovich, *Chem. Phys. Lett.* **256**, 348 (1996).

[2] S Miranda, J. Feldt, F. Pratas, R. A. Mata, N. Roma, P. Tomás, *Int. J. High Perform. Comput. Appl.* DOI: 10.1177/1094342016649420 (2016).

## Structures and Properties of Silicon-Doped Boron Clusters $B_nSi$ , with $n = 15-24$ , and Their Anions

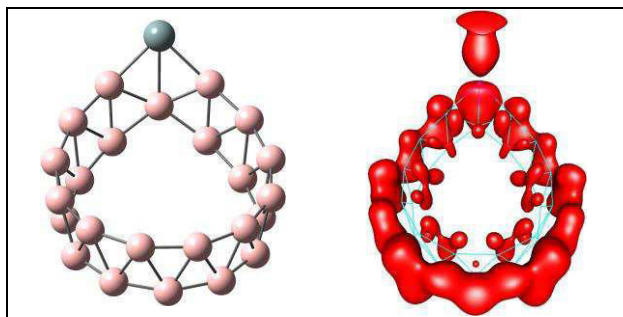
Dang Thi Tuyet Mai,<sup>1</sup> Long Van Duong,<sup>2</sup> and Minh Tho Nguyen<sup>1,\*</sup>

<sup>1</sup>Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium

<sup>2</sup>Institute for Computational Science and Technology (ICST), Quang Trung Software City,  
Ho Chi Minh City, Viet Nam

\*E-mail: [minh.nguyen@kuleuven.be](mailto:minh.nguyen@kuleuven.be)

An investigation on silicon-doped boron clusters  $B_nSi$  ( $n = 15-24$ ) in both neutral and anionic states has been explored systematically using quantum chemical calculations. Thermochemical properties of the lowest-lying isomers of  $B_nSi^{0/-}$  clusters such as average binding energies, detachment energies, dissociation energies, etc. were predicted by using CCSD(T) method. The growth behavior for  $B_nSi^{0/-}$  with  $n = 15-24$  can be established as follows: i)  $B_nSi^{0/-}$  clusters tend to be form by substituting B-atom by Si-atom or adding one Si-impurity into the parent  $B_n$  neutral or anionic clusters, and ii) Si prefers an external position of the  $B_n$  framework. Our calculated results reveal that similar to pure boron clusters, the tubular drum-shape appears at size  $n = 20$  and 24 of impurity  $B_nSi$  clusters. Especially, the double ring  $B_{24}Si$  exhibits the enhanced stability due to possessing high average binding energy and  $\pi$  aromatic character based on the MOs and ELF analysis.



[1] Tai, T. B., Kadłubański, P., Roszak, S., Majumdar, D., Leszczynski, J., Nguyen, M. T., *ChemPhysChem*. **12**, 2948–2958 (2011).

[2] Mai, D. T. T., Duong, L. V., Tai, T. B., Nguyen, M. T., *J. Phys. Chem. A*. **120**, 3623–3633 (2016).

## Spectroscopic Properties of the Redox Active Tyrosine-D in Photosystem II

**Abhishek Sirohiwal, Frank Neese, Dimitrios A. Pantazis**

*Max Planck Institute for Chemical Energy Conversion, Stiftstrasse 34, 45470 Mülheim an der Ruhr, Germany.*

Photosystem II contains two redox-active tyrosine residues, D1-Tyr161 ( $Y_Z$ ) and D2-Tyr160 ( $Y_D$ ). These tyrosines play vital roles [1] when there is a light-driven charge separation in the reaction center, which triggers the redox chemistry. The  $Y_Z$  is involved in direct electron transfer to reduce the reaction center, and the  $Y_Z$  radical subsequently oxidizes the oxygen evolving complex (OEC), which in return oxidizes water to produce dioxygen. The other tyrosine,  $Y_D$ , being spatially far from OEC ( $\sim 20$  Å) plays two important roles, i.e. *redox* and *electrostatic*. In its redox role, it reduces the reaction center; in addition, it participates in redox control of the OEC, where the  $S_2$  state is reduced by  $Y_D$ -OH to  $S_1$  in the dark to form  $Y_D$ -O $\cdot$  and electron transfer from  $S_0$  to  $Y_D$ -O $\cdot$ , which results in the dark-stable  $S_1$  state. The formation of the tyrosyl radical is coupled with proton transfer, facilitated by a robust hydrogen bonding network [2]. The crystallographic structure [3] depicts only one water molecule occupying two positions, proximal and distal, near  $Y_D$ -OH. The proximal water molecule ( $\sim 2.7$  Å from phenolic oxygen atom) is hydrogen bonded to hydroxyl group of  $Y_D$ -OH, whereas the distal one forms a proton transfer pathway starting from Arg180. In this work, we present the correlation between the proposed positions of the water molecule and the spectroscopic properties of the tyrosine radical. The electronic structure of the  $Y_D$ -O $\cdot$  radical is deciphered in terms of its EPR parameters and comparisons are made with the available experimental data in order to understand how the local hydrogen bonding network and the positioning of the mobile water molecule regulate the redox properties of Tyr160.

[1] A. W. Rutherford, A. Boussac, P. Faller, *Biochim. Biophys. Acta* **1655**, 222 (2004).

[2] K. Saito, A. W. Rutherford, H. Ishikita, *Proc. Natl. Acad. Sci. USA* **110**, 7690 (2013).

[3] Y. Umena, K. Kawakami, J. R. Shen, N. Kamiya, *Nature* **473**, 55 (2011).

## Evaluation of Heats of Formation of Giant Fullerenes using Density Functional Tight Binding with Isodesmic Reactions

**Simone Waite<sup>1</sup>, Bun Chan<sup>2</sup>, Amir Karton<sup>3</sup>, Alister Page<sup>1\*</sup>**

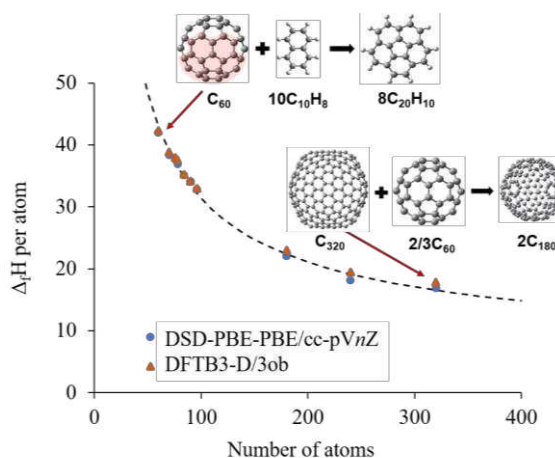
<sup>1</sup>Newcastle Institute for Energy and Resources, University of Newcastle, Callaghan, NSW, Australia

<sup>2</sup>Department of Chemistry, Nagasaki University, Nagasaki, Japan

<sup>3</sup>School of Molecular Sciences, University of Western Australia, Crawley, WA, Australia

\*alister.page@newcastle.edu.au

Carbon-based nanomaterials (fullerenes, nanotubes, graphene, etc) have attracted particular interest due to their unique electronic, optical, thermal, mechanical and chemical properties. In 1985 the first of these carbon nanostructures to be discovered was buckminsterfullerene, (I<sub>h</sub>)C<sub>60</sub> [1]. Despite the wealth of investigation into this remarkable molecule, the  $\Delta_f H$  for C<sub>60</sub> (2560 kJ mol<sup>-1</sup> according to NIST) remained uncertain, with experimental values spanning  $\pm 100$  kJ mol<sup>-1</sup> [2]. Recently, double hybrid density functional theory and W1h theory [3] have been employed to obtain an accurate  $\Delta_f H$  for C<sub>60</sub> (2520.0  $\pm$  20.7 kJ mol<sup>-1</sup>) [4] and some higher fullerenes [5] via isodesmic reaction schemes. However, such high-level approaches are impractical for comprehensively studying giant fullerenes, due to their size and the huge number of cage isomers. Here we demonstrate the utility of dispersion-corrected 3<sup>rd</sup>-order density functional tight binding (DFTB3-D/3ob) method for predicting  $\Delta_f H$  in larger fullerenes using isodesmic reactions. Errors in  $\Delta_f H$  are minimised through judicious choice of reaction schemes, which conserve the fullerene curvature, minimize the total number of species involved, and utilize complementary species with adequate uncertainties. The DFTB3-D/3ob theoretical heat of formation for C<sub>60</sub> ( $\Delta_f H$  = 2539.4 kJ mol<sup>-1</sup>) is shown to be within an acceptable range of the DSD-PBE-PBE/cc-pVQZ value ( $\Delta_f H$  = 2520.0  $\pm$  20.7 kJ mol<sup>-1</sup>) [5]. We also show that DFTB3-D/3ob performs very well in predicting trends in  $\Delta_f H$  for larger fullerenes (Figure 1).



**Figure 1.** Comparison of DSD-PBE-PBE/cc-pVnZ and DFTB3-D/3ob  $\Delta_f H$  (kJ mol<sup>-1</sup>) values for giant fullerenes.

- [1] H. W. Kroto, *et. al.*, *Nature* **318**, 162 (1985).
- [2] H. Y Afeefy *et. al.*, *NIST Chemistry WebBook*, **69**; see <http://webbook.nist.gov>
- [3] J. M. Martin, G. J. de Oliveira, *Chem. Phys.* **111**, 1843 (1999)
- [4] A. Karton *J. Phys. Chem. A.* **117**(8), 1834-42 (2013).
- [5] B. Chan, *et. al.*, *J. Am. Chem. Soc.*, **138** (4), 1420–1429 (2016).

## Theoretical study on the optical properties of *fac*-Ir(ppy)<sub>3</sub> and its derivatives

Yoshiki Natori, Shogo Aoki, Yasutaka Kitagawa, Masayoshi Nakano

Department of Materials Engineering Science, Graduate School of Engineering Science,  
Osaka University, Toyonaka, Osaka 560-8531, Japan

Recently, organic electroluminescence (EL) devices are often used as next-generation flat panel displays and illuminations. Ir(III) complexes have attracted much attention as important materials for such organic EL devices due to their high quantum yields and their phosphorescence emission. It is known that *fac*-Ir(ppy)<sub>3</sub> complex, where ppy denotes 2-phenylpyridine, shows a luminescence property[1][2]. This compound exhibits high quantum yields, but little is known about their optical properties when the coordination species are changed to others. There have also been no specific design guidelines especially for the substituent effect on optical properties. In this study, therefore, a difference in the optical properties among substituted *fac*-Ir(ppy)<sub>3</sub> complexes is examined in detail by DFT and TD-DFT calculations. In addition, the structure, absorption spectrum and maximum emission wavelength of several unreported complexes are also predicted. Finally, we summarize the effect of electron-withdrawing and electron-donating functional groups of substituents on the optical properties of the complexes.

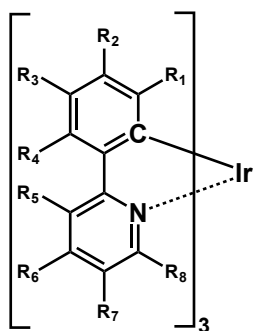


Fig.1 Framework of *fac*-Ir(ppy)<sub>3</sub>.

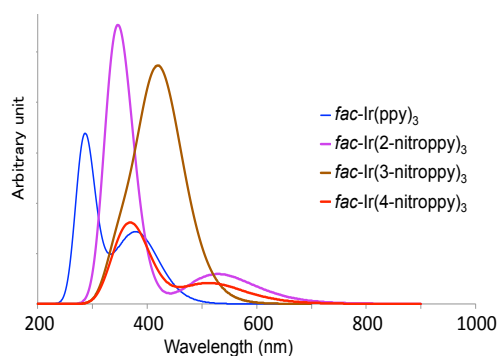


Fig.2 Calculated UV-Vis absorption spectra of *fac*-Ir(*x*-nitroppy)<sub>3</sub>. (*x* = 2, 3, 4)

### References

- [1] M. A. Baldo, S. Lamansky, P. E. Burrowa, M. E. Thompson and S. R. Forrest, *Appl. Phys. Lett.* **75**, 4 (1999).
- [2] S. Ikawa, S. Yagi, T. Maeda, H. Nakazumi, H. Fujiwara, Y. Sakurai, *Dye and Pigments* **95**, 695 (2012).

## Investigating the Interactions of Novel Anti-Cancer Therapeutics with DNA using Computational Modelling and Spectroscopic Techniques

Eunice S. H. Gwee<sup>1</sup>, Bayden R. Wood<sup>1</sup>, Ekaterina I. Izgorodina<sup>1</sup>

<sup>1</sup>*School of Chemistry, Monash University, Wellington Rd, Clayton, 3800, VIC, Australia*

Platinum-based drugs, such as cisplatin, carboplatin, oxaliplatin and nedaplatin, are among the most commonly used drugs to combat cancer.<sup>[1]</sup>

Infrared (IR) spectroscopy is a non-disruptive analytical method that can provide structural information of a sample. With the development of new techniques, it is now possible to study samples in the far IR (FIR) region ( $<600\text{ cm}^{-1}$ ). This would provide information on the platinum-based drugs as the vibrational modes between Pt-ligand would fall in the FIR region. This is important as the activity of metal-based drugs is directly related to the changes in metal coordination to its ligand, making it necessary to assign the vibrational bands to the respective vibrational modes.<sup>[2]</sup>

Another area of interest is the Donor-Acceptor bonds of these platinum-based between the Pt and its ligands, differing them to typical covalent bonds, thus requiring the use of more accurate quantum chemical methods. The Donor-Acceptor bonds are usually observed in the FIR region. It has been noted that stretching vibrations that reflect the strength of the bond are more likely to be affected by the accuracy of the selected level of theory, making it vital to select the appropriate level of theory to study such complexes.

In this work, we incorporate the use of computational chemistry methods to predict FIR spectra of four platinum anti-cancer drugs (cisplatin, carboplatin, oxaliplatin and nedaplatin). A series of factors such as functionals (PBE, PBE0, M06-L and M06-2X), basis sets (cc-pVDZ, cc-pVTZ, aug-cc-pVDZ and aug-cc-pVTZ) and solvation models (PCM, CPCM and SMD) were utilised to predict vibrational frequencies in the far IR region with the view of identifying the importance of each factor. With statistical analysis to compare data between experimental and theoretical spectra, the best combination of DFT functional, basis set and solvent model was identified to predict vibrational frequencies of the platinum complexes in the far IR region.

In addition, the identity of the activated form of cisplatin was investigated by comparing the calculated vibrational frequencies of both the mono- and di-hydrated forms to experimental data, with cisplatin being measured in either serum or saline solutions.

- [1] aR. Barnett, V. Loretta, E. T. James, H. M. Virginia, *Nature* **1969**, 222, 385; bG. Markus, K. K. Bernhard, *Anti-Cancer Agents in Medicinal Chemistry* **2007**, 7, 55-73.
- [2] aA. V. Klein, T. W. Hambley, *Chemical Reviews* **2009**, 109, 4911-4920; bP. Umapathy, in *Coord. Chem. Rev.*, Vol. 95, **1989**, pp. 129-181.

## Electron fate and mutational robustness in the mechanism of (6-4) photolyase-mediated DNA repair

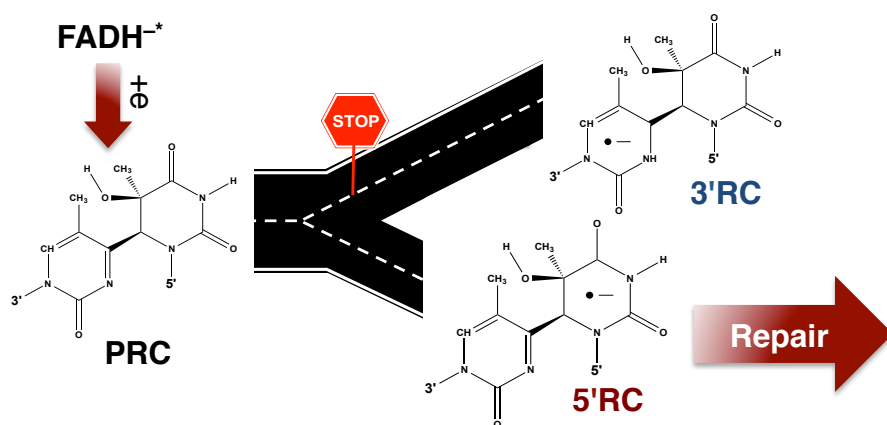
Hisham M. Dokainish<sup>1</sup>, Daichi Yamada<sup>2</sup>, Tatsuya Iwata<sup>2,3</sup>, Hideki Kandori<sup>2,3</sup> and Akio Kitao<sup>1</sup>

Hisham M. Dokainish<sup>1</sup>, Daichi Yamada<sup>2</sup>, Tatsuya Iwata<sup>2,3</sup>, Hideki Kandori<sup>2,3</sup> and Akio Kitao<sup>1</sup>

<sup>1</sup>Institute of Molecular and Cellular Biosciences, The University of Tokyo, 1-1-1, Yayoi, Bunkyo-ku, Tokyo, 113-0032, Japan

<sup>2</sup>Department of Life Science and Applied Chemistry, Nagoya Institute of Technology, Showa-ku, Nagoya 466-8555, Japan

<sup>3</sup>OptoBioTechnology Research Center, Nagoya Institute of Technology, Showa-ku, Nagoya 466-8555, Japan



(6-4) photolyase ((6-4) PHR) are evolutionally ancient enzymes that are essential in maintaining genetic integrity by repairing UV induced cytotoxic DNA lesions, pyrimidine(6-4)pyrimidone photoproduct ((6-4) PP)<sup>1-3</sup>. It harvests sunlight to repair the DNA covalently linked pyrimidine bases via structurally and chemically challenging reaction<sup>1</sup>. Due to biological importance of the (6-4) PP repair, extensive experimental and computational studies have been performed, however, the mechanism is still elusive and debated, because of its challenging assignment and reaction complexity<sup>1-3</sup>. Here we synergistically use molecular dynamics simulations, quantum mechanical/molecular mechanical (QM/MM) calculations, Large-QM/MM which includes 982 atoms in the QM layer, Marcus theory and Fourier transform infrared (FTIR) spectroscopic measurement, to first investigate the electronic nature of reactive complex (RC) after forward electron transfer (FET) and subsequently to investigate in detail the photorepair cycle.

[1] D. Zhong, *Annu. Rev. Phys. Chem.* **66**, 691 (2015).

[2] J. Li, *et al. Nature* **466**, 887 (2010).

[3] H. M. Dokainish and A. Kitao, *ACS Catal.* **6**, 5500 (2016).



## Computational Study of MEA Adsorption on Hydroxylated Cr<sub>2</sub>O<sub>3</sub> Surfaces

Theodorus de Bruin,<sup>1</sup> Aurélie Gouron,<sup>1,2</sup> A.C.T. van Duin,<sup>3</sup> D. van Duin,<sup>3</sup>  
Boubakar Diawara,<sup>2</sup> François Ropital<sup>4</sup>

<sup>1</sup>*Department of Thermodynamics and Molecular Modeling / IFP Energies nouvelles, 1 et 4  
avenue de Bois Préau, Rueil-Malmaison, France*

<sup>2</sup>*Institut de Recherche de Chimie Paris, CNRS / Chimie Paris Tech, 11 rue Pierre et Marie  
Curie, Paris, France*

<sup>3</sup>*RxFF Consulting, LLC, State College, PA 16801, USA*

<sup>4</sup>*Department of Electrochemistry and Materials / IFP Energies nouvelles, Rond-Point de  
l'échangeur de Solaize, BP 3, Solaize, France*

Aqueous alkanolamine – and more specifically monoethanolamine (MEA) – solution are frequently used for the removal of CO<sub>2</sub> from flue gas and natural gas. However, corrosion represents one of the major operational issues in these processes. It is therefore essential to evaluate the stability of the protective Cr<sub>2</sub>O<sub>3</sub> layer of stainless steels, when it is in contact with different species found in CO<sub>2</sub> capture processes, e.g. water, MEA CO<sub>2</sub>, and the reaction products like bicarbonate and the carbamate of MEA.

The adsorption of MEA on the hydroxylated (0001)-Cr<sub>2</sub>O<sub>3</sub> surface was investigated by periodic density functional theory, using both static and dynamics calculations [1]. Two different adsorption modes were investigated: by direct adsorption of MEA onto the surface and by the substitution of a surface water molecule by MEA. Several MEA coverages were studied (from 0.25 to 1 monolayer), as well as temperature and solvation effects. The calculations show that MEA adsorption onto the surface with a density up to 2.37 MEA per nm<sup>2</sup> (0.5 ML) is exergonic at 298 K in an aqueous environment, while the substitution process was found to be endergonic at all coverages at temperatures of 298 K and above.

In an analogous way to MEA, we also studied the adsorption of carbonic and carbamic acid [2].

We are currently fine-tuning the parameters of the ReaxFF reactive force field, allowing us to model larger systems, including the most abundant species in the aqueous phase and to explore larger time scales [3].

[1] A. Gouron, J. Kittel, T. de Bruin, B. Diawara, *J. Phys. Chem. C* **119**, 22889 (2015).

[2] A. Gouron, F. Ropital, T. de Bruin, B. Diawara, *to be submitted*.

[3] A. Gouron, C.T.A. van Duin, D. Diawara, T. de Bruin, *in progress*.

## Empirical Force Fields for Simulating Proton Transfers: Molecular Dynamics and Spectroscopy

Zhen-Hao Xu , Markus Meuwly\*

*Department of Chemistry, University of Basel, Klingelbergstrasse 80., Basel-City, Switzerland*

### Abstract:

The empirical force field method of Molecular Mechanics with Proton Transfer (MMPT) follows concepts from a QM/MM scheme which treats the proton transfer (PT) process in its full dimensionality while improving on three important aspects of the problem: speed, accuracy, and versatility. In a recent generalization, MMPT was extended to treat proton transfer in the condensed phase. This was possible by combining MMPT with multi-surface adiabatic reactive molecular dynamics (MS-ARMD). In this approach, a global potential energy for proton transport is built by mixing multiple potential energy surfaces, each of which corresponds to a localized PT reaction. That enables, for instance, all hydrogen atoms in a bulk phase with excess protons to equally participate into the transfer reactions in a force field regime. The integrated MMPT-MS-ARMD method was applied to performing MD simulations for  $[\text{H}_2\text{O}]_n\text{H}^+$  clusters at the gas phase and results were compared with quantum mechanical (QM) and semi-empirical QM MD simulations.

Complementary to this, recent applications focused on the computation of infrared signatures for the shared proton between a donor and an acceptor site. This was complemented and - in part - motivated by recent experiments. Both, conventional molecular dynamics and more advanced ring polymer MD simulations were carried out to characterize the energetics, dynamics and spectroscopy of transferring protons in topical systems including FAD, AcAc, protonated oxalate. The simulations were found reproducing absorption spectra in good agreement with experimental results.

- [1] S. Lammers, S. Lutz, M. Meuwly. *J. Compu. Chem.* **29**, 1048-1063 (2008).
- [2] K. Mackeprang, Z.-H. Xu, Z. Maroun, M. Meuwly, H. G. Kjaergaard. *Phys. Chem. Chem. Phys.*, **18**, 24654-24662 (2016)
- [3] Z.-H. Xu, M. Meuwly. *J. Phys. Chem. A*, *accepted*.
- [4] T. Nagy; J. Yosa, M. Meuwly. *J. Compu. Theore. Chem.* **10**, 1366-1375 (2014).
- [5] C. T. Wolke, A. F. DeBlase, C. M. Leavitt, A. B. McCoy, M. A. Johnson, *J. Phys. Chem. A* **119**, 13018-13024 (2015).
- [6] D. L. Howard, H. G. Kjaergaard, J. Huang, M. Meuwly. *J. Phys. Chem. A* **119**, 7980-7990 (2015).

## Quantum chemical modelling of magnetic anisotropy and exchange interactions in lanthanide systems with $4f^n5d^m$ configurations

Akseli Mansikkamäki<sup>1,2</sup>, Naoya Iwahara<sup>1</sup>, Liviu F. Chibotaru<sup>1</sup>

<sup>1</sup>*Theory of Nanomaterials Group, Chemistry Department, Katholieke Universiteit Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium.*

<sup>2</sup>*Department of Chemistry, Nanoscience Center, University of Jyväskylä, P. O. Box 35, Jyväskylä, FI-40014, Finland.*

Lanthanide ions in molecular complexes are most often encountered in their trivalent oxidation states. The anisotropic magnetic properties of such systems can be efficiently modeled by *ab initio* multireference methodology developed over the past decade.[1] Much less computational studies have been performed on low-valent systems where the lanthanide ions possess  $4f^n5d^m$  configurations as opposed to the more common  $4f^n$  case encountered in the trivalent ions. The spatial extent of the 5d orbitals is much greater than that of the strongly contracted 4f shell leading to both strong covalent interactions with the ion surroundings and to much stronger exchange coupling. This introduces considerable challenges in the quantum chemical description of the  $4f^n5d^m$  systems as first-order spin-orbit coupling and static electron correlation effects outside the 4f shell both play an important role. In the present contribution we will discuss the quantum chemical modelling of the electronic structures and magnetic properties in low-valent monometallic  $4f^n5d^m$  lanthanide complexes and endohedral metallofullerenes encapsulating mixed valence lanthanide dimers. The calculations utilize methods based on multireference wave function theory, DFT, and *ab initio* model Hamiltonians. The results provide insight into the magnetic anisotropy of the monometallic complexes and to the complicated energy spectrum of the lanthanide dimers resulting from interplay of spin-dependent delocalization and strong spin-orbit coupling.

- [1] L. Ungur, L. F. Chibotaru, in *Lanthanides and Actinides in Molecular Magnetism* (Eds.: R. A. Layfield, M. Murugesu), Wiley-VCH, Germany, **2015**, pp. 153–184.

## Potential energy surface interpolation with neural networks for instanton rate calculations

April Cooper<sup>1</sup>, Johannes Kästner<sup>1</sup>

<sup>1</sup>*Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, Stuttgart, Germany*

For the calculation of reaction rate constants with instanton theory an accurate description of the sector of the potential energy surface (PES) containing the transition state and the reactant state of the reaction of interest is needed. However, obtaining information on the PES on the fly during the rate constant calculation is computationally very demanding. Therefore, we interpolate the PES with artificial neural networks (NNs) and calculate the reaction rate constants with the instanton method using this NN PES. In instanton theory it is assumed that the energy, but also the gradient and the Hessian of the energy with respect to the input coordinates are continuous functions of the input coordinates. Therefore we incorporate not only information on the energy, but include also information on the gradient and Hessian in the NN-fit to ensure their continuity and accuracy.

To demonstrate the capabilities of this approach we calculated reaction rate constants with the instanton method for the reaction  $\text{CH}_3\text{OH} + \text{H} \rightarrow \text{CH}_2\text{OH} + \text{H}_2$  on an average NN PES fitted to CCSD(T)-F12/VTZ-F12 data. We demonstrate that these rate constants are in excellent agreement with rate constants that were calculated on the same level of theory performing energy, gradient and Hessian calculations on the fly, while the computational effort of the rate calculation is significantly lower if a NN PES is used instead of on the fly calculations.

## Electronic Properties and Reorganization Energies of the Metal-Metal-to-Ligand Charge Transfer Transition in Pt(II) Complexes

Wei-Chih Chen<sup>1</sup> and Yuan-Chung Cheng<sup>1</sup>

<sup>1</sup>*Department of Chemistry, National Taiwan University, No.1, Sec. 4, Roosevelt Rd., Taipei 10617, Taiwan (R.O.C)*

**Abstract:** The phosphorescence emission from the metal-metal-to-ligand charge transfer (<sup>3</sup>MMLCT) state of dinuclear transition metal complexes can be used for high-performance near-infrared (NIR) organic light-emitting diodes (OLEDs).<sup>[1]</sup> However, the molecular factors controlling the quantum yields of these NIR dyes remain elusive. In particular, the effects of electron-vibration coupling have not been clearly elucidated previously. In this study, we employ density functional theory calculations to investigate the electronic properties and reorganization energies of a series of Pt(II) complexes in both the monomer and dimer cases. We reveal that the lowest excited state of the monomers are delocalized on the ligands and consequently the intramolecular reorganization energies of the excited state ( $\lambda_{in}$ ) are dominated by the ligand stretching vibration modes. On the other hand, the bond length alternations on the ligands are significantly reduced in the dimers, because the lowest excited state are predominantly located on the two Pt atoms. Therefore, the values of  $\lambda_{in}$  can be significantly reduced in the Pt complex dimers with emission from the <sup>3</sup>MMLCT state. The reduced  $\lambda_{in}$  indicates that NIR emitters with weak electron-vibration coupling could suppress the non-radiative emission to achieve high quantum yield according to the energy gap law.<sup>[2]</sup> In summary, on the basis of the magnitude of the  $\lambda_{in}$ , we provide a ligand design perspective for effective formation excimers and importance rules to improve NIR OLED materials.

[1] K. T. Ly, R. W. Chen-Cheng, H. W. Lin, Y. J. Shiau, S. H. Liu, P. T. Chou, C. S. Tsao, Y. C. Huang, Y. Chi, *Nat. Photon.* **11**, 63 (2017).

[2] R. Englman, J. Jortner, *Mol. Phys.* **18**, 145 (1970).

## Calculation of reaction rate constants via instanton theory in the microcanonical ensemble

Andreas Löhle, Johannes Kästner

<sup>1</sup>*Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany*

The phenomenon of quantum tunneling is crucial in order to make accurate predictions for chemical reaction rates, particularly for those involving the transfer of light atoms such as hydrogen. This is especially true for reactions that take place in extremely cold environments as for instance in gas clouds in interstellar space.

A widely used method to describe tunneling effects in large systems is the use of instanton theory in the canonical ensemble which allows the calculation of reactions rates at well defined temperatures. However, canonical instanton theory is fundamentally restricted to temperatures below the crossover temperature  $T_c$ . Additionally it can be challenging to obtain instanton solutions at very low temperatures as well.

An alternative approach to obtain thermal rates is provided by a microcanonical formulation of instanton theory which in principle is able to provide thermal rates at all temperatures. The objective is therefore to obtain microcanonical rates first in order to calculate thermal rates later while circumventing the existing limitations of using canonical instanton theory directly.

[1] S. R. McConnel, A. Löhle, J. Kästner, J. Chem. Phys. 146, 074105 (2017)

## **DFT+D calculations of non-binding interactions of oligopyrrole aggregates doped with heptafluorotantalate (V) ions in presence of different solvents**

**Felipe Giraldo, Georg Jansen**

*Fakultät für Chemie, Universität Duisburg Essen*

*Universitätstr. 2 45141 Essen*

Polypyrrole is a long known conducting material. It has interesting properties, like mechanical flexibility, good charge storage capacity and is quite easy to synthesize<sup>1,2</sup>. However, not much is known about its structure and, in particular, about the structural changes accompanying insertion of metallic ion dopants, such as heptafluorotantalate,  $\text{TaF}_7^{2-}$ , which enhance the material's conducting properties. Furthermore, the joint system (polypyrrole and the heptafluorotantalate) must be affected in an environment of solvent molecules. In order to shed some light on the interactions between  $\text{TaF}_7^{2-}$  ions and polypyrrole, dispersion corrected density functional theory<sup>3</sup> (DFT+D) calculations were carried out, investigating aggregates between two to four pentapyrrole molecules and two  $\text{TaF}_7^{2-}$  ions. These were submitted to environments of randomly distributed solvent molecules in controlled numbers. The solvent species chosen for this work were water and acetonitrile. Water, because of its facility to interact with both, ions and oligomers through hydrogen bridges and its capacity to form hydrogen bond networks. The results are contrasted to those obtained with acetonitrile solvent molecules, the latter being the aprotic solvent which was used by the experimentalists<sup>4</sup> to synthesize the material.

[1]. Yoon, C. O. ; Sung, H.K. ; Kim, J. H. ; Barsoukov, E. ; Lee, H. *Synthetic Metals* **1999**, 9,(3), 201-212.

[2]. Ma, H. ; Liu, C. ; Jiang, Y. *J. Phys. Chem. B* **2006**, 110, (51), 26488-26496.

[3]. Grimme, S. , *WIREs Comp. Mol. Sci.* , **2011**, 1, 211-228

[4] M. Sc. Thesis Document Gamarra, Jorge, “ Síntesis electroquímica y caracterización de películas de polipirrol dopadas con el anión heptafluorotantalato con potencial de alta capacitancia” Universidad de Los Andes Aug. **2012**.

## The Influence of Chemical Change on Protein Dynamics: A Case Study with Pyruvate Formate-lyase

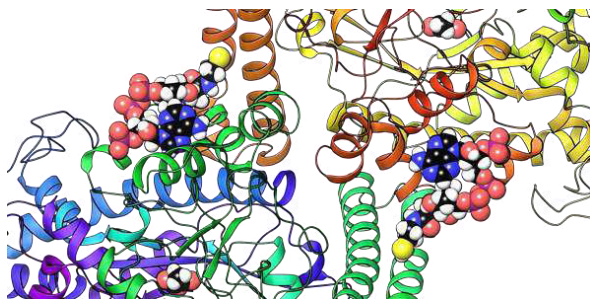
Hanževački Marko<sup>1</sup>, Čondić-Jurkić Karmen<sup>2</sup>, Smith Ana-Sunčana<sup>3</sup>, Smith David M.<sup>1,3</sup>

<sup>1</sup> Division of Physical Chemistry, Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia

<sup>2</sup> Research School of Chemistry, Australian National University, Canberra, ACT, Australia

<sup>3</sup> Institute for Theoretical Physics, FAU Erlangen, Staudtstraße 7, Erlangen, Germany

Pyruvate formate-lyase (PFL) is a glycyl radical enzyme requiring activation by a member of the radical SAM enzyme superfamily.[1] Such radical enzymes are receiving increased interest because of their possible applications in biotechnology.[2] PFL catalyzes the break down of pyruvate into formate and the acetyl group upon the addition of a thiyl radical located at Cys418.[3] The radical is initially stored at Gly734 is shuttled to Cys418 via Cys419. The addition of radical Cys418-S<sup>•</sup> to pyruvate leads to C-C bond dissociation, resulting with formation of formyl radical and acetyl-Cys418. The latter species acts as a temporary acetyl carrier and a reactant in the subsequent half-reaction with the second substrate CoA to produce acetyl-CoA. Formation of AcCoA, the final product, closes the catalytic cycle of PFL.[4]



The investigated aspect of this mechanism concerns the process that allows CoA to enter the active site, which is a prerequisite for the second half-reaction. The problem with this step is that the binding site of CoA is located at the protein surface, while the active site is buried in the protein

interior.[5] In search for possible solutions to this problem, the PFL system was subjected to long unrestrained molecular dynamics simulations. The models representing the PFL system before and after the first half-reaction with pyruvate were used to examine the possible effect that acetylation of the enzyme has on the necessary conformational changes.

[1] J. M. Buis, et al. *Archives of Biochemistry and Biophysics* **433**, 288 (2005).

[2] L. Zelcbuch, et al. *Biochemistry* **55**, 2423 (2016).

[3] J. Knappe, et al. *Eur. J. Biochem.* **50**, 253 (1974).

[4] J.-D. Guo et al. *J. Phys. Chem. B* **108**, 15347 (2004).

[5] A. Becker, et al. *J. Biol. Chem.* **277**, 40036 (2002).



## Energies of Molecular Crystals from Many Body Expansion combined with Frozen Density Embedding

Daniel Schmitt-Monreal<sup>1</sup>, Julia Brüggemann<sup>1</sup>, Christoph R. Jacob<sup>1</sup>

<sup>1</sup>*Institut für Physikalische und Theoretische Chemie, TU Braunschweig  
Gaußstraße 17, Braunschweig, Deutschland*

Molecular crystals are relevant in different research fields such as pharmaceuticals or organic based semiconductor technologies. Of particular interests are the energy difference between different polymorphic structures of molecular crystals. Predicting these small energy differences with quantum chemical methods is an incredibly difficult task [1].

Wave-function based electronic structure methods are a powerful tool for describing inter-molecular interactions, but are in general not available for periodic crystal structures. Instead, (dispersion-corrected) DFT is routinely available for periodic crystal structures, but often does not provide the required accuracy. The many-body expansion provides an appealing approach for calculating the lattice energies of molecule crystals by decomposing it into contributions of subsystems such as dimers, trimers, etc. The decomposition into smaller subsystems allows for the use of wave-function based methods to calculate the interaction energies with sufficiently high accuracy [2].

However, the convergence with respect to the subsystem order in the many-body expansion remains a bottleneck, because the contributions of trimers and tetramers can in general not be neglected. Here, we explore the use of quantum-chemical embedding methods to implicitly account for such high-order contributions. Specifically, we employ frozen-density embedding (DFT-in-DFT and WFT-in-DFT) for the monomer, dimer and trimer calculations. As test cases, we consider ice as well as two organic compounds (acetylsalicylic acid, oxalyldihydrazide) in different crystal structures [3].

- [1] Gregory J. O. Beran, *Chem. Rev.* **116** (9), 5567 - 5613 (2016).
- [2] Ryan M. Richard, Ka Un Lao, John M. Herbert, *J. Chem. Phys.* **141**, 014108-1-11 (2014).
- [3] Christoph R. Jacob, Johannes Neugebauer, *WIREs Comput. Mol. Sci.* **4**, 325-362 (2013).

## Assessment of density functionals for computing thermodynamic properties of lanthanide complexes

Arnaud Jaoul<sup>1</sup>, Grégory Nocton<sup>1</sup>, Carine Clavaguéra<sup>2</sup>

<sup>1</sup>LCM, CNRS, Ecole polytechnique, Université Paris-Saclay, Route de Saclay, 91128 Palaiseau Cedex, France

<sup>2</sup>Laboratoire de Chimie Physique, CNRS - Université Paris Sud, Université Paris-Saclay. 15 avenue Jean Perrin, 91405, Orsay Cedex, France

*carine.clavaguera@u-psud.fr*

Electron transfer using lanthanide complexes has found numerous applications in the last decades, e.g. for the reduction of small molecules such as CO<sub>2</sub> or the development of newly designed luminescent and magnetic compounds.

Recently, it was shown experimentally that the electron transfer from a divalent lanthanide complex to the phenanthroline ligand induces a coupling reaction with the formation of a new C-C [1, 2]. The evaluation of the thermodynamic properties of this coupling reaction is a real challenge for computational chemistry and we propose to assess a variety of density functionals in order to reproduce the available experimental data of this equilibrium between the radical phenanthroline complex  $Cp_2^*Sm(phen)$  and the coupling product  $(Cp_2^*Sm(phen))_2$ . The role of the Hartree-Fock exchange in the functional is pointed out. Finally, the PBE0-D3 and M06-2X functionals lead to a good evaluation of the energies and enable a correct description of the ligand to metal charge transfer, both in the 4f and 5d metal orbitals [3]. Furthermore, topological analyses pointed out that the C-C bond created has a partial covalent character explaining why both the monomeric and the dimeric forms exist in equilibrium.

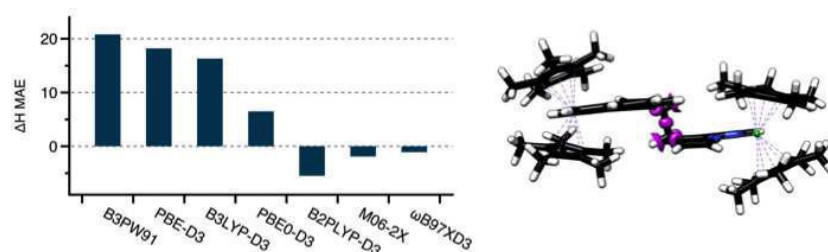


Figure 1: Mean Average Signed Deviation between the theoretical and experimental  $\Delta H$  (kcal/mol) for samarium complexes using different density functionals (left) and ELF representation of the V(C,C) synaptic basin (right)

[1] G. Nocton, L. Ricard, Chem. Commun. **51**, 3578 (2015).

[2] G. Nocton, W. W. Lukens, C. H. Booth, S. S. Rozenel, S. A. Medling, L. Maron, R. A. Andersen, J. Am. Chem. Soc. **136**, 8626 (2014).

[3] A. Jaoul, G. Nocton, C. Clavaguéra, submitted (2017).

## Azobenzene photoisomerization in the strong coupling regime

J. Fregoni<sup>1,2</sup>, G. Granucci<sup>3</sup>, M. Persico<sup>3</sup>, S. Corni<sup>2,4</sup>

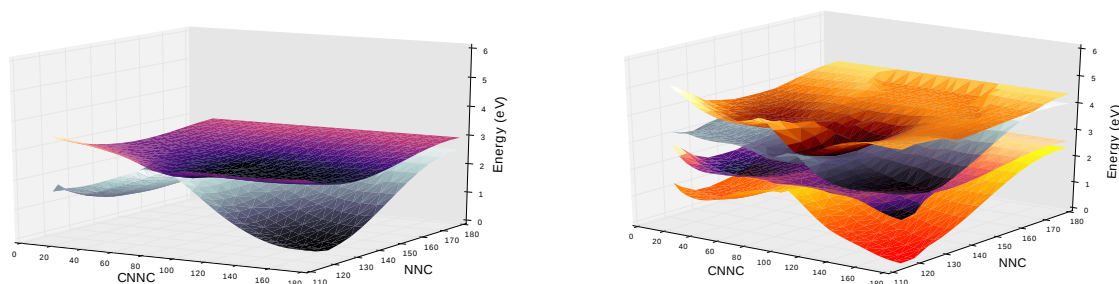
<sup>1</sup>*F.I.M. Dept., University of Modena and Reggio Emilia, Via G. Campi 213/a, Modena, Italy*

<sup>2</sup>*CNR - Institute of Nanosciences, Via G. Campi 213/a, Modena, Italy*

<sup>3</sup>*Dept. of Chemistry and Industrial Chemistry, University of Pisa, Via Moruzzi 13, Pisa, Italy*

<sup>4</sup>*Dept. of Chemical Sciences, Univeristy of Padova, via F. Marzolo 1, Padova, Italy*

The experimental achievement of single-molecule strong coupling regime in nanocavities for organic molecules [1] has risen a deep interest in the theoretical comprehension of such phenomenon [2]. Such regime can be achieved as the resonant frequency of a cavity coupled to the excited states of a molecule. Under this condition, the Rabi oscillations of a single molecule inside the cavity are much faster than the dissipation effects. Therefore, the coupling allows stable hybrid light-matter states to be formed (polaritonic states). Various theoretical treatments on model molecules show the possibility to manipulate the dynamics of photochemical processes, such as photocatalysis and photoisomerizations [3]. However, no realistic molecules have been theoretically treated so far. Here, we present the formation of polaritonic states in a photopolarizable molecule at different resonant energies. As it was recently argued by Flick *et al.* [4], the correct description of the coupling term is still controversial. In order to clarify the problem, we compare such term within two different gauges: the dipolar hamiltonian and the minimal coupling hamiltonian. Finally, the influence of the strong coupling on the photoisomerization process in azobenzene is investigated through direct (on-the-fly) trajectory surface hopping (DTSH). The electronic problem is solved by exploiting the semiempirical wavefunction approach devised by Persico, Granucci and coworkers [5]. The photoisomerization is studied in vacuum for the time being, comparing the results to the state-of-the-art literature references for the photochemistry of azobenzene.



Uncoupled and coupled azobenzene PESs

- [1] R. Chikkaraddy, B. De Nijs, F. Benz, S. Barrow, O. Scherman, E. Rosta, A. Demetriadou, P. Fox, O. Hess, J. Baumberg, *Nature*, **535**, 127 (2016).
- [2] R. Li, D. Pérez, F. Vidal, A. Domínguez, *Phys. Rev. Lett.*, **117**, 107401 (2016).
- [3] M. Kowalewski, K. Bennett, S. Mukamel, *J. Chem. Phys.*, **144**, 054309 (2016).
- [4] J. Flick, M. Ruggenthaler, H. Appel, A. Rubio, *PNAS*, **114**, 5063 (2017).
- [5] T. Cusati, G. Granucci, E. Nùñez, F. Martini, M. Persico, and S. Vázquez, *J. Phys. Chem. A*, **116**, 98 (2012).

## Interpolation of Potential Energy Surfaces using Gaussian Process Regression

Alexander Denzel<sup>1</sup>, Johannes Kästner<sup>1</sup>

<sup>1</sup>*Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55,  
Stuttgart, Germany, denzel@theochem.uni-stuttgart.de*

One of the fundamental problems in theoretical chemistry is the steep scaling of electronic structure calculations with the system size. In many calculations one needs many evaluations of the potential energy surface and its derivatives (often up to second order).

It is well known that one can use interpolation schemes like Shepard interpolation to overcome this problem to a certain extend.

Over the last years the increasing usability of machine learning methods like neural networks and Gaussian process regression (GPR) lead to many scientific advancements in several fields. Many of these methods aim at interpolating high dimensional functions and therefore, they seem well suited for the purpose of interpolating a potential energy surface as well.

We already studied the usability of neural networks for the interpolation of potential energy surfaces in our group. In our work we are currently investigating Gaussian process regression as an alternative approach. In contrast to neural networks this method is more tractable, easier and faster to set up for a new system, and also, formulated in a Bayesian setting, has the capability of giving uncertainty measurements and the possibility of optimizing its parameters with e.g. the maximum likelihood method. In both methods we include derivative informations up to second order to train our model and improve the inference of derivative information.

We apply this method to interpolate several potential energy surfaces to be able to do geometry optimization and instanton calculations with fewer electronic structure calculations and therefore, faster than before.

## $\pi$ Electron Effects Control Diels-Alder Regioselectivity to Empty Fullerenes

Paula Pla<sup>1</sup>, Yang Wang<sup>1, 2</sup>, Manuel Alcamí<sup>1, 2, 3</sup>

<sup>1</sup>Dpto. de Química, Módulo 13, Universidad Autónoma de Madrid, 28049 Madrid, Spain

<sup>2</sup>Institute for Advanced Research in Chemical Sciences (IAdChem), Universidad Autónoma de Madrid, 28049 Madrid, Spain

<sup>3</sup>Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanociencia), 28049 Madrid, Spain

Diels-Alder (DA) cycloadditions are a powerful tool for the introduction of a six-membered ring to a fullerene cage. They have enabled the preparation of many functionalized derivatives of empty and endohedral fullerenes with applications in material and biological sciences.[1] Due to the existence of different types of bonds, regioselectivity is commonly exhibited. For instance, for C<sub>60</sub> fullerene, the [6,6] cycloadduct is distinctly preferred over the [5,6] one.[2] In the case of larger and less symmetrical cages, many possible regioadducts may be formed. In that context, several descriptors based on different physical arguments such as bond lengths, pyramidalization angles and fullerene LUMO shapes have been used to predict the DA selectivity of fullerenes, but none of them seem to be universally applicable.[3]

In this contribution, we show that the regioselectivity of DA cycloadditions to empty fullerenes is governed by the stabilization of the global  $\pi$  system of adducts. Reaction energies obtained from DFT calculations can be well reproduced by a computationally almost costless Hückel-based simple model.[4, 5] An extensive and systematic study of a whole range of fullerenes from C<sub>60</sub> to C<sub>180</sub> reveals that DA cycloaddition occurs preferentially at a few simple bond patterns. These simple rules provide us a visual guide for rapid prediction of DA regioselectivity. Moreover, we have proposed two quantitative reactivity descriptors that have a direct chemical interpretation in terms of bond forming and breaking ability and in terms of local aromaticity.

- [1] R. Caballero, P. de la Cruz, F. Langa in *Fullerenes: Principles and Applications*, Vol. 2 (Eds.: F. Langa, J.-F. Nierengarten), RSC, Cambridge, pp. 66-124 (2011).
- [2] A. Rodríguez-Forteza, S. Irle, J. M. Poblet, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **1**, 350–367 (2011).
- [3] S. Osuna, M. Swart, J. M. Campanera, J. M. Poblet, M. Solà, *J. Am. Chem. Soc.* **130**, 6206–6214 (2008).
- [4] Y. Wang, S. Díaz-Tendero, M. Alcamí, F. Martín *Nat. Chem.* **7**, 927-934 (2015).
- [5] Y. Wang, S. Díaz-Tendero, M. Alcamí, F. Martín *J. Am. Chem. Soc.* **139**, 1609-1617 (2017).

## Application of the Bethe-Salpeter Equation to cationic dyes and $n\text{-}\pi^*$ chromogens

Cloé Azarias<sup>1</sup>, Ivan Duchemin<sup>2,3</sup>, Xavier Blase<sup>3,4</sup>, Denis Jacquemin<sup>1,5</sup>

<sup>1</sup> CEISAM (UMR CNRS 6230), Université de Nantes, 2 rue de la Houssinière 44322  
Nantes, France

<sup>2</sup>INAC, SP2M/L\_Sim, CEA/UJF Cedex 09, Grenoble, France

<sup>3</sup>Institut NEEL, Université Grenoble Alpes, F-38042 Grenoble, France

<sup>4</sup> Institut NEEL, CNRS, F-38042 Grenoble, France

<sup>5</sup> Institut Universitaire de France, 1 rue Descartes, F-75231 Paris cedex 05, France

Among the different approaches that exist for modelling electronically excited-states, the Bethe-Salpeter (BSE) formalism that relies on the GW eigenstates, is becoming increasingly popular due to its good compromise between accuracy and computational cost [1]. Indeed, it offers an alternative to the Time-Dependent Functional Theory (TD-DFT) as it benefits from the same scaling with system size while allowing a significantly more limited dependency on the starting exchange-correlation functional [ADC(2)] [2]. In this contribution, we present the performances of BSE/GW regarding two challenging cases: cationic dyes and  $n\text{-}\pi^*$  chromogens. First, we investigated the excited-state properties of a series of structurally diverse arylcarbonium derivatives. We compared the 0-0 energies as well as auxochromic and acidochromic shifts obtained with the BSE/GW, TD-DFT and the second-order algebraic diagrammatic construction [3]. Second, we studied the lowest singlet transition in twelve  $n\text{-}\pi^*$  compounds based on the nitroso, carbonyl, thiocarbonyl and diazo chromophores. We compared the BSE/GW and TD-DFT descriptions with wavefunction-based theoretical best estimates [4]. This contribution supports the use of BSE/GW for modelling transitions that are not well described with TD-DFT.

[1] D. Jacquemin, I. Duchemin, X. Blase, *J. Phys. Chem. Lett.* **8**, 1524 (2017).

[2] D. Jacquemin, I. Duchemin, X. Blase, *J. Chem. Theory Comput.* **11**, 3290 (2015).

[3] C. Azarias, I. Duchemin, X. Blase, D. Jacquemin, *J. Chem. Phys.* **146**, 034301 (2017).

[4] C. Azarias, C. Habert, S. Budzák, X. Blase, I. Duchemin, D. Jacquemin, submitted to *J. Phys. Chem. A*.

## Flexible water docking and virtual screening using PLANTS combined with tuned water selection criteria

Xiao Hu<sup>1</sup> and Alessandro Contini<sup>1</sup>

<sup>1</sup>*Dipartimento di Scienze Farmaceutiche, Università degli Studi di Milano*

*Via Venezian, 21 20133 Milano, Italy*

*xiao.hu@unimi.it*

Role of explicit water molecules in docking and virtual screening remains debatable and contradictory. In this study, we have assessed the docking performance including flexible water molecules using the PLANTS docking package[1]. This could provide a potential resolution to the efficient virtual screening including flexible water molecules. To enable the efficient assessment, a set of automatised selection criteria for water molecules within both the *holo* and *apo* structures was applied. The water molecules were selected from both crystal resolved water position and 3D-RISM calculations. Good correlation was demonstrated between the two and an ideal amount of water molecules can be preserved. Moreover, the selection procedures are also applicable to apo binding site, which allows further feasibility. We have demonstrated improved docked poses after inclusion of flexible water assessed using three test sets, two of which derived from CCDC-Astex “clean” list [2] and DUD-E database [3], and an additional apo test set. The performance of virtual screening was also assessed using several testing systems.

[1] O. Korb, T. Stützle, T. E. Exner, *J. Chem. Inf. Model.* **49**, 84-96 (2009).

[2] J. W. M. Nissink, C. Murray, M. Hartshorn, M. L. Verdonk, J. C. Cole, R. Taylor, *Proteins: Struct., Funct., Genet.* **49**, 457-471 (2002).

[3] M. M. Mysunger, M. Carchia, J. J. Irwin, B. K. Schoichet, *J. Med. Chem.* **55** (14), 6582-6594 (2012).

X. Hu is funded by the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant (No. 675527)

## Theoretical investigation of Herzberg-Teller effects in resonance Raman spectra

Julien Guthmuller<sup>1</sup>

<sup>1</sup>*Faculty of Applied Physics and Mathematics, Gdańsk University of Technology,  
Narutowicza 11/12, 80-233 Gdańsk, Poland*

Vibrational resonance Raman (RR) spectroscopy is a useful tool to provide information on structures and properties of molecular excited states [1]. Therefore, an accurate simulation of absorption and RR spectra, by quantum chemistry methods, can help in the interpretation of experimental data as well as in the design of new compounds for specific applications e.g. in dye-sensitized solar cells or as photocatalysts [2,3]. Moreover, the calculation of RR intensities and their comparison with experimental data offers an opportunity to assess the ability of standard quantum chemistry methods to predict excited state properties [4,5].

In this contribution, simplified sum-over-state expressions are presented to calculate RR intensities [6], which allow inclusion of Franck-Condon (FC) and Herzberg-Teller (HT) effects. The molecular properties are calculated with density functional theory and the different methods are applied to the molecule of Rhodamine 6G [6]. Additionally, HT effects are considered for the molecule of Porphycene and for a Ruthenium-Palladium supramolecular photocatalyst [3] and are shown to have a significant impact on the RR intensities.

### Acknowledgments

The author is grateful to the Narodowe Centrum Nauki (Project No. 2014/14/M/ST4/00083) for financial support. The calculations have been performed at the Universitätsrechenzentrum of the Friedrich-Schiller University of Jena.

### References

- [1] M. Wächtler, J. Guthmuller, L. González, B. Dietzek, *Coord. Chem. Rev.* **256**, 1479 (2012).
- [2] S. Kupfer, J. Guthmuller, M. Wächtler, S. Losse, S. Rau, B. Dietzek, J. Popp, L. González, *Phys. Chem. Chem. Phys.* **13**, 15580 (2011).
- [3] J. Guthmuller, L. González, *Phys. Chem. Chem. Phys.* **12**, 14812 (2010).
- [4] J. Guthmuller, *J. Chem. Theory Comput.* **7**, 1082 (2011).
- [5] M. Staniszevska, S. Kupfer, M. Łabuda, J. Guthmuller, *J. Chem. Theory Comput.* **13**, 1263 (2017).
- [6] J. Guthmuller, *J. Chem. Phys.* **144**, 064106 (2016).



## Automated Analysis of Exchange Pathways in Spin-Coupled Systems

Torben Steenbock, Carmen Herrmann

*Institute for Inorganic and Applied Chemistry, University of Hamburg,  
Martin-Luther-King-Platz 6, 22761 Hamburg, Germany*

Spin coupling between spin centers plays an important role in systems containing transition metals such as enzymes and molecular magnets, and in organic di- and polyradicals. A reliable and efficient computation of spin-state energy splittings and magnetic exchange coupling constants is therefore an important task of theoretical chemistry.

We rederived, inspired by Ozaki and coworkers [1], an approach from solid-state physics based on Green's functions [2] by employing local projection operators and successfully applied it to various transition-metal complexes [3]. This methodology has the advantage that the coupling constant can be obtained from the electronic structure of the high-spin state only and does not require the calculation of the low-spin state.

Additionally, the Green's-function approach allows for a decomposition of the total coupling constant into molecular orbital (MO) contributions [4]. We also developed a scheme which can be used to obtain atomic contributions to the total coupling constant. This scheme allows us to evaluate the contributions to spin coupling from different fragments of the system (as for example ligands or surfaces; see Figure 1). Both decomposition schemes were successfully applied to transition-metal complexes in order to establish an automated analysis of exchange pathways in such compounds [4].

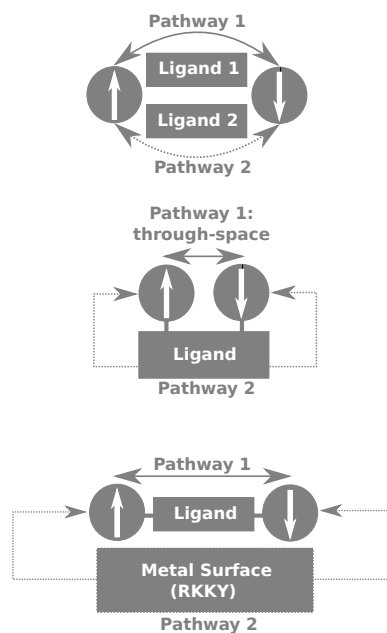


Figure 1: Three examples for systems with competing spin coupling pathways.

- [1] M.J. Han, T. Ozaki, J. Yu, *Phys. Rev. B* **70**, (2004) 184421.
- [2] A.I. Liechtenstein, M.I. Katnelson, V.P. Antropov, V.A. Gubanov, *J. Magn. Magn. Mater.* **67**, (1987) 65.
- [3] T. Steenbock, J. Tasche, A.I. Lichtenstein, C. Herrmann, *J. Chem. Theor. Comput.* **11**, (2015) 5651–5664.
- [4] T. Steenbock, C. Herrmann, *submitted*.

## New materials designed for absorption of non-steroidal antiinflammatory drugs

**Mariana Kozłowska<sup>1</sup>, Dorota Chełminiak-Dutkiewicz<sup>2</sup>,  
Marta Ziegler-Borowska<sup>2</sup>, Anna Kaczmarek-Kędziera<sup>2</sup>**

<sup>1</sup>*Institute of Chemistry, University of Białystok, Ciołkowskiego 1K, 15-245 Białystok, Poland*

<sup>2</sup>*Faculty of Chemistry, Nicolaus Copernicus University in Torun, Gagarina 7, 87-100 Torun, Poland*

Design of the efficient and selective non-steroidal antiinflammatory drugs (NSAIDs) sorbents is crucial for various branches of science and technology, starting from the pollution detection and removal from the environment and finishing in nanomedicine and designing of the drug delivery systems. NSAIDs are available over-the-counter and are applied widely in chronic diseases and popular ailments. Among their adverse effects the gastrointestinal problems, cardiovascular risk and erectile dysfunction can be mentioned. NSAIDs themselves and their metabolites are discharged to the environment and can undergo the further photodegradation or other transformations that can possibly increase their hazardous action on living organisms. Despite their small amounts in environment (ppb) one does not know the precise influence of NSAIDs on the organisms assuming the long exposition times. Thus the current European Union regulations add diclofenac to the list of the most hazardous chemicals. Therefore, it is of particular importance to develop the methodology of NSAIDs detection and removal from the wastewaters and soils. Hence, the thorough knowledge of the mutual interaction of NSAIDs and their sorbents is essential. In the current project chitosan-based materials are proposed as the efficient sorbents. Computational study includes the characteristics of intramolecular interaction in chitosan chains, conformational study of chosen NSAIDs, their dimerization, and the influence of the chitosan modification on the mutual NSAID-biopolymer interaction.

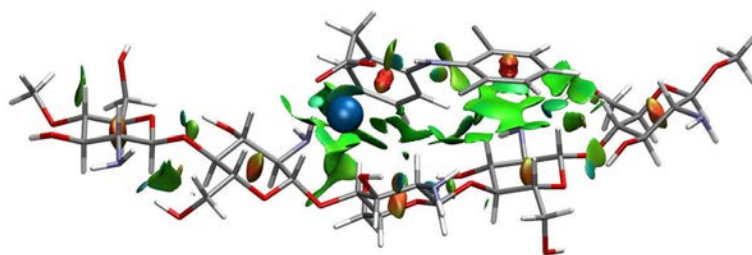


Figure 1: Diclofenac sodium-chitosan unit interaction

### Acknowledgements

Support from National Science Centre, Poland grant No. UMO-2014/13/B/ST8/04342 is gratefully acknowledged. Calculations were performed in Wrocław Centre for Networking and Supercomputing, Poznań Supercomputing and Networking Center and Academic Computer Centre Cyfronet AGH.

## Two-component relativistic density functional theory based on infinite-order Douglas-Kroll-Hess method

Yasuhiro Ikabata<sup>1</sup>, Takuro Oyama<sup>2</sup>, Kenta Hiraga<sup>2</sup>, Masao Hayami<sup>2</sup>, Junji Seino<sup>1</sup>, Hiromi Nakai<sup>1,2,3,4</sup>

<sup>1</sup>*Research Institute for Science and Engineering, Waseda University,  
Shinjuku, Tokyo, Japan*

<sup>2</sup>*Department of Chemistry and Biochemistry, School of Advanced Science and Engineering,  
Waseda University, Shinjuku, Tokyo, Japan*

<sup>3</sup>*CREST, Japan Science and Technology Agency, Kawaguchi, Saitama, Japan*

<sup>4</sup>*Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University,  
Nishikyo, Kyoto, Japan*

The infinite-order Douglas-Kroll-Hess (IODKH) method [1,2] is a promising technique to incorporate relativistic effects into quantum chemical calculations. We have established the accurate and efficient scheme based on the IODKH method within the framework of wavefunction theory. The key for efficiency in molecular systems is the local unitary transformation (LUT) method [3,4], which utilizes the local nature of relativistic effects. The divide-and-conquer (DC) method further accelerates the computation for large systems [5]. We also achieved quantitative agreement with spin-dependent four-component calculations at the post-Hartree-Fock level [6].

In this presentation, we focus on the extension of our scheme to density functional theory (DFT). In addition to the case of wavefunction theory, three points should be addressed: (1) picture change of the density operator [7,8], (2) noncollinear treatment of electronic spin, and (3) relativistic formulation of exchange-correlation functionals. We will present recent progress of theoretical development, together with the performance of DFT calculations.

- [1] M. Barysz and A. J. Sadlej, *J. Chem. Phys.* **116**, 2696 (2002).
- [2] J. Seino and M. Hada, *Chem. Phys. Lett.* **461**, 327 (2008).
- [3] J. Seino and H. Nakai, *J. Chem. Phys.* **136**, 244102 (2012).
- [4] J. Seino and H. Nakai, *J. Chem. Phys.* **137**, 114101 (2012).
- [5] J. Seino and H. Nakai, *J. Chem. Phys.* **139**, 034109 (2013).
- [6] M. Nakano, J. Seino, and H. Nakai, *Chem. Phys. Lett.* **675**, 137 (2017).
- [7] J. Seino, W. Uesugi, and M. Hada, *J. Chem. Phys.* **132**, 164108 (2010).
- [8] T. Oyama, Y. Ikabata, J. Seino, and H. Nakai, *Chem. Phys. Lett.* **680**, 37 (2017).

## Phosphorescent mechanism of arylboronic esters at room temperature

Qi Wang<sup>1,2</sup>, Yasuhiro Iwabata<sup>1</sup>, Junji Seino<sup>1</sup>, Yoshiaki Shoji<sup>3</sup>, Takanori Fukushima<sup>3</sup>, Hiromi Nakai<sup>1,2,4,5</sup>

<sup>1</sup>Research Institute for Science and Engineering, Waseda University, Shinjuku, Tokyo, Japan

<sup>2</sup>CREST, Japan Science and Technology Agency, Kawaguchi, Saitama, Japan

<sup>3</sup>Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, Midori, Yokohama, Japan

<sup>4</sup>Department of Chemistry and Biochemistry, School of Advanced Science and Engineering, Waseda University, Shinjuku, Tokyo, Japan

<sup>5</sup>Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Nishikyo, Kyoto, Japan

Recently, the phosphorescence of arylboronic esters has been experimentally<sup>[1]</sup> observed with a long lifetime in the solid state at room temperature (Fig. 1). Phosphorescence occurs via spin-forbidden transition, which is in general inefficient in the absence of heavy atoms. Thus, the phosphorescence of heavy-metal-free arylboronic esters is interesting. In this presentation, quantum chemistry calculations were performed to investigate the phosphorescent mechanism of arylboronic esters.

To achieve room-temperature phosphorescence, it is important to facilitate the intersystem crossing process and to suppress the non-radiative decay of triplet states. First, phosphorescent wavelengths and frontier orbitals of arylboronic esters were investigated by DFT calculations. The calculated wavelengths were in reasonable agreement with the experimental values. Next, the spin-orbit coupling constant was calculated to investigate the intersystem crossing process between singlet and triplet states for arylboronic esters. The structural deformation at T<sub>1</sub> state due to the boron functionality is responsible for the nonzero spin-orbit coupling. Finally, the minimum energy crossing point between S<sub>0</sub> and T<sub>1</sub> states was calculated to investigate the non-radiative decay process. The results will be shown in detail in the poster.

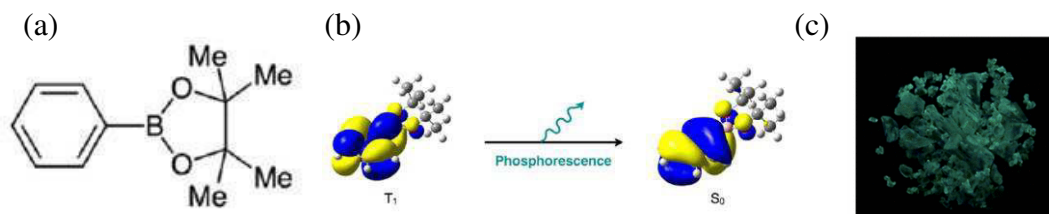


Fig. 1. (a) Molecular structures, (b) Kohn-Sham orbitals, and (c) phosphorescence emission of phenylboronic acid pinacol ester.

[1] Y. Shoji, Y. Iwabata, Q. Wang, D. Nemoto, A. Sakamoto, N. Tanaka, J. Seino, H. Nakai, and T. Fukushima, *J. Am. Chem. Soc.* **139**, 2728 (2017).

## A coupled state-averaged second-order MCSCF solver with fast convergence

David A. Kreplin<sup>1</sup>, Peter J. Knowles<sup>2</sup>, Hans-Joachim Werner<sup>1</sup>

<sup>1</sup>*Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany*

<sup>2</sup>*School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom*

We present a new second-order MCSCF solver including the coupling between CI coefficients and orbitals and the capability of state-averaged calculations. The solver is based on the second-order energy expansion in the unitary transformation of the orbitals introduced by Werner and Meyer [1]. This energy expansion ensures fast convergence and a reduced number of the four index integral transformations. It is used in the solver of Werner and Knowles [2, 3], where the CI coefficients and orbitals are optimized in an alternating way (micro-iterations). In some cases, the indirect coupling through the alternating optimization yields convergence problems. Our new solver considers the simultaneous and coupled optimization of CI coefficients and orbitals, based on the same energy expansion. Through the direct coupling of CI coefficients and orbitals, the convergence of the micro-iterations is improved. The CI coefficients and orbitals are calculated by a level-shifted second-order optimization and the coupling is realized by considering the mixed derivatives in the Hessian matrix similar to [4]. Also, we found a way to perform state-averaged calculations with a second-order optimization by using orthogonal projection operators. Hence, it is possible to perform coupled state-averaged calculations as well. To calculate the update in each optimization step, a system of linear equations with a level shifted Hessian has to be solved. To avoid the construction of the full Hessian matrix, we introduce an iterative subspace solver, where the equation is projected onto a suitable subspace. A good starting guess of the subspace yields fast convergence of the iterative subspace solver (mostly 4-6 iterations).

Through the coupling, our new solver needs half as many micro-iterations than the solver of Werner and Knowles [2, 3] and in some cases, the number of four index integrals transformations is significantly reduced. In all cases, the micro-iterations and subspace iterations converge to the demanded accuracy. This improves the robustness of the solver, such that new approximations will be possible. Also, the timing of calculations can be reduced by parallelization.

[1] H.-J. Werner, W. Meyer, *J. Chem. Phys.* **73**, 2342 (1980)

[2] H.-J. Werner, P. J. Knowles, *J. Chem. Phys.* **82**, 5053 (1985)

[3] P. J. Knowles, H.-J. Werner, *Chem. Phys. Lett.* **115**, 259-267 (1985)

[4] H. Jensen, H. Ågren, *Chem. Phys.* **104**, 229-250 (1986)

## Critical Analysis of Embedding Schemes for QM/MM Calculations in Condensed Phase

Martin Werner, Ricardo A. Mata

*Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Tammannstraße 6,  
37077 Göttingen, Germany*

The use of quantum mechanics/molecular mechanics (QM/MM) hybrid methods is still today the option of choice to describe chemical phenomena within an embedding environment. Its applications reach from reactions in the active sites of enzymes over explicit solvent simulations up to periodic structure calculations in solid states. The interaction between the quantum mechanical and molecular mechanical regions is a key element to the success of these QM/MM calculations[1] and can be included by different embedding schemes. While the interaction is simply calculated at the MM level in *mechanical embedding* schemes, the QM region is embedded in point charges for *electrostatic embedding* allowing for its polarization. The repolarization of the MM region, as taken into account in *polarized embedding* schemes, can have a significant impact in the properties under study.[2]

In this work, we critically address the different embedding schemes used in QM/MM approaches by comparing them to the results of an embedding with fragment Fock potentials.[3, 4] By separation of the Fock potentials into their components one gains insight into the resulting effect of Coulomb and exchange contributions to the description of the QM region. Mutual updates of the potentials in the presence of their environment allows for the analysis of the effect of repolarization. The benchmark systems involve periodic boundary crystal structure simulations and solutes in solution with explicit solvent treatment.

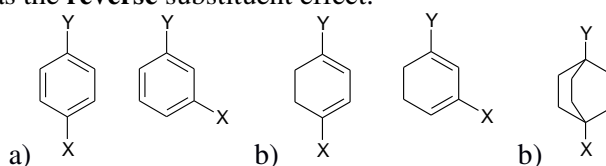
- [1] J. M. H. Olsen, N. H. List, K. Kristensen and J. Kongsted, *J. Chem. Theory Comput.* **11**, 1832 (2015).
- [2] A. Ganguly, E. Boulanger and W. Thiel, *J. Chem. Theory Comput.*, DOI: 10.1021/acs.jctc.7b00016 (2017).
- [3] R. A. Mata and H. Stoll, *Chem. Phys. Lett.* **465**, 136 (2008).
- [4] M. Werner and R. A. Mata, *AIP Conf. Proc.* **1702**, 090069 (2015).

## Towards physical interpretation of the substituent effect.

Halina Szatyłowicz

Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664  
Warsaw, Poland

The general term “substituent effect” can be applied to different kinds of intramolecular interactions in X-R-Y systems. This concept is especially useful in elucidating: (i) the impact of substituent X on the properties of a fixed group Y, known as a **classical** understanding of the substituent effect, (ii) the effect of X on the properties of transmitting moiety R, (iii) interrelations between some properties of Y due to the influence of the distant substituent X, and (iv) influence of the fixed group Y or -R-Y on the properties of substituent X, named as the **reverse** substituent effect.

**Scheme:**

Substituted derivatives of benzene (a), cyclohexa-1,3-diene (b) and bicyclo[2.2.2]octane (c).

B3LYP/6-311++G(d,p) method has been chosen to investigate the electron-donating properties of the Y group in a series of substituted systems (Scheme), where Y = NH<sub>2</sub>, H, NO<sub>2</sub> and X = NMe<sub>2</sub>, NH<sub>2</sub>, OH, OMe, CH<sub>3</sub>, H, F, Cl, CF<sub>3</sub>, CN, CHO, COMe, CONH<sub>2</sub>, COOH, NO<sub>2</sub>, NO. The Hammett substituent  $\sigma$ , charge of the substituent active region (cSAR) and substituent effect stabilization energy (SESE) descriptors are applied as the substituent effect characteristics. The Y group is characterized by structural and cSAR parameters, whereas the transmitting moiety – by aromaticity index HOMA.

All used parameters are found to be mutually interrelated with much better correlations for the *para*- than the *meta*-derivatives. The reverse substituent effect is clearly documented by a comparison of the cSAR(X) characteristics for the studied series of derivatives [1-5].

**Acknowledgements:** The author gratefully acknowledges the Interdisciplinary Center for Mathematical and Computational Modeling (Warsaw, Poland) for providing computer time and facilities and the National Science Centre and Ministry of Science and Higher Education of Poland for supporting this work under the grant no. UMO-2013/11/B/ST4/00531.

[1] O. A. Stasyuk, H. Szatyłowicz, C. Fonseca Guerra, T. M. Krygowski, *Struct. Chem.* **26**, 905 (2015).

[2] H. Szatyłowicz, T. Siodla, O. A. Stasyuk, T. M. Krygowski, *Phys. Chem. Chem. Phys.* **18**, 11711 (2016).

[3] H. Szatyłowicz, T. Siodla, T. M. Krygowski, *ACS Omega* **2**, 1746 (2017).

[4] H. Szatyłowicz, T. Siodla, T. M. Krygowski, *J. Phys. Org. Chem.* in press, DOI: 10.1002/poc.3694 (2017).

[5] H. Szatyłowicz, A. Jezuita, K. Ejsmont, T. M. Krygowski, *Struct. Chem.* in press, DOI: 10.1007/s11224-017-0922-2 (2017).

## Quest for Pb<sup>II</sup> Hydrides: When Theory Guides Experiment

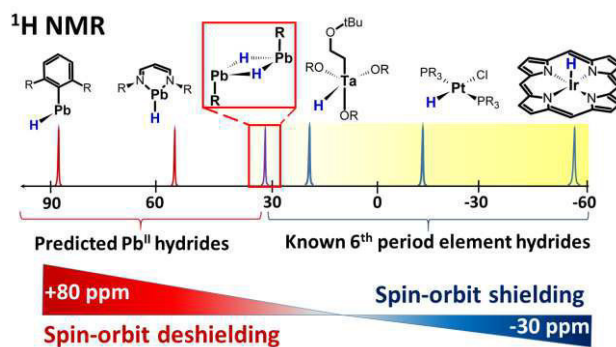
Jan Vicha,<sup>†</sup> Radek Marek,<sup>‡</sup> Michal Straka<sup>§</sup>

<sup>†</sup>Center of Polymer Systems, University Institute, Tomas Bata University in Zlín, Třída T. Bati, 5678, CZ-76001, Zlín, Czech Republic

<sup>‡</sup>CEITEC - Central European Institute of Technology, Masaryk University, Kamenice 5/A4, CZ-62500 Brno, Czech Republic

<sup>§</sup>Institute of Organic Chemistry and Biochemistry, Academy of Sciences, Flemingovo nám. 2, CZ-16610, Prague, Czech Republic

Although heavier low valent Group 14 hydrides are known to be versatile reagents in many chemical reactions, Pb<sup>II</sup> hydride was never observed. Our fully-relativistic calculations of <sup>1</sup>H NMR chemical shifts of model Pb<sup>II</sup> hydrides revealed possible reason. <sup>1</sup>H NMR chemical shifts of model Pb<sup>II</sup> hydrides, including the most stable dimeric  $\mu$ -H-bridged Pb<sup>II</sup> hydride, were predicted in a region between 30 – 90 ppm, well beyond standard <sup>1</sup>H NMR experimental ranges. [1] High-frequency shifts of these <sup>1</sup>H signals originate from relativistic contributions of unprecedented size, up to 80 ppm, caused by spin-orbit coupling at heavy atom. Based on these findings, the preparation of dimeric Pb<sup>II</sup>  $\mu$ -H-bridged hydride was re-examined, and <sup>1</sup>H NMR chemical shift ranges broadened accordingly. [2] Indeed, the hydride <sup>1</sup>H NMR resonance was detected at 31.1 ppm in solid state and 35.6 ppm in solution respectively [3] (theoretical prediction 30.8 ppm *in vacuo*). The last unknown low-valent Group 14 hydride was thus experimentally confirmed.



Acknowledgement: This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic, Program NPU I (LO1504 to JV) and the Czech Science Foundation (grants 16-05961S to JV and 15-09381S to RM).

[1] J. Vicha, R. Marek and M. Straka, *Inorg. Chem.*, **55**, 10302–10309 (2016).

[2] J. Schneider, C. P. Sindlinger, K. Eichele, H. Schubert and L. Wesemann, *J. Am. Chem. Soc.*, **139**, 6542–6545 (2017).



## Molecular Dynamics Study of the Thermoresponsive Polymer: poly(*N*-*n*-propylacrylamide) (PNnPAm).

Tiago E. de Oliveira<sup>1</sup>, Carlos Marques<sup>1</sup>, Paulo A. Netz<sup>2</sup>

<sup>1</sup>*Institut Charles Sadron, CNRS, Strasbourg, France*

<sup>2</sup>*Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil*

The breadth of technological applications of smart polymers relies on the possibility of tuning their molecular structure to respond to external stimuli. In this context, we present numerical simulation results on the phase transition of poly(*N*-*n*-propylacrylamide) (PNnPAm) oligomers. PNnPAm is a smart polymer that exhibits a coil-to-globule collapse transition in aqueous solutions when the temperature is increased above its lower critical solution temperature (LCST) (297 K). Compared with the better known *N*-substituted acrylamide-based polymer (poly(*N*-isopropylacrylamide))(PNIPAm), PNnPAm has a *n*-propyl group instead of the isopropyl group present on PNIPAm. Experiments show that the lower critical solution temperature of PNnPAm is lower than that of PNIPAm and that in PNnPAm solutions the collapsing transition steeper and stronger than in PNIPAm. We carried out all-atom molecular dynamics simulations to understand, from a microscopic point-of-view, the influence of chain size and concentration on the LCST of PnPAm. Our analysis not only shows that the oligomer chain length has a strong influence on the LCST but allow also to discriminate the role of the intra- and inter-chain non-bonded interactions in the collapsed transition.

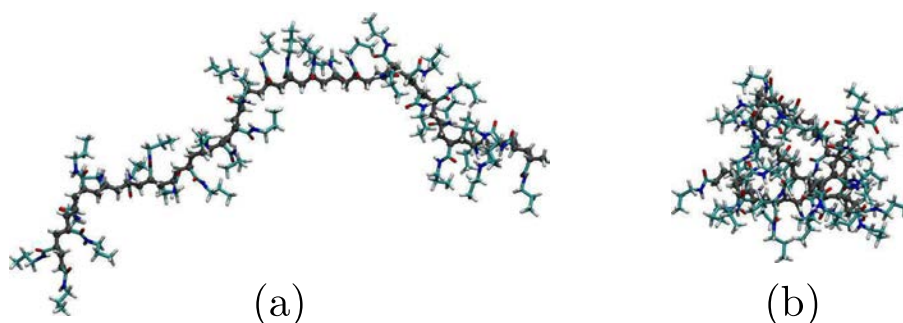


Figure 1: Snapshot of a PNnPAm chain for 32-mers at the end of 50 ns at two different temperatures: (a) below the LCST (280 K) and (b) above the LCST (340 K). The carbon backbone are shown in gray and water molecules have been omitted for clarity.

[1] T. E. de Oliveira *et al.* - *to be submitted*, (2017).

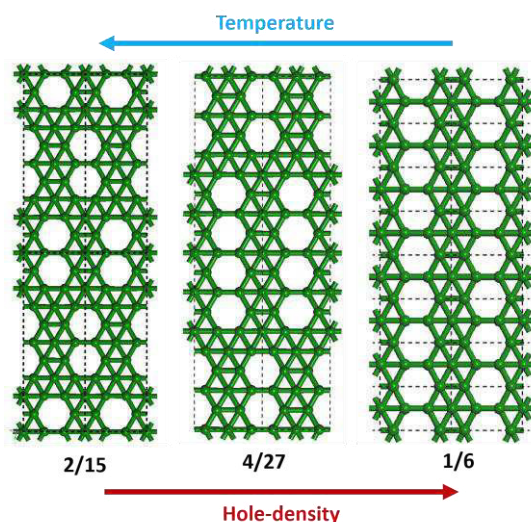
[2] B. Wedel, Y. Hertle, O. Wrede, J. Bookhold, and T. Hellweg, *Polymers* **8**, 162 (2016).

## The role of holes in borophenes, an *ab-initio* study of structural stability on Ag(111) surface.

Naiwrit Karmodak and Eluvathingal D. Jemmis

*Department of Inorganic and Physical Chemistry  
Indian Institute of Science, Bangalore, Karnataka-560012*

The discovery of 2D boron phases is one of the remarkable developments in the last few years.<sup>[1,2,3]</sup> The hexagonal hole density (HD) is explained by comparing to the electronic structure of  $\text{MgB}_2$ . The HD and distribution of holes determine the relative stability of the borophene phases on Ag (111) surface.<sup>[4]</sup> Several polymorphs of boron are energetically competitive on Ag surface. The conditions during the growth process control the nature of these phases. Sheets with higher HD are formed at lower temperatures. Upon increasing the temperature, the metal to sheet interaction decreases and the boron atoms rearrange to reduce the HD of the sheet. Detailed studies of first principles based simulations will be presented.



### The temperature dependence of borophene phases

#### References:

- [1] A. J. Mannix, et al., *Science* **350**, 1513 (2015).
- [2] (a) B. Feng, et al., *Nat Chem* **8**, 563 (2016). (b) Z. Qing, et al., *J. Phys. Condens. Matter* **29**, 095002 (2017).
- [3] (a) H. Tang and S. Ismail-Beigi, *Phys. Rev. Lett.* **99**, 115501 (2007). (b) X. Wu, J. Dai, Y. Zhao, Z. Zhuo, J. Yang, and X. C. Zeng, *ACS Nano* **6**, 7443 (2012).
- [4] N. Karmodak and E. D. Jemmis, *Angew. Chem., Int. Ed.*, (2017). DOI: 10.1002/anie.201610584.

## Nonlinear Optical Properties in Helical Molecules with Pancake Bonding

Shota Takamuku<sup>1</sup>, Masayoshi Nakano<sup>1</sup>

<sup>1</sup>Department of Materials Engineering Science Graduate school of Engineering Science,  
Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan

In our previous studies, we have revealed the correlation between the diradical character ( $\gamma$ ), which is defined by twice the weight of doubly excited configuration in ground states, and the second hyperpolarizability ( $\gamma$ ), which is the molecular level property of third-order nonlinear optical (NLO) properties. On the basis of this “ $\gamma$ - $\gamma$  correlation”, we have predicted large enhancement of  $\gamma$  values in a variety of open-shell singlet molecular systems with intermediate  $\gamma$  values [1]. To realize such an electronic structure, several molecular structures have been investigated, like polyaromatic hydrocarbon, main group systems, metal-metal bonded systems, and open-shell aggregates. Among them, pancake bonded systems, which has the covalent-like bonding between the stacked  $\pi$ -radicals [2], are found to show the intermediate diradical systems and large  $\gamma$  value in the stacking direction [3]. Recently, we have theoretically investigated helical molecules with pancake bonding (Figure 1) [4], and have found that some of them have intermediate diradical character (Figure 2). Furthermore, azulene-like molecules (Figure 2c) have been predicted to have asymmetric charge distribution, leading to further enhancement of the  $\gamma$  values [1]. Based on these studies, we expect that these helical pancake bonded systems are good candidates for highly-efficient NLO materials. In this study, therefore, we investigate those  $\gamma$  values using the LC-BLYP( $\mu = 0.33$ ) method with 6-31+G(d) basis set. For example, the orientationally-averaged  $\gamma$  value of **7AZ** is found to be about 9 times larger than that of 7helicene, which is the closed shell reference to **7AZ**. This demonstrates that intermediate diradical character enhances the  $\gamma$  values in helical pancake bonded systems.

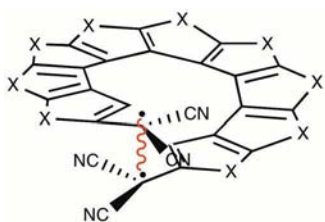


Figure 1. Helical pancake bond

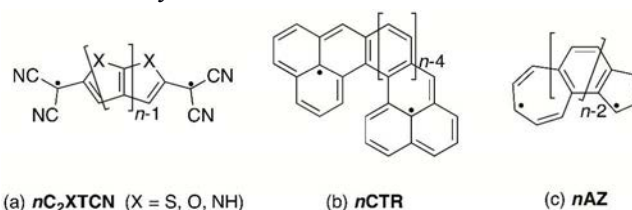


Figure 2. Model helical molecules with pancake bonds

- [1] M. Nakano, B Champagne, *J. Chem. Phys. Lett.* **6**, 3236 (2015). [2] Y-H. Tian, M. Kertesz. *J. Am. Chem. Soc.* **132**, 10648 (201) [3] K. Yoneda et al. *Chem. Eur. J.* **20**, 11129 (2014). [4] S. Takamuku, M. Nakano, M. Kertesz. *Chem. Eur. J.* **23**, 7474 (2017).

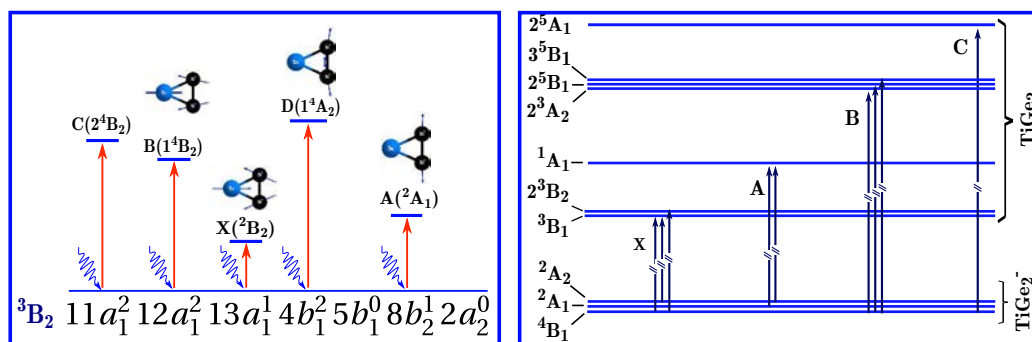
# ScSi<sub>2</sub><sup>-0</sup> AND TiGe<sub>2</sub><sup>-0</sup>: ELECTRONIC STRUCTURES AND INSIGHTS INTO ANION PHOTOELECTRON SPECTRA

Le Nhan Pham<sup>1, 2</sup>, Minh Tho Nguyen<sup>1</sup>

<sup>1</sup>Department of Chemistry, University of Dalat, 01 Phu Dong Thien Vuong, Dalat, Vietnam

<sup>2</sup>Division of Quantum Chemistry and Physical Chemistry, KULeuven, Leuven, Belgium

Theoretical studies on clusters containing transition metals are one of the interesting and challenging topics. The main reason is electronic structures of these systems need to be described with appropriate wave functions. Usually, single reference wave functions can describe electronic structures of many systems. For several systems especially those containing transition metals, single reference wave functions cannot be used efficiently with regard to correlation energy. In such situations, multireference wave functions are believed to be a positive alternative. Therefore, we utilize both single reference and multireference quantum wave function types (DFT, RCCSD(T), CASSCF, MRCI(Q), CASPT2 and NEVPT2) to synergistically investigate electronic structures of tiny clusters containing transition metals (ScSi<sub>2</sub><sup>-0</sup> and TiGe<sub>2</sub><sup>-0</sup>). On the basis of their electronic structures, possible one-electron ionization processes, which are the removals of one electron from anionic clusters, are predicted. Ionization energies of these transitions, the so-called adiabatic and vertical detachment energy (ADE and VDE), are also calculated at several levels of theory mentioned above. These calculated ADEs and VDEs provide reliable evidences to understand nature of all experimental photoelectron bands in the spectra. In addition, multidimensional Franck-Condon factor simulations can be employed to confirm electronic transitions and/or to provide more details about experimental results.



[1] L. N. Pham, M. T. Nguyen *J. Phys. Chem. A* **120**, (2016).

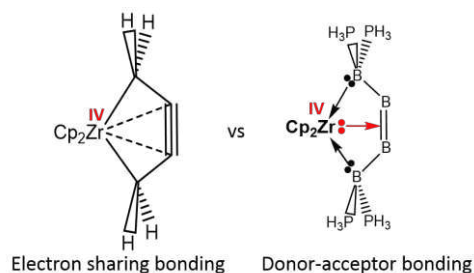
[2] L. N. Pham, M. T. Nguyen *J. Phys. Chem. A* **121**, (2017).

## Stabilization of B-B triple bond in a metallaborocycle: Contrast between boron and carbon analogs

Sagar Ghorai and Eluvathingal D. Jemmis\*

*Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, Karnataka, India*

High strain energy resisted the synthesis of cyclic allenes, cumulenes, and alkynes. An effective way to stabilize these cyclic systems is the incorporation of metal fragments that induce stabilizing trans-annular interactions.<sup>[1]</sup> We present strategies to incorporate the B-B triple bond in a metallacycle and ways to stabilize it. Electronic structure of  $(\eta^5\text{-Cp})_2\text{Zr}(\text{NH}_2\text{-BB-NH}_2)$  suggests it to be a candidate for boron-boron triple bond in the cyclic system; however, computational study shows that it is a very high energy isomer on its potential energy surface. Replacement of amines with tricoordinate nucleophilic boron groups  $(\eta^5\text{-Cp})_2\text{Zr}[\text{B}(\text{PH}_3)_2\text{-BB-B}(\text{PH}_3)_2]$  reduces the relative energy dramatically. The B-B triple bond arises by the donation of two electrons from the metal fragment,  $\text{ZrCp}_2$ , to the in-plane  $\pi$ -bonding orbital of the central B-B unit. The stabilization of metal center (Zr) comes from the donation of electron pairs from terminal tricoordinate nucleophilic B-centers. The characteristic donor-acceptor bonding feature in metallacycloboryne contrasts with the electron-sharing bonding in metallacycloalkyne. Strong  $\sigma$ -donating and chelating bis-phosphine ligands ( $\text{L}_2 = \text{Me}_2\text{P}(\text{CH}_2)_n\text{PMe}_2$ ), which stabilize donor-acceptor bonding interaction in gem-diborene  $\text{L}_2\text{B-BBr}_2$ , would be a good choice along the synthetic path towards,  $(\eta^5\text{-Cp})_2\text{Zr}[\text{B}_4(\text{Me}_2\text{P}(\text{CH}_2)_3\text{PMe}_2)_2]$ . A comparison of the energetics of the reaction leading to cyclic boryne system, with the linear boryne isomer  $[(\text{B}_2\text{NHC}^{\text{Ph}})_2]$  shows that the angle strain from cyclization is compensated by stabilization from the metal.<sup>[2, 3]</sup>



[1] S. Roy, U. Rosenthal, E. D. Jemmis, *Acc. Chem. Res.* **2014**, *47*, 2917-2930.

[2] H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radacki, A. Vargas, *Science* **2012**, *336*, 1420-1422.

[3] S. Ghorai, E. D. Jemmis, *Chem. Eur. J.* DOI: 10.1002/chem.201702422.

## Coupled electron-nuclear dynamics: A comparison of methods and dimensionality

**Thomas Schnappinger, Julius P. P. Zauleck, Robert Siemering,  
Regina de Vivie-Riedle**

*Department of Chemistry, Ludwig-Maximilians-Universität,  
Butenandtstr. 5-13, Munich, Germany*

The purpose of this work is a first comparison of two methods describing a coupled electron-nuclear dynamics: the purely quantum mechanical ansatz NEMol and the Real-Time Time-Dependent Density Functional Theory (RT-TDDFT) based Ehrenfest dynamics. The NEMol ansatz was developed in our group to describe the coupled electron-nuclear dynamics of a photoexcited system. We introduce a novel form of the NEMol ansatz which is formulated for a single electronic state in a one-dimensional subspace. The comparison between this NEMol ansatz and the RT-TDDFT Ehrenfest dynamics is so far limited due to the difference in dimensionality. Therefore an approach for one-dimensional RT-TDDFT Ehrenfest dynamics is presented.

As an example the dynamics of (Z)-3-aminocarolein in the electronic ground state was analyzed. Using different quantum chemical methods the potential profile of the tautomerism was calculated and the critical points of the reaction were identified to set up the one-dimensional potential energy surface along the reaction coordinate. Using this surface we were able to compare the coupled electron-nuclear dynamics calculated purely quantum mechanical (snapshots are shown in Figure 1) with the semiclassical Ehrenfest dynamics and observed significant differences for the electron motion. In order to probe the influence of the reduced dimensionality the full-dimensional RT-TDDFT based Ehrenfest dynamics simulation was performed, too. In addition a short outlook is provided how to select and evaluate the chosen dimensions for a dynamic simulation using the principal component analysis (PCA).

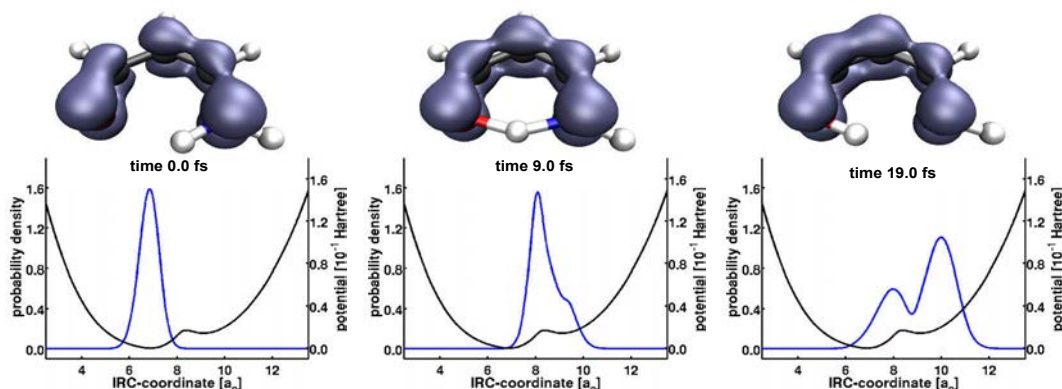


Figure 1: Snapshots of the coupled electron-nuclear dynamics of (Z)-3-aminocarolein calculated using the NEMol ansatz.



## Reaction-prediction scheme based on quantum chemical information and machine learning

M. Fujinami<sup>1</sup>, J. Seino<sup>2</sup>, H. Nakai<sup>1,2,3,4</sup>

<sup>1</sup>*Department of Chemistry and Biochemistry, Waseda University,  
3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan*

<sup>2</sup>*Research Institute for Science and Engineering, Waseda University,  
3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan*

<sup>3</sup>*CREST, Japan Science and Technology Agency,  
4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan*

<sup>4</sup>*Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University,  
Katsura, Kyoto 615-8520, Japan*

Predictions of products from reactants in chemical reactions are important in chemistry. Various reaction-prediction systems, which solve this problem using a computer, have been developed since 1980 [1]. Recently, the systems based on inductive data analysis methods have attracted attentions due to the high accuracy. Especially, the schemes utilizing the machine learning for organic reactions showed the great performances [2-5]. These schemes use a topological fingerprint of a molecule as a descriptor. The fingerprint is a suitable descriptor for organic molecules because of the small computational costs and its abundant information to describe variations of molecular structures. However, physical information beyond a two-dimensional molecular structure might be essential especially to predict elementary reactions including arbitrary elements such as transition metal elements.

In the present study, we extended the reaction-prediction scheme based on the machine learning [6]. The present scheme utilizes descriptors obtained by quantum chemical calculations. Polar and radical reactions extracted from a textbook in organic chemistry are predicted. The scheme gives close results to the previous studies with the topological fingerprint. Especially, the descriptors have an advantage in the prediction of radical reaction. An analysis of a relationship between descriptors and a reaction is performed in order to obtain the physicochemical knowledge in the reaction [7].

- [1] T. D. Salatin, W. L. Jorgensen, *J. Org. Chem.* **45**, 2043 (1980).
- [2] M. A. Kayala, C. A. Azencott, J. H. Chen, P. Baldi, *J. Chem. Inf. Model.* **51**, 2209 (2011).
- [3] J. N. Wei, D. Duvenaud, A. A.-Guzik, *ACS Cent. Sci.* **2**, 725 (2016).
- [4] M. H. S. Segler, M. P. Waller, *Chem. Eur. J.* **23**, 5966 (2017).
- [5] C. W. Coley, R. Barzilay, T. S. Jaakkola, W. H. Green, K. F. Jensen, *ACS Cent. Sci.* **3**, 434 (2017).
- [6] M. Fujinami, J. Seino, H. Nakai, *J. Comput. Chem. Jpn.* **15**, 63 (2016).
- [7] M. Fujinami, J. Seino, H. Nakai, *in preparation*.

## From structure to electronic properties of poly[methyl(phenyl)silylene] with DFT approach

**Barbora Hanulikova, Ivo Kuritka, Pavel Urbanek**

*Tomas Bata University in Zlín, Centre of Polymer Systems, tr. Tomase Bati 5678, Zlín,  
Czech Republic*

Poly[methyl(phenyl)silylene] (PMPSi) belongs to a group of  $\sigma$ -conjugated polymers, which are valuable materials due to their unique electron-optical properties induced by  $\sigma$ -orbital delocalization along their single-bonded Si backbones. Therefore, these properties, e.g. absorption maximum ( $\lambda_{max}$ ), are strongly dependent on the extent of electron delocalization and thus on conformation of the backbone chains [1]. Maximal  $\sigma$ -conjugation is related with helical arrangement of PMPSi. However, various disruptions of ideal conformation, such as bends of backbones, which are connected with adoption of semi-crystalline structure, are normally found in its chains. This evoked the aim of the investigation of the structural disruptions in backbone and their effect on the electronic properties [2, 3]. A kink of approximately *gauche* ( $60^\circ$ ) conformation that consists of four consecutive Si atoms was virtually introduced to several oligo[methyl(phenyl)silylene] (OMPSi<sub>n</sub>, n=1-10) backbones and these molecules were subjected to DFT and TDDFT study with B3LYP, M06 and  $\omega$ B97X-D functionals, and 6-31G\* basis set.

It was discovered that delocalization of molecular orbitals is affected by the presence of the kink because it causes their asymmetric distribution to non-disrupted parts of the backbone and to phenyl (Phe) rings in the kink vicinity. A position of the kink in Si chain also influences the value of HOMO-LUMO gap and therefore  $\lambda_{max}$ . Bandgap becomes wider as the kink shifts closer to the center of the backbone that reflects in experimental and calculated spectra. Further, the employment of  $\pi$ - $\pi$  interactions between Phe groups was confirmed on decamers and tetramers by Phe-Phe angle-distance dependence and molecular energy. It was found that the kink is viable folding element in PMPSi polymer.

### *Acknowledgement*

This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic – Program NPU I (LO1504). Computational resources were provided by the CESNET LM2015042 and the CERIT Scientific Cloud LM2015085, provided under the programme "Projects of Large Research, Development, and Innovations Infrastructures".

- [1] S. Nespurek et al., *J. Optoelectron. Adv. M.* **7**, 223 (2005).
- [2] B. Hanulikova et al., *Macromol. Symp.* **339**, 100 (2013).
- [3] B. Hanulikova et al., *Chem. Cent. J.* **10**, 28 (2016).



**[Sb<sub>n</sub>Au<sub>n</sub>Sb<sub>n</sub>]<sup>m</sup> (n= 4,5,6; m= -2, -1, -2) sandwich complexes as host of elements from groups I and II of periodic table.**

**Rafael Grande Aztatzi<sup>1</sup>, Jose M. Mercero<sup>1</sup>, Jesus M. Ugalde<sup>1</sup>**

<sup>1</sup> *Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU) and Donostia International Physics Center (DIPC), Donostia, 20080, Spain.*

Sandwich complexes have been widely explored during the last sixty years, since the ferrocene was synthesized in the early 1950s; its discover gave rise to a new area of research in chemical and materials sciences, having abundant applications as catalysts, nanodevices, polymers or as building block for new materials. Sandwich compounds are not only confined within carbon-containing ligands, but have also been synthesized carbon-free metallocenes and poly-metallic sandwich compounds, as is the case of [Sb<sub>3</sub>Au<sub>3</sub>Sb<sub>3</sub>]<sup>3-</sup> in 2015; the first all-metal layer sandwich species; which has inspired the design of new nanoscale building blocks with hollow structure, since that can increase their functional features, and depending on the size cavity, they can encapsulate a second material. In this sense, Zhu *et al.* theoretically have studied the Sb-Au sandwich complexes increasing the size of their metal rings from 3 up to 6, keeping the integrity of sandwich and thus growing up their hollow interior.[1-3]

In this work, we evaluate the capacity of the [Sb<sub>n</sub>Au<sub>n</sub>Sb<sub>n</sub>]<sup>m</sup> (n= 4,5,6; m= -2, -1, -2) sandwich complexes to capture inside them elements from groups I and II of the periodic table. Within density functional theory framework, the neutral and charged structures were optimized and characterized as minima by frequency analysis, we use the non-empirical exchange-correlation functional PBE0 and the def2-TZVP basis sets with the corresponding pseudopotential for heavy atoms.

Our results shown that in most of the cases, the guest is located in the center of the gold ring causing its elongation and therefore modifying the stacking of the three metal layers, preserving thus the sandwich integrity.

- [1] F. Pan, *et al. JACS*, **137**, 10954 (2015)
- [2] W. Tian, *et al. JCP*, **145**, 044308 (2016)
- [3] T. Zhu, *et al. AIP Advances*, **7**, 025012 (2017)

## Energetics of ion binding of the Na<sup>+</sup>/H<sup>+</sup> antiporter MjNhaP1

Judith Warnau<sup>1,3</sup>, Kei-ichi Okazaki<sup>1</sup>, Ana P. Gamiz-Hernandez<sup>3</sup>,  
David Wöhlert<sup>2</sup>, Özkan Yildiz<sup>2</sup>, Werner Kühlbrandt<sup>2</sup>, Ville R. I. Kaila<sup>3</sup>,  
Gerhard Hummer<sup>1</sup>

<sup>1</sup>Department of Theoretical Biophysics and <sup>2</sup>Department of Structural Biology, Max Planck Institute of Biophysics, Max-von-Laue-Straße 3, Frankfurt am Main, Germany.

<sup>3</sup>Department Chemie, Technische Universität München, Lichtenbergstraße 4, Garching, Germany.

Sodium proton transport is essential for the viability of the cell by controlling pH and salt concentration, and maintaining volume homeostasis. Originally described as Na<sup>+</sup>/H<sup>+</sup> exchangers, several cation/proton antiporter (CPA) were recently shown to also transport K<sup>+</sup> [1,2]. By contrast the electroneutral NhaP1 of *Methanocaldococcus jannaschii* (MjNhaP1) does not transport potassium ions [3]. To understand the ion selectivity of MjNhaP1, we estimate the free-energy of ion binding using classical free-energy perturbation (FEP) calculations. In a fully atomistic molecular-dynamics (MD) simulation, a sodium ion is alchemically transformed to a potassium ion, which sheds light on the molecular mechanism of ion specificity.

[1] M. Gierth, P. Mäser, *FEBS Lett.* **581**, 2348-56 (2007).

[2] C. L. Brett, M. Donowitz, R. Rao, *Am J Physiol Cell Physiol* **288**, C223-C239 (2005).

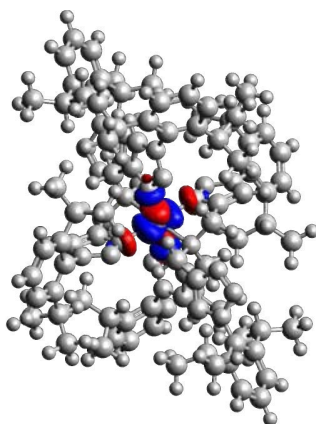
[3] C. Paulino, D. Wöhlert, E. Kapotova, Ö. Yildiz, W. Kühlbrandt, *elife*, **3**:e03583 (2014).

## Embedded Multireference Coupled Cluster Theory

David J. Coughtrie<sup>1</sup>, Robin Giereth<sup>1</sup>, Hans-Joachim Werner<sup>1</sup>, Andreas Köhn<sup>1</sup>

<sup>1</sup>*Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55,  
70569 Stuttgart, Germany*

Many chemical reactions are dominated by a small number of atoms and electrons in an active region of the molecule. This has led to the development of embedded electronic structure methods, which strive to combine an accurate description of the active region with a computationally less expensive approach for the rest of the system. This is of particular importance for multireference systems, which require more complex and expensive theories, for example internally contracted multireference coupled cluster (icMRCC) theory[1]. We have implemented an embedding procedure that uses truncated sub-spaces of the occupied and virtual molecular orbitals, rendering expensive multireference calculations viable by restricting them to the active region of the molecule. The occupied molecular orbitals are localised and partitioned into active and environment regions, and a reduced virtual space made by merging projected atomic orbitals within the active region. Embedded icMRCC calculations are further incorporated into less expensive perturbative methods [2] using a simple subtractive approach. We present benchmark calculations for the embedding procedure using small molecules, including homolytic bond breaking and carbenes. Further application to much larger systems is also demonstrated, including transition metal complexes consisting of hundreds of atoms and thousands of basis functions (see figure).



[1] M. Hanauer and A. Köhn, *J. Chem. Phys.* **136**, 204107 (2012).

[2] F. Menezes, D. Kats and H.-J. Werner, *J. Chem. Phys.* **145**, 124115 (2016).

## Computational study of biologically active naphthylisoquinoline alkaloids: an overview of obtained results

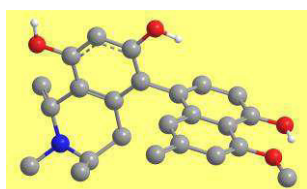
Mireille K. Bilonda<sup>1</sup>, Liliana Mammino<sup>2</sup>

<sup>1,2</sup>*Department of Chemistry / University of Venda / University Road, Thohoyandou,  
South Africa*

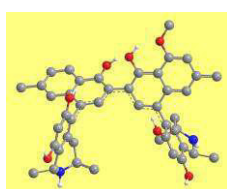
<sup>1</sup>*E-mail: mireillebilonda@yahoo.fr*

<sup>2</sup>*E-mail: sasdestria@yahoo.com*

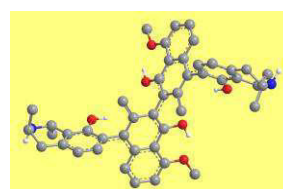
Naphthylisoquinoline alkaloids are alkaloids found in plants of the *Ancistrodaceae* and *Dioncophyllaceae* families. They exhibit remarkable biological activities - antimalarial, anti-HIV, anti-trypanosomal, anti-leishmanial and others [1-2]. Their molecules may contain one unit consisting of one isoquinoline moiety and one naphthalene moiety (monomeric structures) or two such units (dimeric structures). The presentation offers an overview of the results obtained for 33 monomeric alkaloids with antimalarial activity [3] and two dimeric alkaloids – jozimine A<sub>2</sub> [4], with antimalarial activity, and michellamine A [5], with anti-HIV activity. Calculations were carried out at the HF/6-31G(d,p) and DFT/B3LYP/6-31+G(d,p) levels in vacuo and in three different solvents. The results show that the conformational preferences and other molecular properties are influenced by intramolecular hydrogen bond (IHB) patterns, i.e., the number and type of IHBs present in a conformer, and by the mutual orientations of the moieties, with preference for mutual perpendicularity [3-5]. The solvent shows non-negligible effects on the molecular properties, mostly depending on the solvent nature and on the conformer's IHB pattern.



Ancistrocongoline



Michellamine A



Jozimine A<sub>2</sub>

- [1] M. R. Boyd, *J. Med. Chem.* **37**, 1740 (1994).
- [2] G. Bringmann, D. Feineis, *J. Exp. Bot.* **52**, 2015 (2001).
- [3] L. Mammino, M.K. Bilonda, *Theor. Chem. Acc.* **135**:101 (2016).
- [4] M. K. Bilonda, L. Mammino, *J. Mol. Mod.* Submitted.
- [5] L. Mammino, M.K. Bilonda, *J. Mol. Mod.* (2017) in press

## **Modern Coupled Cluster Approaches for the Spin-State Energetics of Carbenes**

**Reza Ghafarian-Shirazi, Frank Neese, Dimitrios A. Pantazis**

*Max Planck Institute for Chemical Energy Conversion, Stiftstr. 34-36, 45470 Mülheim an der Ruhr, Germany*

Carbenes constitute a large class of organic compounds that are not only of high practical interest because of their rich and varied chemistry, but also of fundamental interest owing to the complexity of their electronic structure. The stability and accessibility of the spin singlet and triplet states determines to large extent their physical and chemical properties. It is therefore of great importance to have widely applicable quantum chemical methods that can accurately predict the relative energies of these states for any given carbene. This often presents a challenge because of the fundamentally different closed or open-shell electronic configurations that contribute to the each possible state, the presence of near-degeneracies, and the substituent effects. In the present work we compile a benchmark set of aryl carbenes that span a range of singlet-triplet gaps and include both singlet and triplet ground state species. The performance of various correlated wave function methods is evaluated for the prediction of the ground spin state and the singlet-triplet gap. The comparison includes modern linear-scaling domain-based local pair natural implementations of coupled cluster theory, and critically examines the convergence and reliability of explicitly correlated F12 coupled cluster methods for open-shell species.

## Modelling the electronic states of polyphenylene-ethynylenes

Emmeline Ho<sup>1</sup>, Thibaud Etienne<sup>1</sup>, Marie-Liesse Doublet<sup>1</sup>, Benjamin Lasorne<sup>1</sup>

<sup>1</sup>*Institut Charles Gerhardt, Université de Montpellier, 2 place Eugène Bataillon,  
Montpellier, France*

Hydrocarbon dendrimers are macromolecules experimentally well-known for their exceptional optoelectronic properties [1]. Polyphenylene-ethynylene (PPE) dendrimers behave as light-harvesting antennae in which unidirectional exciton transfer occurs along a series of linear, conjugated building blocks connected *via* the *meta*-substitution of phenylene rings. Thus, PPE dendrimers have received much interest as artificial photosynthetic systems. Recent theoretical investigations based on semi-classical dynamics simulations [2] have indicated that the unidirectional energy transfer involves a cascade of conical intersections between excited states localized on different linear fragments. Yet, the calculations of full-dimensional potential energy surfaces (PES) remains out of reach for any level higher than semi-empirical, due to the size of the systems.

Different types of calculations (TDDFT, extended Hückel) enlightened a strong hierarchy within the interactions governing the electronic structure of *meta*-PPEs; in particular, their first excited states result from weak couplings among the excited states of the corresponding *para*-PPEs. This allows us to build a new type of diabatic representation for the PES under the form of a Hubbard matrix, whose eigenvalues are expected to reproduce the adiabatic energies at a TDDFT level of theory. The dependence on the nuclear coordinates will be expressed through the Hubbard parameters that are involved in the energies of the diabatic states (diagonal) and their couplings (off-diagonal); as all are local, each will only depend on a few nuclear coordinates, thus simplifying drastically the potential energy functions. The explicit expression of the Hubbard matrix elements through their constituting parameters as functions of the nuclear coordinates will be based on a multiscale approach.

[1] S. F. Swallen, R. Kopelman, J. S. Moore, C. Devadoss, *J. Mol. Struct.* **485-486**, 585 (1999).

[2] S. Fernandez-Alberti, V. D. Kleiman, S. Tretiak, A. E. Roitberg, *J. Phys.Chem.A* **113**, 7535 (2009).

**Relativistic calculations for identifying new chemical species at ultra-trace concentrations:  $\text{AtO}(\text{OH})_2^-$  and  $\text{IAtBr}^-$  revealed**

**Dumitru-Claudiu Sergentu<sup>1,2</sup>, Ning Guo<sup>1</sup>, David Teze<sup>1,2</sup>, Julie Champion<sup>1</sup>, Gilles Montavon<sup>1</sup>, Nicolas Galland<sup>2</sup>, Rémi Maurice<sup>1</sup>**

<sup>1</sup>*SUBATECH, UMR 6457, IN2P3/IMT Atlantique/Université de Nantes, Nantes, France*

<sup>2</sup>*CEISAM, UMR 6230, Université de Nantes, Nantes, France*

Revealing the occurrence of and identifying new chemical species at ultra-trace concentrations may turn out to be practically impossible from the sole experimental point of view. In such conditions, standard analytical chemistry tools such as spectroscopy ones cannot be used, and little information can be convincingly obtained. The molecular charge of a given species can be determined with electromigration experiments or chromatography, and speciation changes can be indirectly characterized by means of competition experiments.

In this work, we will focus on the identification of new astatine (At,  $Z = 85$ ) species. Actually, this work is of fundamental interest owing the high potential of the  $^{211}\text{At}$  radionuclide in radiotherapy and the current lack of knowledge on the chemistry of astatine [1]. Note that due to the minute quantities of astatine than can be produced in cyclotrons, one is in this case obliged to work at ultra-trace concentrations. Since At is a heavy element and since its  $6p$  shell may not be fully occupied in the compounds it can form, calculations must account for relativistic effects and in particular for spin-orbit coupling (SOC).

In this presentation, we will first show that the spin-orbit DFT (SO-DFT) method is accurate enough to compute or predict equilibrium constants of reactions between astatine basic units and inorganic ligands [2]. Then, we will show that SO-DFT calculations can discriminate two hypotheses arising from experiments concerning the identification of a new species belonging to the Pourbaix ( $E$ -pH) diagram of astatine, leading to the firm identification of  $\text{AtO}(\text{OH})_2^-$  [3]. Finally, we will show that SO-DFT calculations can be used to target the tiny experimental domain to be covered for evidencing an "exotic" interhalogen compound,  $\text{IAtBr}^-$  [4].

[1] D. S. Wilbur, *Nat. Chem.* **5**, 246 (2013).

[2] D.-C. Sergentu, G. David, G. Montavon, R. Maurice and N. Galland, *J. Comput. Chem.* **37**, 1345 (2016).

[3] D.-C. Sergentu, D. Teze, A. Sabatié-Gogova, C. Alliot, N. Guo, F. Bassal, I. da Silva, D. Deniaud, R. Maurice, J. Champion, N. Galland and G. Montavon, *Chem. Eur. J.* **22**, 2964 (2016).

[4] N. Guo, D.-C. Sergentu, D. Teze, J. Champion, G. Montavon, N. Galland and R. Maurice, *Angew. Chem. Int. Ed.* **55**, 15369 (2016).

## Potential energy surfaces for dissociative collisions of atmospheric molecules

**Yuliya Paukku, Zoltan Varga, and Donald G. Truhlar**

*Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN, USA*

We are developing potential energy surfaces for collisions of atmospheric molecules. Reactions of atmospheric molecules like  $O_2$ ,  $N_2$ , and  $NO$  play an important role in atmospheric chemistry and are also of interest for re-entry chemistry in aerospace applications. Hypersonic vehicles, spacecraft, and re-entry vehicles are in the atmosphere for extended periods of time, and their surface is exposed to interactions with high-temperature gases. The currently applied chemical models in hypersonic flow simulations are partially based on outdated data and assumptions. Accurate global potential energy surfaces (PESs) are needed for realistic computational fluid dynamics (CFD) simulations of shock layers around hypersonic vehicles.

Construction of potential energy surfaces involves electronic structure calculations and fitting of potential energy surfaces and their couplings. These surfaces can be further used for to calculate reaction rates and energy transfer. Due to the highly multi-reference characters of the reactants, intermediate structures, and products, construction of the PESs is very challenging from the theoretical point of view and requires application of expensive methods and significant amounts of computational time. A global ground-state potential energy surface describes all kinds of collisions of two diatomic molecules, as well as a triatomic molecule interacting with an atom, and a triatomic surface as a sub-surface of the four-body PES. Although the spin state of the whole system is constrained in a four-body system, the spin states of sub-systems are not conserved. Thus, individual three-body PESs are also important for the investigation of atom-diatom collisions. The surfaces are based on electronic structure calculations by multi-state complete-active-space second-order perturbation theory with minimally augmented correlation-consistent polarized valence triple-zeta basis sets. Potential energy surfaces are obtained by fitting the many-body interaction to electronic structure data points with a fitting function that is a permutationally invariant polynomial in terms of bond-order functions of the six interatomic distances. The resulting surfaces are used to carry out dynamical simulations that allow one to get reaction rate constants and energy transfer rate constants to model heat transport.

The authors are grateful to Tom Schwartzentruber and Graham Candler for collaboration on the overall project. This work was supported in part by the Air Force Office of Scientific Research by grant no. 3002-11098-00056269.



## Computational Approach to Organic Reactions Mechanisms in Ionic Liquids

**Christian Silvio Pomelli<sup>1</sup>, Cinzia Chiappe<sup>1</sup>**

<sup>1</sup>*Department of Pharmacy, University of Pisa, Via Bonanno 33, 56126, Pisa, Italy*

Ionic Liquids have extended, remarkably, the possibilities of tuning organic reactions taking advantage of the environmental effects [1]. Although only a small part of all hypothetic ionic liquids has been effectively synthesized and used as reaction media they are enough to provide a large variability of effects on reactions affecting reaction efficiency and selectivity not easy to rationalize. Ionic liquids cannot be localized along the classic coordinates of polarity, acidity, etc. used for molecular solvent classification. These categories can be used but they are not sufficient to full classify and rationalize them.

Ionic liquids can be considered as an equimolar mix of an anion and a cation. The effect of ions' net charges is quenched at macroscopic level but can be important at molecular level. This weakens one of the axioms of the solvent polarity theory: the importance of the dielectric constant value is limited in this context. Specific chemical properties of anion or cation or both can influence the reaction mechanism while their combination determines the physico-chemical nature of the ionic liquid.

Here we will present some computational studies [2] about reaction mechanisms in ionic liquids. The aim of these studies is to rationalize the experimentally observed effects in terms of specific chemical roles taken by anion or cation or both. These effects influence heavily mechanism and selectivity of the reaction studied.

The chemical nature of these effects is related to phenomena like hydrogen bond, steric hindering, inductive effect, acid/base properties, etc. Some mechanism in which ionic liquids present catalytic effects in molecular solvents will be also presented.

[1] T. Welton, P. Wasserscheid (Editors) *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim (2006).

[2] C. S. Pomelli, C. Chiappe *Phys. Chem. Chem. Phys.* **15**, 413 (2013).

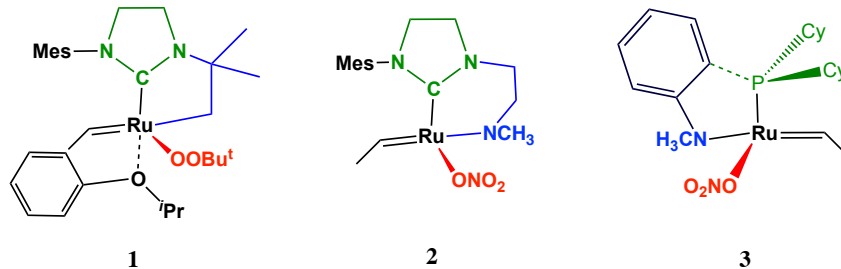
## DFT MECHANISM OF CHELATING RUTHENIUM CATALYSTS NEW FOR RING OPENING METATHESIS POLYMERIZATION (ROMP).

Katherine Paredes-Gil,<sup>a</sup> Xavier Solans-Monfort,<sup>b</sup> Luis Rodríguez-Santiago,<sup>b</sup> Mariona Sodupe,<sup>b</sup> Fernando Mendizábal,<sup>a</sup>

<sup>a</sup> *Facultad de Ciencias, Departamento de Química, Universidad de Chile, Las Palmeras 3425, Santiago, Chile*

<sup>b</sup> *Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain*

The Ring Opening Metathesis Polymerization (**ROMP**) is nowadays a highlighted area to the production of novel polymeric materials.<sup>1</sup> In this direction, the polynorbornadiene has been widely studied through well-defined Schrock catalysts. For instance, [Mo(NR)(=CHR<sub>2</sub>)(biphenolate)<sub>2</sub>] give to rise to *cis*-isotactic polymers, while the called MAP catalysts [Mo(NR)(=CHR<sub>2</sub>)(OR<sub>1</sub>)(Pyr)] produce the highly stereoregular or *cis*-syndiotactic polymers.<sup>2,3</sup> On the other hand, in the 2013 was reported the first Grubbs catalysts **1** that also conduce to *cis*-syndiotactic polymers.<sup>4</sup> This belongs to the *Z*-selective catalyst's family for Cross Metathesis (**CM**) which has allowed to obtain in the last decade high yield of *cis*-olefins.<sup>5,6</sup> In sense, we recently have studied the ancillary and chelating ligand effect on ruthenium complexes and found that the catalysts **2** and **3** are also *Z*-selective.<sup>7</sup> Therefore, these new catalysts that have similar characteristic to **1** could also lead to highly stereoregular polymers. For research this premise, we studied the **DFT** mechanism of these catalysts on **ROMP** reactions using norbornadiene as substrate. Specifically, were found the initiation and propagation step, and the rotameric change of the metal-carbene bond on the 14e- propagation specie, which has been postulated as the determinant step in the stereoregular polymer formation using Mo-complexes. All calculations were performed in the Gaussian 09 program, using the M06 functional. The Ru was described by the pseudopotential, called MWB28, which replaces the 28 inner electrons by a nonlocal effective potential. The others elements were described by the 6-31+G(*d,p*) basis sets. Finally, we carried out the vibrational analysis of all located stationary points to ensure their nature as intermediate or transition structure.



### References

- [1] Grubbs, R. H.; Khosravi, E. *Handbook of Metathesis, Volume 3: Polymer Synthesis*; WILEY, Ed.; 2015.
- [2] Schrock, R. R. *Dalton Trans.*, **40**, 7484 (2011)
- [3] Schrock, R. R. *Acc. Chem. Res.*, **47**, 2457 (2014)
- [4] Rosebrugh, L. E.; Ahmed, T. S.; Marx, V. M.; Hartung, J.; Liu, P.; López, J. G.; Houk, K. N.; Grubbs, R. H. *J. Am. Chem. Soc.*, **138**, 1394 (2016)
- [5] Endo, K.; Grubbs, R. H. *J. Am. Chem. Soc.*, **133**, 8525 (2011)
- [6] Smit, W.; Koudriavtsev, V.; Occhipinti, G.; To, K. W.; Jensen, V. R. *Organometallics*, **35**, 1825 (2016)
- [7] Paredes-Gil, K.; Solans-Monfort, X.; Rodríguez-Santiago, L.; Sodupe, M.; Jaque, P. In *Preparation*.

## Towards an Accurate First-Principles Description of Excited States in Dielectric Environments: The Versatile ADC(0-3)/SS-PCM Approach

Jan-Michael Mewes<sup>1</sup>, Andreas Dreuw<sup>2</sup>

<sup>1</sup>*Centre for Theoretical Chemistry and Physics, The New Zealand Institute for Advanced Study (NZIAS), Massey University Albany, Private Bag 102904, Auckland 0745, New Zealand*

<sup>2</sup>*Interdisciplinary Center for Scientific Computing, Rupprechts-Karls University, Im Neuenheimer Feld 205, 69120 Heidelberg, Germany*

We present a combination of the state-specific polarizable-continuum model (SS-PCM) with the ADC family of excited-state methods (ADC: algebraic-diagrammatic construction for the polarization propagator). Using a self-consistent scheme for “long-lived” solvent-equilibrated states as well as a perturbation-theoretical approach (ptSS-PCM) for vertical transitions in the non-equilibrium limit, ADC/SS-PCM can rigorously model all common photophysical processes. These include ground- and excited-state (one and two photon) absorption, fluorescence and phosphorescence. The SS-PCM is available for all variants of ADC implemented in Q-CHEM 5.0, i.e., canonical ADC, spin-flip ADC for multi-reference problems, CVS-ADC for core-valence excitations, as well as ri- and SOS-ADC(2) for increased efficiency and accuracy. By computing excited-state wavefunctions via the efficient intermediate-state representation formalism, the computational overhead for the SS-PCM is kept small, such that applications to systems with 500+ basis functions are possible with riADC(2). One example is the large (ca. 400 bf.) push-pull system (ZMSO2, Fig. 1), for which we demonstrate how solvent-polarity governs the extent of charge-separation in the lowest excited state. Modeling the solvent-relaxed excited-state PES of DMABN in polar and non-polar solvents, we establish that ADC(2)/SS-PCM affords excellent agreement with experimental fluorescence data. However, the observed solvent-dependent dual fluorescence can only be explained at the ADC(3)/SS-PCM level of theory.

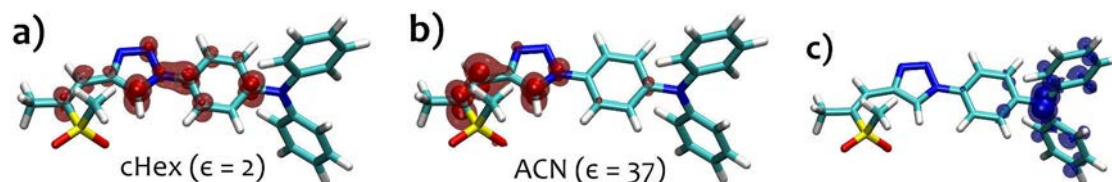


Figure 1: Isodensity plots of electron (red, a&b) and hole (blue, c) for the solvent-relaxed lowest excited state of ZMSO2 in cyclo-hexane and acetonitrile @ riADC(2)/SV(P)/SS-PCM

[1] J.M. Mewes, J.M. Herbert, A. Dreuw, *PCCP* **19**, 2 (2017).

[2] J.M. Mewes, Z.Q. You, M. Wormit, T. Kriesche, J.M. Herbert, A. Dreuw, *JPCA*, Jacopo Tomasi Festschrift (2015).

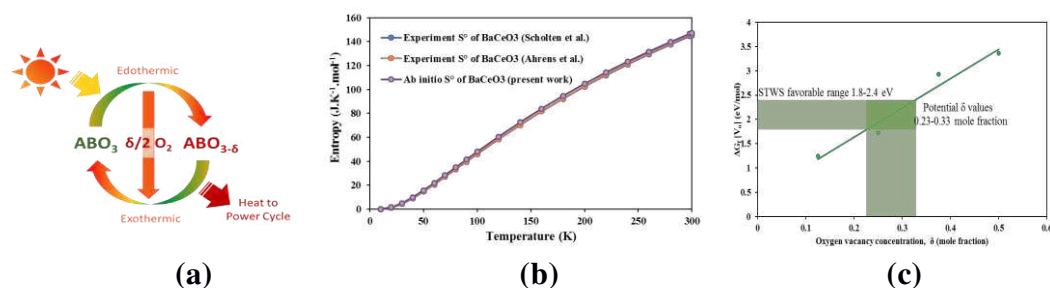
## Thermochemical Properties of BaXO<sub>3</sub> (X=Mn, Zr, Ce) Perovskite Materials using First Principles Phonon Calculations

Krishna K. Ghose<sup>1</sup>, Alicia Bayon Sandoval<sup>2</sup>, Jim Hinkley<sup>2</sup>, Alister J. Page<sup>1</sup>

<sup>1</sup>The University of Newcastle, Callaghan 2308, Australia

<sup>2</sup>CSIRO Energy Technology, Newcastle 2304, Australia

Perovskites metal oxides (ABO<sub>3</sub>) are attractive candidates for energy applications such as solar thermal water splitting (STWS), solar fuel production and photocatalysis due to their mixed oxidation states [1]. In STWS process, these materials can be reduced under solar-driven, high-temperature conditions, to produce reduced perovskite metal oxides (ABO<sub>3-δ</sub>) and oxygen (δ/2O<sub>2</sub>) (Figure 1(a)). This reduced metal oxide can subsequently be oxidized by water, to release heat and hydrogen (H<sub>2</sub>) via an exothermic reaction. The performance of such metal oxides as redox materials is dominated by their free energy associated with the formation/removal of oxygen vacancies in the reduction/oxidation reactions, respectively. Here, we predict the redox thermochemistry of BaXO<sub>3</sub> (X = Mn, Zr, Ce) using density functional theory (DFT). Thermochemical properties obtained here are in excellent agreement with experimental data (Figure 1(b)). For BaCeO<sub>3</sub>, our calculations show that energetically optimal formation energies ( $\Delta G_f[V_0]$ ) are achieved with vacancy concentrations of  $\delta = 0.23$ -0.33. Furthermore, our predicted  $\Delta G_f[V_0]$  values for BaCeO<sub>3-δ</sub> demonstrate, for the first time, that BaCeO<sub>3</sub> is a potentially useful, yet unexplored, perovskite for solar thermal water splitting applications. Comparison of BaCeO<sub>3</sub> with BaMnO<sub>3</sub> and BaZrO<sub>3</sub> reveals the electronic and structural origins of this improved performance.



**Figure 1:** (a) STWS redox reaction, (b) PBE-PAW+U+J, entropy  $S^\circ$  of present and experimental work (J K<sup>-1</sup> mol<sup>-1</sup>) of bulk BaCeO<sub>3</sub> [2,3], (c) PBE-PAW+U+J,  $\Delta G_f[V_0]$  of BaCeO<sub>3-δ</sub> (298.15 K, 1 atm) as a function of  $\delta$ . The green zone indicates the optimum  $\Delta G_f[V_0]$  range 1.8-2.4 eV [4].

[1] C. L. Muhich, et al. *WIREs Energy Environ.* **5**, 261–287 (2016).

[2] M. J. Scholten, et al. *Thermochimica Acta.* **268**, 161-168 (1995).

[3] M. Ahrens, J. Maier. *Thermochimica Acta.* **443**, 189-196 (2006).

[4] A. M. Deml, et al. *Energy & Environmental Science.* **7**, 1996-2004 (2014).

## Behavior of finite uniform electron gases at high and low density.

Marat Sibaev<sup>1</sup>, Peter M.W. Gill<sup>1</sup>

<sup>1</sup>*Research School of Chemistry, Australian National University, Canberra, Australia*

Traditional concept of uniform electron gas consists of a homogeneous system of electrons at constant density contained in an infinite volume. In spite of its simplicity many real phenomena in solid-state physics can be adequately explained by this model,[1] i.e. electronic structure of metals, superconductivity and quantum hall effect.

Similarly, the importance of uniform electron gas to chemistry cannot be overstated. After all, at the crudest level an electron cloud in a molecule is just a collection of minuscule chunks of uniform electron density. This is the main idea behind local density approximation and forms a starting point for most density functionals. However, is an infinite electron gas the best starting point for studying a finite molecular system?

Recently, a new paradigm of finite uniform electron gases has been introduced by Loos and Gill.[2, 3] It consists of electrons confined to the surface of  $(n+1)$ -dimensional ball, or an  $n$ -sphere, with fixed radius. Two electron systems in such space have been studied extensively, and behavior of electrons on a 3-sphere is most reminiscent of realistic systems.[3, 4] However, practical utilisation of this paradigm in density functional theory necessitates going beyond just two electron systems and requires solving the many body problem.

This presentation will give a brief introduction to finite uniform electron gases, and our progress in finding methods for solving the corresponding many body problem, with particular emphasis on high and low density regimes.

- [1] G. Giuliani, G. Vignale, *Quantum Theory of The Electron Liquid* (Cambridge University Press, Cambridge, 2005)
- [2] P. M. W. Gill, P. F. Loos, *Theor. Chem. Acc.* **131**, 1069 (2012)
- [3] P. F. Loos, P. M. W. Gill, *Phys. Rev. Lett.* **103**, 123008 (2009)
- [4] P. F. Loos, P. M. W. Gill, *Chem. Phys. Lett.* **500**, 1 (2010)

## Is a post-self-consistent-field addition of the non-local correlation kernel in van-der-Waals density functionals sufficient?

Asim Najibi<sup>1</sup>, Lars Goerigk<sup>1</sup>

<sup>1</sup>*School of Chemistry, The University of Melbourne, Melbourne, Australia*

Addressing the inability of Kohn-Sham density functional theory (KS-DFT) to properly describe London-dispersion forces has attracted a lot of attention in recent years. One technique for DFT that describes London-dispersion forces is the addition of a non-local correlation kernel to the exchange-correlation density functional. The resulting functional is then called a van-der-Waals density functional (vdW-DF), and various formulations exist.

Adding the non-local correlation functional in a post-self-consistent-field (post-SCF) fashion can be accurate [1], which is beneficial to reduce computational cost. Yet, implementations of newer functionals recommend a fully self-consistent usage of the non-local correlation term[2].

To the best of our knowledge, there has not been any thorough assessment of whether or not adding the non-local correlation kernel in the post-SCF fashion is accurate for a broad range of chemical problems (including large systems), compared to employing it during the SCF procedure.

In this work, we thoroughly investigate this issue by examining various exchange-correlation functionals augmented with the accurate[3] VV10 non-local correlation kernel for an extended database that encompasses general main-group thermochemistry, kinetics and non-covalent interactions.

Our results suggest that the accuracy of vdW-DFs is not compromised when the non-local correlation functional is added to the exchange-correlation functional after the SCF procedure. Finally, we also conduct an in-depth analysis of how using a non-local correlation functional influences other molecular properties, such as electron densities. Our findings provide insights for future method developments.

[1] W. Hujo, S. Grimme, *Phys. Chem. Chem. Phys.* **13**, 13942 (2011).

[2] N. Mardirossian, et al., *J. Phys. Chem. Lett.* **8**, 35 (2017).

[3] O. A. Vydrov, T. Van Voorhis, *J. Chem. Phys.* **133**, 244103 (2010).

## Exciton Transference in Natural and Hypothetical Bacteriochlorophyll Arrangements. Is Singlet Fission a Possible Photosynthetic Mechanism?

Joaquín Barroso-Flores<sup>1</sup>, María Eugenia Sandoval-Salinas<sup>1</sup>, Gustavo Mondragón Solórzano<sup>1</sup>

<sup>1</sup>*Centro Conjunto de Investigación en Química Sustentable UAEM – UNAM Personal de la UNAM Carr. Toluca – Atlacomulco km 14.5 Toluca, Mexico.*

Several excitation energy transfer (EET) processes are known to occur during the first stages of photosynthesis, with timescales ranging from a few fs to several tens of ps, however their full assignment is still a matter of controversy [1]. Singlet fission (SF) is a photochemical in which an exciton in a singlet state decays to two coupled–degenerate triplet excitons with half the energy of the original excited singlet [2]. The resulting multiexcitonic (ME) state can later decouple in vicinal molecules, thus propagating the original excitation. SF has been extensively observed in polyaromatic hydrocarbons [3] but not in chlorophyll–related photosynthetic pigments.

Bacteriochlorophylls (Bchl) *–a* through *–d* are the light–harvesting pigments used by anaerobic photosynthetic bacteria; the structural simplicity of their photosystem II complexes makes them attractive for electronic structure calculations [3]. Time Dependent Density Functional Theory (TD–DFT) at the CAM–B3LYP/6-31G(*d*) level of theory and Restricted Active Space–Spin Flip (RAS–SF) calculations were undertaken to get a full description of the excited states on each pigment molecule and their dimers at various conformations. Pigment dimers in the Fenna–Matthews–Olson (FMO) complex and the bchQRU chlorosome from *C. tepidum* (a 600 Bchl–*d* toroid) were studied as candidates for SF in photosynthesis.

- [1] T. Fujita, J. Huh, S. K. Saikin, J. C. Brookes, A. Aspuru–Guzik, *Photosynth. Res.* **120** (3), 273 (2014).
- [2] M. B. Smith, J. Michl, *Chem. Rev.* **110** (11), 6891 (2010).
- [3] D. Casanova, *J. Chem. Theory Comput.* **2014**, 10 (1), 324
- [4] D. E. Tronrud, J. Wen, L. Gay, R. E. Blankenship, *Photosynth. Res.* **100** (2), 79 (2009).

## An efficient method for calculating effective core potential integrals.

Simon C. McKenzie<sup>1</sup>, Evgeny Epifanovsky<sup>2</sup>, Andrew T.B. Gilbert<sup>1</sup>, Peter M.W. Gill<sup>1</sup>

<sup>1</sup>Research School of Chemistry, Australian National University, ACT 2601, Australia

<sup>2</sup>Q-Chem Inc., 6601 Owens Dr, Pleasanton, CA 94588, USA

Effective core potential (ECP) integrals are one of the most difficult one-electron integrals due to their constituent projected integrals. Several authors<sup>1</sup> have provided methods to compute these difficult projected integrals yet there remains no dominant method that is both efficient and reliable.

Taking inspiration from efficient algorithms to calculate two-electron repulsion integrals, we develop efficient recurrence relations and rigorous upper bounds for ECP integrals. Our recurrence relations are founded upon a previously derived simple fundamental projected integral<sup>2</sup> and our rigorous upper bounds reduce the number of total ECP integrals from  $O(M \times N^2)$  to  $O(M)$  significant ECP integrals, where  $N$  and  $M$  are the the number of basis and ECP functions, respectively. We implement the present method into Q-Chem 5.0 and demonstrate significantly faster ECP integral computation as compared to Q-Chem 4.4<sup>3</sup> and GAMESS (US).<sup>4</sup>

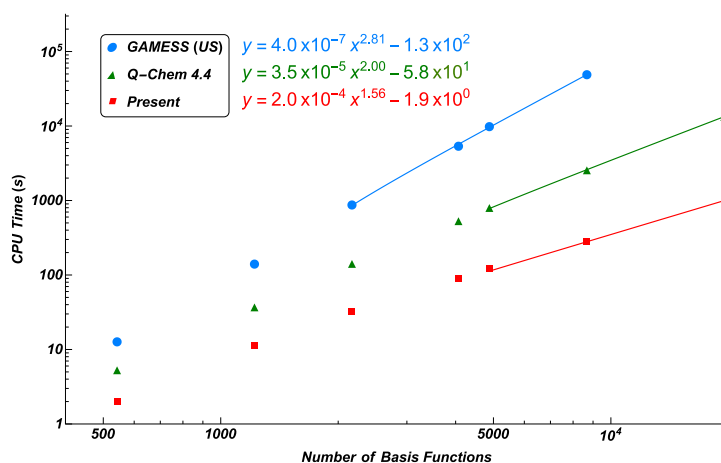


Figure 1: ECP integral timings for a Pt SBKJC slab.

- [1] R. Flores-Moreno et al., *Journal of Computational Chemistry* **27**, 1009 (2006).
- [2] J. C. Barthelat et al., *Molecular Physics* **33**, 159 (1977).
- [3] Y. Shao et al., *Molecular Physics* **113**, 184 (2015).
- [4] M. W. Schmidt et al., *Journal of Computational Chemistry* **14**, 1347 (1993).



## Evaluation of aromaticity based on magnetically induced current using the GIMIC method for open-shell molecules

Takanori Nagami<sup>\*,1</sup>, Jun-ya Fujiyoshi<sup>1</sup>, Kenichiro Watanabe<sup>1</sup>, Masaki Yamane<sup>1</sup>, Ryohei Kishi<sup>1</sup>, Masayoshi Nakano<sup>1,2</sup>, Benoît Champagne<sup>3</sup>, Vincent Liégeois<sup>3</sup>

<sup>1</sup>Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

<sup>2</sup>Center for Spintronics Research Network (CSRN), Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

<sup>3</sup>Department of Chemistry, Faculty of Science, University of Namur, Rue de Bruxelles 61 - 5000 Namur, Belgium

Aromaticity is a familiar concept for chemists that can help probing the electronic structures of  $\pi$ -conjugated molecules. So, when applying an external magnetic field perpendicular to the plane of an aromatic molecule, both diatropic and paratropic currents, associated with aromaticity and antiaromaticity, respectively, are induced. The magnetically induced current (MIC) strength,  $J$ , is a quantitative indicator of aromaticity. The gauge including magnetically induced current (GIMIC) method has recently been developed for various levels of electronic structure theory and quantum chemistry packages to evaluate such currents for a variety of electronic states including open-shell systems [1].

We investigate here at the DFT level the aromaticity of open-shell singlet molecules, dicyclopenta-fused acenes (DPA) [2] and polyacenes (PA), for clarifying the relationships between open-shell character and the MIC. For DPA,  $J$  values are significantly different between closed-shell and open-shell wave-functions (Fig. 1): open-shell show larger aromaticity in the 6-membered rings than closed-shell ones. We also present the results on PA together an analysis of the relationship between the spatial current and odd electron distributions.

- [1] (a) J. Jusélius, D. Sundholm, J. Gauss, *J. Chem. Phys.*, **121**, 3952 (2004). (b) S. Taubert, D. Sundholm, J. Jusélius, *J. Chem. Phys.*, **134**, 054123 (2011). (c) M. Rauhalahti, S. Taubert, D. Sundholm, V. Liégeois, *Phys. Chem. Chem. Phys.*, **19**, 7124 (2017).  
[2] S. Motomura, M. Nakano et al., *Phys. Chem. Chem. Phys.* **13**, 20575 (2011).

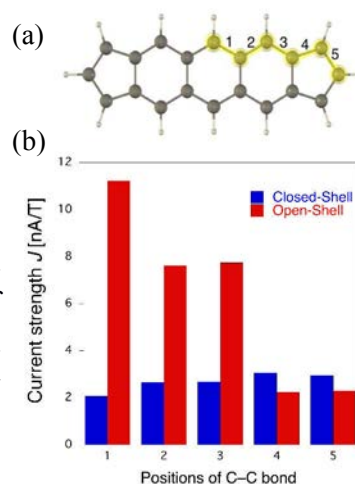


Fig. 1 (a) Molecular structure of DPA(5). (b) Current strength  $J$  across each C–C bond of DPA(5) for closed-shell (blue) and open-shell (red) solutions.

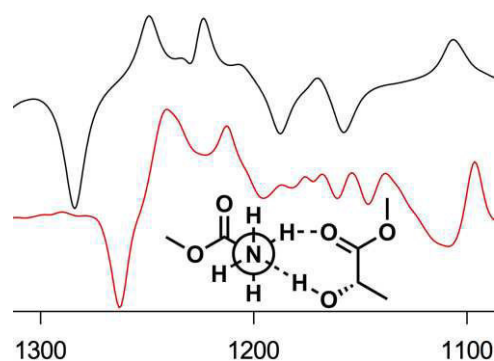
## Chiral glycine methyl ester – Chirality transfer in matrix-isolation vibrational circular dichroism (MI-VCD) spectroscopy

**Dennis Gerbig, Sarina Desch, and Peter R. Schreiner\***

*Institute of Organic Chemistry, Justus-Liebig University*

*Heinrich-Buff-Ring 17, 35392 Giessen, Germany*

The origin of homochirality of even the most fundamental biomolecules, such as amino acids or sugars, is still vividly debated. Current hypotheses often invoke the interaction of racemic mixtures with circularly polarized light (CPL), *e.g.*, preferential photolysis of one enantiomer [1]. Indeed, photolysis of various amino acids in extraterrestrial ice analogs with CPL in the UV/Vis range [2] yields small enantiomeric excesses (*ee*) similar to those found in the Murchison meteorite [3]. Since CPL has been detected in the interstellar medium [4], the initial generation of chiral biomolecules on extraterrestrial bodies, *e.g.*, on comets, is now being regarded as a viable scenario [1]: Fixation of suitable (organic) precursors in cometary ices may lead to accumulation of sufficiently high reactant concentrations and protects volatiles against evaporation.



Combination of chiroptical methods, such as vibrational circular dichroism (VCD) spectroscopy with matrix-isolation (MI) enables the investigation [5] of chiral species and their interactions under realistic model conditions. We recently found that the achiral amino acid derivative glycine methyl ester (Gly-OMe) forms binary complexes with either L- or D-methyl lactate in solid dinitrogen matrices upon mild annealing. As a result, Gly-OMe acquires unique VCD activity of its ester moiety and thus “inherits” chirality from the methyl lactate template (*cf.* inset; *red*: experimental VCD trace of L-methyl lactate:Gly-OMe complex; *black*: VCD trace of complex computed at B3PW91/aug-cc-pVTZ). In subsequent CPL-enabled transformations, this transfer of chirality may provide a means for the proliferation of chiral information even across the boundaries of different classes of biologically relevant compounds (*vide supra*).

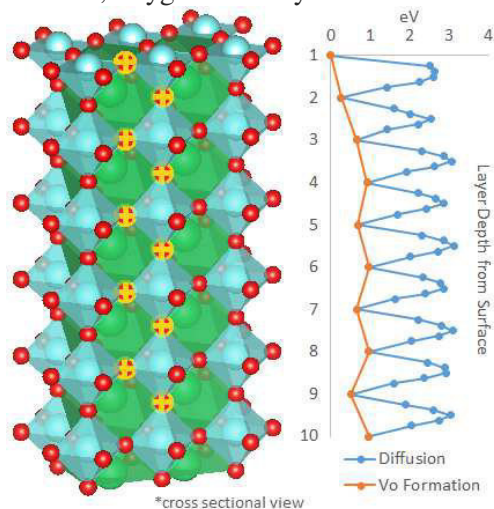
- [1] E. Rubenstein *et al.*, *Nature* **306**, 118 (1983).
- [2] M. Paola *et al.*, *Astrophys. J.* **788**, 79 (2014).
- [3] M. H. Engel, S. A. Macko, *Nature* **389**, 265 (1997).
- [4] J. Bailey *et al.*, *Science* **281**, 672 (1998).
- [5] C. Merten, Y. Xu, *Angew. Chem. Int. Ed.* **52**, 2073 (2013).

# Surface Effects on Vacancy Diffusion in Titanate Perovskites $\text{ATiO}_3$ ( $\text{A} = \text{Sr}^{2+}$ , $\text{Ba}^{2+}$ , $\text{Ca}^{2+}$ )

Joshua J. Brown<sup>1</sup> and Alister J. Page<sup>1</sup>

<sup>1</sup>Newcastle Institute for Energy and Resources, University of Newcastle, Newcastle, Australia

The formation, stability and mobility of oxygen vacancy defects in  $\text{ABO}_3$  perovskites has great influence on their potential use in energy applications, such as fuel cell electrodes and thin film technologies. Tuning  $\text{A}^{\text{II}}\text{Ti}^{\text{IV}}\text{O}_3$  titanate perovskites has attracted considerable attention in this respect due the various electronic, optical and thermal properties which are useful for hydrogen and oxygen evolution reactions. Across this perovskite series, variation of the A-site cation results in various structural effects in the titanate crystal, inducing changes that tailor the individual titanates towards different applications. Recent studies have highlighted the importance of lattice oxygen diffusion in catalytic surface water splitting reactions,<sup>1</sup> while surface oxygen vacancies deprotonate adsorbed water molecules.<sup>2</sup> Several other simulations reported in the literature have investigated the propensity for surface defect formation and defect aggregation in bulk  $\text{SrTiO}_3$ .<sup>3,4</sup> In contrast, oxygen vacancy diffusion near the catalytic interface (i.e. the surface/subsurface region) remains unexplored, despite the fact that it potentially limits the utility of  $\text{SrTiO}_3$  in most real-world energy applications. Herein we investigate oxygen vacancy diffusion at the  $[0001]\text{ATiO}_3$  interface ( $\text{A} = \text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ) using PBE-PAW+U+J (Figure 1), and demonstrate how the A-site cation can promote/limit oxygen diffusion near the catalyst interface. Our results show that the size of the A-site cation has a substantial impact on the stability and mobility of oxygen defects in both the AO and  $\text{TiO}_2$  sublattices. A geometrical energy decomposition analysis also reveals that the interaction and deformation energy contribution to the oxygen vacancy formation and migration correlates to the ease of the AO sublattice structurally housing a defect compared to the  $\text{TiO}_2$  sublattice.



**Figure 1.** PBE-PAW+U+J oxygen formation energies ( $V_o$ ) and diffusion barriers, eV, for the  $[0001]\text{SrTiO}_3$  interface.

- [1] X. Rong, J. Parolin, A. M. Kolpak, *ACS Catal.*, **6**, 1153 (2016).
- [2] T. Sarkar, S. Ghosh, M. Annamalai, A. Patra, *et al.*, *RSC Adv.*, **6**, 110 (2016).
- [3] L. Zhang, B. Liu, H. Zhuang, P.R.C. Kent, *et al.*, *Comput. Mater. Sci.*, **118**, 309 (2016).
- [4] H. O. Jeschke, J. Shen, R. Valenti, *New. J. Phys.*, **17**, 023034 (2015)

## Short-Range Spin-Dependent Interaction Energies between Chiral Molecules

Steffen M. Giesen<sup>1</sup>, Robert Berger<sup>1</sup>

<sup>1</sup>*Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Str. 4, 35032 Marburg, Germany*

The interaction between two closed-shell chiral molecules has been investigated for enantioselective discrimination in the long-range region[1]. To find a discriminating and non-negligible energy difference for the interaction in homo- and hetero-chiral dimers, a method for short- and medium-range interaction energies has to be employed[2]. The group function approach allows for the direct calculation of the interaction energy, decomposed into contributions whose physical interpretations are discussed in Ref. [3]. The overlap region of electron distributions of the interacting systems becomes accessible by suspending the strong-orthogonality condition between their individual wave functions. Expanding the non-orthogonality contributions in order of transpositions between the systems, spin-dependent terms arise via a coupling of the corresponding spin tensor operators[4]. The implementation of this scheme starting from broken-symmetry Hartree-Fock determinants is presented with applications to simple systems. The convergence of the expansion and the interpretation of the arising contributions is discussed.

- [1] B. Martire, P. E. Schipper, *Chem. Phys.* **1986**, *108*, 461–472.
- [2] D. B. Craig, E. A. Power, T. Thirunamachandran, *Chem. Phys. Lett.* **1970**, *6*, 211–214.
- [3] C. Amovilli, R. McWeeny, *Chem. Phys.* **1990**, *140*, 343–361.
- [4] P. D. Dacre, R. McWeeny, *Proc. R. Soc. London. A. Math. Phys. Sci.* **1970**, *317*, 435–454.

**Concerted Proton Transfer in Mixed Acid-Water Clusters:** **$[(\text{HCl})(\text{H}_2\text{O})]_2$  and  $[(\text{HF})(\text{H}_2\text{O})]_4$** **Itay Zakay<sup>1</sup>, Mychel E. Varner<sup>2</sup>, R. Benny Gerber<sup>1,3</sup>**<sup>1</sup>*Institute of Chemistry and The Fritz Haber Research Center, The Hebrew University,  
Jerusalem 91904, Israel*<sup>2</sup>*Department of Chemistry, Iona College, NY 10801, USA*<sup>3</sup>*Department of Chemistry, University of California Irvine, CA 92697, USA*

Molecular dynamics simulations using directly *ab initio* potentials are carried out for the ionically-bonded clusters:  $[(\text{Cl}^-)(\text{H}_3\text{O}^+)]_2$  and  $[(\text{F}^-)(\text{H}_3\text{O}^+)]_4$ , to explore their transitions to the hydrogen-bonded structures:  $[(\text{HCl})(\text{H}_2\text{O})]_2$  and  $[(\text{HF})(\text{H}_2\text{O})]_4$ , respectively. Both the ionic and H-bonded structures are highly symmetric for both clusters. It is found that proton transfers are concerted in all trajectories for  $[(\text{Cl}^-)(\text{H}_3\text{O}^+)]_2$ , whereas for  $[(\text{F}^-)(\text{H}_3\text{O}^+)]_4$  the four-proton concerted transfer is highly dominant but not exclusive. It is suggested that the high symmetry of the ionic and the H-bonded structures plays a role in the preference for concerted transfers. The results predict a major role of collective effects in ionization of acid molecules in concentrated systems.

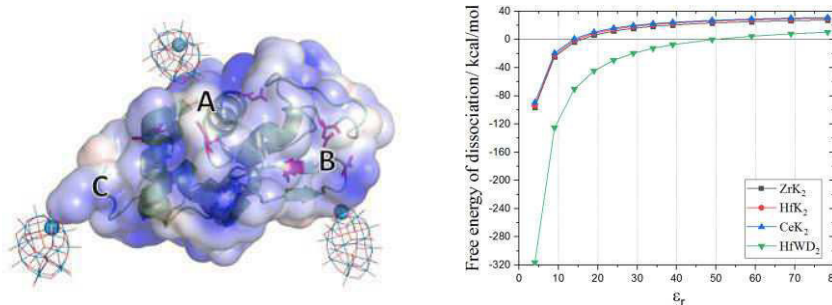
## Insights into the formation of catalytically active metal-substituted polyoxometalates in the presence of proteins

L. Vandebroek<sup>1</sup>, E. De Zitter<sup>1</sup>, H. G. T. Lya<sup>1</sup>, A. Sap<sup>1</sup>, Paul Proost<sup>2</sup>, L. Van Meervelt<sup>1</sup>, D. Conic<sup>1</sup>, T. Mihaylov<sup>1</sup>, K. Pierloot<sup>1</sup> and T. N. Parac-Vogt<sup>1</sup>

<sup>1</sup>Department of Chemistry, KU Leuven, Celestijnenlaan 200F box 2404, Leuven, Belgium

<sup>2</sup>Department of Microbiology and Immunology, KU Leuven, Rega, Herestraat 49 box 1042, Leuven, Belgium

Several metal-substituted polyoxometalates (MSPs) of  $\text{MX}_2$  type ( $\text{M} = \text{Zr(IV)}$ ,  $\text{Hf(IV)}$ ,  $\text{Ce(IV)}$  and  $\text{X} = \text{Keggin (K)}$ , Wells-Dawson (WD) polyoxometalates) have demonstrated a remarkable selectivity towards peptide bond hydrolysis in proteins under mild conditions [1]. The hydrolytic activity has been attributed to the  $\text{MX}$  species, presumably formed through dissociation of the starting  $\text{MX}_2$  compounds [1]. However, the existence of  $\text{MX}$  species in water solutions, at near neutral pH, have not been evidenced experimentally so far. Recently, a monomeric  $\text{ZrK}$  polyoxometalate was identified in a co-crystal with hen egg-white lysozyme (HEWL) [2]. Here, we report on the successful co-crystallization between HEWL and a catalytically active  $\text{HfWD}$  polyoxometalate, which is the first crystallographic evidence for the existence of this species. The crystal structure showed three binding sites (the Figure on the left), one of which lays in the proximity of three cleavage sites. Since in both experiments  $\text{MX}_2$  species were used as starting compounds, the X-ray results strongly suggest that in the presence of a protein the dissociation reaction  $\text{MX}_2 \rightarrow \text{MX} + \text{X}$  becomes favorable, while it is unfavorable in the absence of a protein. Previous studies showed that the dielectric constant  $\epsilon_r$  at the protein surface is much lower as compared to bulk water, ranging from  $\epsilon_r \approx 6$ -7 inside the protein to  $\epsilon_r \approx 20$ -30 at the surface of the protein [3]. To examine the influence of  $\epsilon_r$  on the reaction thermodynamics DFT calculations were performed on a series  $\text{MX}_2$  type MSPs. The results (the Figure on the right) suggest that binding of the MSPs to the protein surface (with low  $\epsilon_r$ ) may promote dissociation by increasing the Coulomb repulsion between the negatively charged X moieties of the  $\text{MX}_2$  complexes, which is otherwise effectively screened in the bulk water.



[1] M. Arefian, M. Mirzaei, H. Eshtiagh-Hosseini, A. Frontera, *Dalton Trans.* **46**, 6812 (2017)

[2] A. Sap, E. De Zitter, L. Van Meervelt, T. N. Parac-Vogt, *Chem. Eur. J.*, **21**, 11692 (2015)

[3] L. Li, C. Li, Z. Zhang, E. Alexov, *J. Chem. Theory Comput.* **9**, 2126-36 (2013)

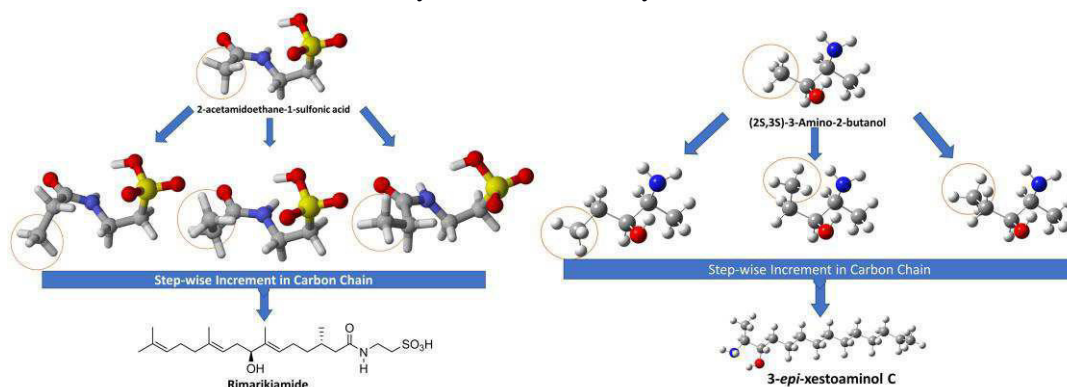
## Conformational Analysis and Accurate Prediction of Molecular Properties for Highly Flexible Chiral Natural Products

Muhammad Ali Hashmi<sup>1</sup>, Matthias Lein<sup>1,2</sup>

<sup>1</sup> School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington, 6012 (New Zealand)

<sup>2</sup> Centre for Theoretical Chemistry and Physics, New Zealand Institute for Advanced Study, Massey University Auckland, Private Bag 102904, North Shore MSC 0632 Auckland (New Zealand)

Despite advances in electronic structure theory, the theoretical prediction of spectroscopic properties remains a computational challenge. This is especially true for natural products that exhibit very large conformational freedom and hence need to be sampled over many different accessible conformations. We report a strategy, *MICE-PES* (Method for the Incremental Construction and Exploration of the Potential Energy Surface) which can predict NMR chemical shifts and more elusive properties like the optical rotation with great precision, through step-wise incremental increases of the conformational degrees of freedom. This method maps the potential energy in a systematic incremental approach using high level quantum chemical calculations in a much shorter time than a normal systematic conformational search will take even at a very low level of theory. The application of this method is demonstrated for 3-*epi*-xestoaminol C [1] and rimarikiamide. Both compounds are chiral natural products, one with a long, linear alkyl chain of 14 carbon atoms, the other also includes intramolecular hydrogen bonding and unsaturated carbon-carbon bonds. Comparisons with experimental NMR and  $[\alpha]_D$  values are reported to validate the results of the Density Functional Theory calculations.



### References:

- [1]. M. A. Hashmi, S. K. Andreassend, R. A. Keyzers, and M. Lein, *PCCP*, **18**, 24506 (2016).



## Density-Functional Tight-Binding Molecular Dynamics Simulations of Proton Diffusion in the Bulk Ices and Liquid Water

Aditya Wibawa Sakti<sup>1</sup>, Yoshifumi Nishimura<sup>2</sup>, Chien-Pin Chou<sup>2</sup>,  
Hiromi Nakai<sup>1,2,3,4</sup>

<sup>1</sup>*Department of Chemistry and Biochemistry, Waseda University, Shinjuku-ku, Tokyo 169-8555, Japan*

<sup>2</sup>*Research Institute for Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 169-8555, Japan*

<sup>3</sup>*Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST), Kawagu-cho, Saitama 332-0012, Japan*

<sup>4</sup>*Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Kyoto 615-8520, Japan*

A fast proton diffusion in the bulk water is governed by the combination of vehicular and Grotthuss diffusion processes[1]. Fluorescence quenching study confirmed that hydronium ion moves faster in the ice  $I_h$  phase rather than in the liquid one[2]. However, current theoretical study of the proton transfer in the ice phase is limited to the empirical molecular dynamics simulation, which is only specific for the ice  $I_h$  phase[3]. Extension of molecular dynamics simulation at the ab-initio level is difficult due to the limitation of the computational cost. In the present work[4], the structural, dynamical, and energetic properties of the excess proton in the bulk water, low-density ( $I_h$  and  $I_c$ ), and high-density (III and melted VI) ice phases were studied using the density-functional tight-binding (DFTB) method, which has a good balance between computational cost and accuracy. Moreover, divide-and-conquer scheme in DC-DFTB-K[5] code enables to perform large size simulations of the bulk water systems. The estimated proton transfer rates in the low-density ice structures are faster than in the high-density one. It is owing to the low density ices conserve the perfect tetrahedral structure of hydrogen bond networks, which are necessary for facilitating the proton transfer. The present study has reproduced the experimental tendency of the proton transfer rate in the ice phases.

- [1] H. Nakai, A. W. Sakti, Y. Nishimura, *J. Phys. Chem. B* **120**, 217 (2016).
- [2] A. Urtski, I. Presiado, Y. Erez, R. Gepshtein, D. Huppert, *J. Phys. Chem. C* **113**, 10285 (2009).
- [3] K. Park, W. Lin, F. Paesani, *J. Phys. Chem. B* **118**, 8081 (2014).
- [4] A. W. Sakti, Y. Nishimura, C.-P. Chou, H. Nakai, *in preparation*.
- [5] H. Nishizawa, Y. Nishimura, M. Kobayashi, S. Irle, H. Nakai, *J. Comput. Chem.* **37**, 1983 (2016).



## Accurate Prediction of One-Electron Reduction Potentials of Transition Metal Complexes.

**Daniel Bím<sup>1</sup>, Mauricio Maldonado Domínguez<sup>2</sup>, Lubomír Rulíšek<sup>1</sup>, Martin Srnec<sup>2</sup>**

*<sup>1</sup>Institute of Organic Chemistry and Biochemistry, The Czech Academy of Sciences,  
Flemingovo nám. 2, Prague 6, 16000, Czech Republic*

*<sup>2</sup>J. Heyrovský Institute of Physical Chemistry, The Czech Academy of Sciences, Dolejškova  
3, Prague 8, 18223, Czech Republic*

Many chemical transformations that involve metalloenzymes are very closely related to the redox properties of their metal sites. Those arise from variability in transition metals that are involved in reactions, different oxidation, spin and protonation states, total charges, types of ligands and ligand field geometries, different solvent (protein) environments, etc. The calculations of such electronic properties are therefore invaluable in understanding the above biochemical processes. Accurate prediction of reduction potentials is still a formidable task that is complicated by many factors among which solvation of highly charged species plays a crucial role. Herein, we present a robust and efficient theoretical methodology for the calculation of reduction potentials of transition metal complexes. The validation has been done on nearly 50 non-heme iron complexes, where the experimental electrochemical data are known and which often serve as biomimetic models of non-heme iron enzymes. For the subset of these non-heme iron complexes, the redox properties were also investigated along with their effects on H-atom abstraction reactivity. Last but not least, the accurate protocol for calculation of charged species in aqueous solution is presented. Here we introduce the novel H-atom addition/abstraction methodology used to neutralize charged species through several followed thermodynamic cycles. The accuracy has been evaluated on the set of 15 different transition-metal complexes that are considered as extremely challenging systems for computational electrochemistry. It is shown that the absolute error of calculated reduction potentials in comparison with the experiment is in most cases less than approx. 200 mV, which makes our methodology highly useful also in the interpretation of complicated electrochemical data, as well as in the description of electronic and spin state properties of transition metal complexes.

## Concentration dependence of sound velocity in water and methanol mixtures using molecular-dynamics simulations.

Masafumi Yamasaki, Sakuma Shota and Shuji Munejiri

*Graduate School of Integrated Arts and Sciences, Hiroshima University, 1-7-1  
Kagamiyama, Higashi-Hiroshima City Hiroshima, Japan 739-8521*

It is experimentally known that the ultrasonic velocity of water-methanol mixture depends on the methanol concentration  $X_m$  and it takes a maximum when  $X_m$  is about 15% [1]. However, the microscopic mechanism of these features has not yet been elucidated. In our previous study, we had performed molecular-dynamics (MD) simulations of water and methanol mixtures for various concentrations  $X_m$  and calculated the wavenumber-dependent sound velocity  $v(k)$ , where  $k$  is the wavenumber [2]. In that study, SPC/E and TIP4P models for water and OPLS-AA model for methanol were used. The MD simulations were carried out with 10000 molecules for a period of 0.1ns. Though the simulation time of 0.1ns was not long enough to calculate  $v(k)$ , we had obtained the following preliminary results: For a fixed  $X_m$ , with increasing wavenumber from about  $1 \text{ nm}^{-1}$  to about  $7 \text{ nm}^{-1}$ , the value of  $v(k)$  increases. When the wavenumber  $k$  is about  $5\sim 7 \text{ nm}^{-1}$ , with increasing  $X_m$  from 0 to 100%,  $v(k)$  changes almost linearly from the value of pure water to that of pure methanol. With decreasing wavenumber, the concentration dependence of  $v(k)$  changes and when the wavenumber is as small as  $2 \text{ nm}^{-1}$ ,  $v(k)$  shows a maximum near  $X_m=20\%$ .

The purpose of the present study is to calculate the sound velocity with high accuracy from longer time MD simulations and to assure the previous results. To show the results above shown is independent with potential model, we employed a different water model, TIP4P-Ew. The simulations were performed at room temperature for 11 methanol concentrations  $X_m$  from 0 to 100% in steps of 10%. The number of molecules was determined so that the length of the side of the cubic simulation box became 6.28nm. To improve statistical average the MD simulation for a period of 1ns were conducted three times for each  $X_m$ . The wavenumber-dependent sound velocity  $v(k)$  was calculated from the relation  $v(k) = \omega(k)/k$ , where  $\omega(k)$  is peak frequency of  $\omega^2 S(k, \omega)$ . Here,  $S(k, \omega)$  is the dynamic structure factor and  $\omega$  is the angular frequency. We found that sound velocity of several nanometer wavelength in water-methanol mixture shows similar concentration dependence to that of ultrasonic wave. We also discuss temperature dependence of sound velocity.

[1] William D. T. Dale, Peter A. Flavelle, and Peeter Kruus, *Can. J. Chem.* **54**, 355 (1976).

[2] Y. Tachibana and S. Munejiri, POSTER 39, 16th International Conference on Liquid and Amorphous Metals (LAM-16)



# POSTER SESSION 2



## A new approach for the balanced description of dynamic correlation and spin-dependent relativistic effects

**Lucas Lang, Shubhrodeep Pathak, Frank Neese**

*Max Planck Institute for Chemical Energy Conversion,  
Stiftstr. 34-36, D-45470 Mülheim an der Ruhr, Germany*

Nowadays there exist a plethora of accurate and efficient methods to approach the electron correlation problem for molecular systems with single-determinant character. However in many situations, like bond-breakings, excited states and also for many electronic ground states at equilibrium geometry, the electronic structure becomes intrinsically multi-configurational. The situation is particularly complicated if several different electronic states need to be described at the same level of accuracy, as is necessary for the interpretation of the spectroscopy and magnetism of transition metal compounds. The latter case additionally requires the correct description of relativistic effects like spin-orbit coupling (SOC) and the Zeeman effect. One usual approach consists in accounting for dynamic correlation first and doing a subsequent first-order quasi-degenerate perturbation theory (QDPT) treatment in a small basis of preselected non-relativistic roots to account for relativistic effects [1]. This two-step procedure obviously has limitations whenever dynamic correlation and spin-orbit effects become comparable in size to the zeroth-order energy splittings. We therefore propose an extension of the recently developed second-order dynamic correlation dressed complete active space method (DCD-CAS(2)) [2] in order to obtain a dressed CASCI Hamiltonian that includes the effects of dynamic correlation and relativity at the same time. The main properties of the method are discussed and the performance for relativistic energies and derived spectroscopic and magnetic quantities is evaluated.

[1] D. Ganyushin and F. Neese, *J. Chem. Phys.* **125**, 024103 (2006).

[2] L. Lang, S. Pathak and F. Neese, *submitted*.

## Cooperative effect in water cluster

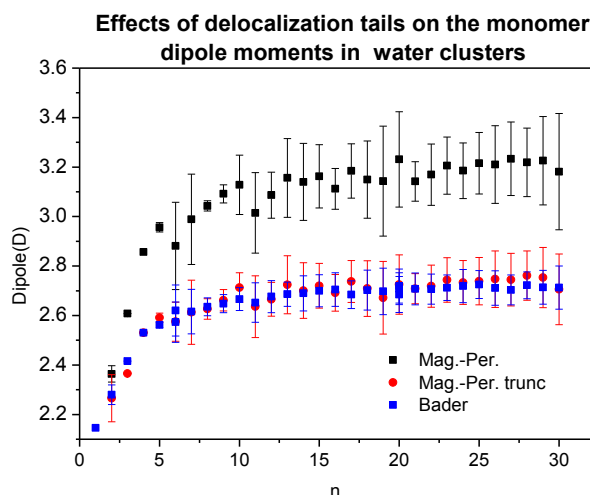
Imre Bakó<sup>1</sup>, István Mayer<sup>1</sup>

<sup>1</sup> *Institute of Organic Chemistry Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar tudósok körútja 2 519, P.O. Box 286 Budapest, Hungary*

The cooperativity of hydrogen bonds means that the local hydrogen bond strengths and other electronic properties of the different water clusters have been subjects of intensive study in the literature. One of the reasons of these works was to understand better the origin and the size of these collective effects. We will present the values of dipole moments of individual water molecules as well as the results of the intra- and intermolecular bond order calculations indicating the big importance of collective electrostatic effects caused by the non-immediate environment in liquid water models [1,2]. It will also be discussed how these collective effects build up as consequences of the electrostatic and quantum chemical interactions in water clusters. Additionally, we characterize how several local properties of water molecule (dipole moment, polarizability, relaxation energy) depend on the H-bonding environment and on the cluster size (Fig. 1). It has been shown using energy partition method (CECA) [3] that the local H-bond strength depends on the H-bonding state of donor and acceptor molecules. We calculated the ratio of two body and three body energy terms using the Mayer-Valiron hierarchy too [4].

- [1] I. Bakó, I. Mayer . *J. Phys. Chem A.* **120**, 4408 (2016)
- [2] I. Bakó, I. Mayer . *J. Phys. Chem A.* **120**, 631 (2016)
- [3] I. Mayer, I. Mayer, *Chem. Phys. Letter* **332**, 381 (2000)
- [4] I. Mayer, Valiron, *J. Chem. Phys.* **109**, 3360 (1998)

Fig.1



## Exploring and pushing the limits of *ansa*-aminoborane reactivity

Dénes Berta<sup>1</sup>, Konstantin Chernichenko<sup>2</sup>, Vendel Nagy<sup>1</sup>, Eszter Albert<sup>1</sup>, Imre Pápai<sup>1</sup>

<sup>1</sup>Research Centre for Natural Sciences, Hungarian Academy of Sciences

Magyar tudósok körútja 2, H-1117, Budapest, Hungary

<sup>2</sup>Department of Chemistry, University of Helsinki

A. I. Virtasen aukio 1, P.O. Box 55, 00014 Helsinki, Finland

The *ansa*-aminoborane compounds are fascinating family of frustrated Lewis pairs (FLPs). As many other counterparts, they are capable of reversible hydrogen uptake [1], but the special orientation of the acidic and basic centers enables the heterolytic activation of C-H bonds of unsaturated substrates [2]. Although there is a huge synthetic potential for  $sp$  and  $sp^2$  C-H activation, the reactions with  $sp^3$  substrates in the same fashion seems only feasible in quite specific circumstances [3].

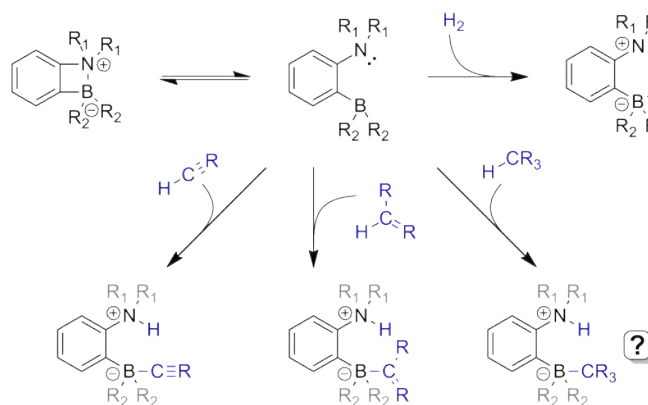


Figure 1: Summary of *ansa*-aminoborane chemistry.

In our continuing studies we aim to explore the natural limitations of *ansa*-aminoborane reactivity with the tools of computational chemistry. We demonstrate the differences between thoughtfully chosen representative reactions and show why they result in reduced reactivity in case of  $sp^3$  substrates. The understanding of well-defined trends guides us to design new *ansa*-aminoboranes, which can unleash the full potential of its structure in C-H activation.

- [1] K. Chernichenko, Á. Madarász, I. Pápai, M. Nieger, M. Leskelä, T. Repo, *Nat. Chem.* **5**, 718 (2013).
- [2] K. Chernichenko, M. Lindqvist, B. Kótai, M. Nieger, K. Sorochkina, I. Papai, T. Repo, *J. Am. Chem. Soc.* **138**, 4860 (2016).
- [3] É. Rochette, M.-A. Courtemanche, F.-G. Fontaine, *Chem. Eur. J.* **23**, 3567 (2017).

## Intramolecular Singlet Fission: Insights from Multireference Perturbation Theory and Quantum Dynamical Simulations

**Pedro B. Coto<sup>1</sup>, Seelam R. Reddy<sup>1</sup>, Michael Thoss<sup>1</sup>**

*<sup>1</sup>Institute of Theoretical Physics and Interdisciplinary Center for Molecular Materials (ICMM), Friedrich-Alexander Universität Erlangen-Nürnberg, Staudtstrasse 7/B2, Erlangen, Germany  
E-mail: pedro.coto@fau.de*

Singlet fission (SF) is a spin-allowed process by which two triplet excitons are generated from a singlet exciton [1]. It has received great attention recently as a feasible way to overcome the Shockley-Queisser limit [2], which could enable the development of more efficient solar cells. In this contribution, we analyze intramolecular SF (iSF) in a series of modified pentacene dimers covalently bonded to conjugated, cross-conjugated and non-conjugated spacers employing multireference perturbation theory and quantum dynamical methods [3-5]. The systems investigated provide insight into the key roles that the molecular and electronic structure of the spacer, the electronic states involved in the process and the coupling to molecular vibrations play in iSF. The impact that these aspects have in the relative contributions of the direct and mediated mechanisms of iSF is also discussed.

- [1] M. B. Smith, J. Michl, *Chem. Rev.* **110**, 6891 (2010).
- [2] W. Shockley, H. J. Queisser, *J. Appl. Phys.* **32**, 510 (1961).
- [3] J. Zirzmeier, D. Lehnher, P. B. Coto, E. T. Chernick, R. Casillas, B. Basel, M. Thoss, R. R. Tykwinski, D. M. Guldi, *Proc. Natl. Acad. Sci. (USA)* **112**, 5325 (2015).
- [4] J. Zirzmeier, R. Casillas, S. R. Reddy, P. B. Coto, D. Lehnher, E. T. Chernick, I. Papadopoulos, M. Thoss, R. R. Tykwinski, D. M. Guldi, *Nanoscale* **8**, 10113 (2016).
- [5] B. S. Basel, J. Zirzmeier, C. Hetzer, B. T. Phelan, M. D. Krzyaniak, S. R. Reddy, P. B. Coto, N. E. Horwitz, R. M. Young, F. White, F. Hampel, T. Clark, M. Thoss, R. R. Tykwinski, M. R. Wasielewski, D. M. Guldi, *Nat. Comm.* **8**, 15171 (2017).

## Charge-transfer states in donor-acceptor pairs connected by the salt bridge

Ivana Antol, Lucija Crnković, Zoran Glasovac, Davor Margetić

Ruđer Bošković Institute, Bijenička cesta 54, HR-10000 Zagreb, Croatia,

E-mail: [iantol@irb.hr](mailto:iantol@irb.hr)

Population of charge-transfer (CT) states is very important step in the charge photo-generation process in different organic photovoltaic devices [1]. The initial electron transfer step from the locally excited (LE) to the CT state may be followed by full charge separation to form dissociated charge carriers or geminate recombination to form the ground state ( $S_0$ ) [1]. To prevent undesired recombination, CT states should be thermodynamically favorable and should have a long lifetime. Based on a cascade values of ionization potentials and electron affinities, multicomponent covalently connected donor-acceptor systems with very long lifetime has been developed.[2] To include concepts of self-assembly and recognition in the design of such systems, covalent connections among donors and acceptors are replaced with soft interactions such as H-bonds in the salt bridges.

In this work the donor-acceptor pairs connected via carboxylate-guanidinium salt bridge [3] are modeled using TD-DFT methods with particular emphasize on the CT states. The results indicate that the charge separation in CT states depend on the orientation of the salt bridge. Also, the salt bridge was flexible enough to allow approaching of two interacting charged subunits in the minimum on the PES of the CT state as exemplified in Fig. 1.

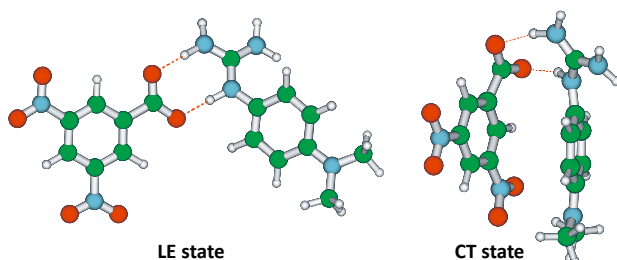


Figure 1. Geometries of 4-dimethylaminophenylguanidinium complex with 3,5-dinitrobenzoic acid in the bright LE and the lowest energy CT state at TD-CAM-B3LYP/6-31+G(d,p) level of theory

Acknowledgment: Support from the Croatian Science Foundation grant No. 9310 is acknowledged. The calculations were performed on the Isabella cluster ([isabella.srce.hr](http://isabella.srce.hr)) at the University of Zagreb Computing Center (SRCE).

- [1] T. M. Clarke, J. R. Durrant, *Chem. Rev.* **110**, 6736 (2010).
- [2] H. Imahori, D. M. Guldi, K. Tamaki, Y. Yoshida, C. Luo, Y. Sakata, S. Fukuzumi, *J. Am. Chem. Soc.* **123**, 6617 (2001).
- [3] I. Antol, Z. Glasovac, D. Margetić, R. Crespo-Othero, M. Barbatti, *J. Phys. Chem. A* **120**, 7088 (2016).



## Non-Adiabatic Dynamics at Metallic Surfaces: Revisiting the NO/Au(111) Puzzle

Tobias Serwatka<sup>1</sup>, Jean Christophe Tremblay<sup>1</sup>, Beate Paulus<sup>1</sup>

<sup>1</sup>*Institut für Chemie und Biochemie, Freie Universität Berlin, Takustraße 3, 14195 Berlin, Germany*

In the present contribution, we aim at the first principle characterization of some key factors affecting vibrational dynamics of adsorbates at metallic surfaces. Our work is motivated by a series of experiments by Wodtke and co-workers for the scattering of oriented NO molecules from a Au(111) surface (e.g., Refs. [1-4]). For molecules in different initial vibrational states, important multiple quanta vibrational relaxations and excitations are observed to take place on the subpicosecond timescale. Previous theoretical simulations have aimed at rationalizing those findings from the perspective of non-adiabatic coupling, both in the strong [5] and weak [6] coupling limits. Despite their great success, many key observed features remain unexplained.

Here, we present a global, flexible functional form for the potential energy surface that includes previously neglected binding sites and captures the subtleties of the potential landscape. In particular, we discuss the role of three-body terms, of charge transfer and of molecular orientation. The static vibrational eigenstates of the system in increasing dimension reveal important inter-mode couplings which were previously neglected. The relaxation behaviour of the adsorbed NO is further studied in static terms.

### References:

1. Y. Huang, C. T. Rettner, D. J. Auerbach, and A. M. Wodtke. *Science* **290** (2000) 111.
2. N. Bartels, K. Golibrzuch, C. Bartels, L. Chen, D.J. Auerbach, A.M. Wodtke, and T. Schäfer. *J. Chem. Phys.* **140** (2014) 054710.
3. N. Bartels, B.C Krüger, D.J. Auerbach, A.M. Wodtke, and T. Schäfer *Angew. Chem.* **126** (2014) 13908.
4. B. C. Krüger, N. Bartels, C. Bartels, A. Kandratsenka, J. C. Tully, A. M. Wodtke, and T. Schäfer. *J. Phys. Chem. C* **119** (2015) 3268.
5. N. Shenvi, S. Roy, and J.C. Tully. *J. Chem. Phys.* **130** (2009) 174107.
6. S. Monturet and P. Saalfrank. *Phys. Rev. B* **82** (2010) 075404.

## Analysis of Electron Correlation Effects in Strongly Correlated Systems ( $N_2/N_2^+$ )

Christian Stemmler<sup>1</sup>, Örs Legeza<sup>2</sup>, Beate Paulus<sup>1</sup>

<sup>1</sup>*Physikalische und Theoretische Chemie - Institut für Chemie und Biochemie, Freie Universität Berlin, Takustraße 3, Berlin, Germany*

<sup>2</sup>*Strongly correlated systems “Lendület” research group, Wigner Research Centre for Physics, P.O.Box 49, Budapest, Hungary*

The dissociation of  $N_2$  and  $N_2^+$  has been studied by using the *ab initio* Density Matrix Renormalization Group (DMRG) method. Accurate Potential Energy Surfaces (PES) have been obtained for the electronic ground states of  $N_2$  ( $X^1\Sigma_g^+$ ) and  $N_2^+$  ( $X^2\Sigma_g^+$ ). Inherently to the DMRG approach, the eigenvalues of the reduced density matrix and their correlation functions are at hand. Thus we can apply Quantum Information Theory (QIT) directly, and investigate how the wave function changes along the PES and depict differences between the different states. Moreover by characterizing quantum entanglement between different pairs of orbitals and analyzing the reduced density matrix, we achieved a better understanding of the multi-reference character featured by these systems.

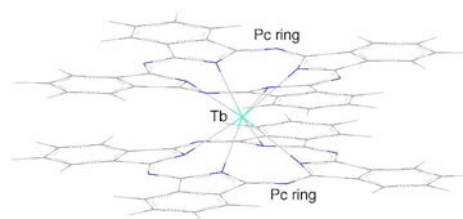
- [1] S. Szalay, M. Pfeffer, V. Murg, G. Barcza, F. Verstraete, R. Schneider, and Ö. Legeza, *Int. J. Quant. Chem.* **115**, 1342-1391 (2015).
- [2] G. Barcza, R.M. Noack, J. Sólyom, and Ö. Legeza, *Phys. Rev. B* **92**, 125140 (2014)

**Theoretical study on exchange interaction between  $f$  and  $\pi$  electrons  
in Tb(III)-phthalocyanine double-decker complex**  
**Yasutaka Kitagawa<sup>1</sup>, Yoshiki Natori<sup>1</sup>, Keiichi Katoh<sup>2</sup>, Masahiro Yamashita<sup>2</sup>  
and Masayoshi Nakano<sup>1</sup>**

<sup>1</sup> *Department of Materials Engineering Science, Graduate School of Engineering Science,  
Osaka University, 1-3 Machikaneyanma, Toyonaka, Osaka 560-8531, Japan.*

<sup>2</sup> *Graduate School of Science, Tohoku University, 6-3 Aramaki-Aza-Aoba, Aoba-ku, Sendai,  
Miyagi 980-8578, Japan.*

About a decade ago, Ishikawa *et al.* found that lanthanide phthalocyanine (Pc) double-decker complexes ( $\text{LnPc}_2^-$ ;  $\text{Ln}=\text{Tb(III)}, \text{Y(III)}$ ) exhibit a single molecular magnet (SMM) behavior.<sup>1</sup> On the other hand, neutral lanthanide double- and multiple-decker complexes with Tb(III) and Y(III) ions have also been reported.<sup>2</sup> Our group has investigated a relationship between molecular structure and electronic structure on the Tb(III) complex illustrated in Figure 1. In a previous paper, we pointed out that a  $\pi$ - $\pi$  dispersion interaction plays an important role in the molecular geometry and the frontier orbitals.<sup>3</sup> On the other hand, the neutral complex includes an exchange (magnetic) interaction between  $f$ -electrons of Tb(III) and  $\pi$  radical of the Pc rings. Usually, the  $f$ - $\pi$  magnetic interaction is considered to be negligible. However, there are no reports on the quantitative analysis of  $f$ - $\pi$  interaction in this complex. In this study, therefore, we examine the  $f$ - $\pi$  magnetic interaction in the neutral  $\text{TbPc}_2$  complex with the use of DFT calculations. The magnetic exchange interaction was estimated by the energy gap between ferromagnetic and antiferromagnetic spin states.<sup>4</sup>



**Figure 1** Illustration of  $\text{TbPc}_2$

1. N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara, Y. Kaizu, Y. *J. Am. Chem. Soc.* **125**, 8694 (2003); N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara, Y. Kaizu, Y. *J. Phys. Chem. B* **108**, 11265 (2004).
2. K. Katoh, Y. Yoshida, M. Yamashita, H. Miyasaka, B.K. Breedlove, T. Kajiwara, S. Takaishi, N. Ishikawa, H. Isshiki, Y.F Zhang, T. Komeda, M. Yamagishi, J. Takeya, *J. Am. Chem. Soc.* **131**, 9967 (2009).
3. Y. Kitagawa, Y. Kawakami, S. Yamanaka, M. Okumura, *Mol. Phys.* **112**, 995 (2014).
4. Y. Kitagawa *et al.*, *in preparation*.

## Fitted potential energy surfaces in non-redundant, translationally and rotationally invariant coordinate systems

Sean McConnell<sup>1</sup>, Johannes Kästner<sup>1</sup>

<sup>1</sup>*Institute for theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany*

Potential energy surfaces (PES) fitted using machine learning methods have become popular as they reduce the time required to obtain a qualitatively accurate picture of the energy landscape of a molecule containing many degrees of freedom.<sup>1-4</sup> We seek to use a fitted PES in the calculation of reaction rate constants using instanton theory, where knowledge of gradients and Hessians is required at the different molecular configurations along the instanton path. If the input coordinates are cartesian, the learning algorithm must be trained to learn about the rotational and translational independence of the properties of interest (energies, gradients and Hessians). This requires the training and test sets be artificially padded with a large amount of excess data. Naturally there exist a number of remedies, most commonly, the input data is transformed into a normal coordinate representation. We propose the use of a coordinate system which is intrinsically independent of any rotational or translational degrees of freedom for the purpose of fitting not just energies, but also gradients and Hessians. Moreover, this coordinate system should be *non-redundant*, i.e. it will contain only the minimum necessary  $3N - 6$  degrees of freedom, where  $N$  is the number of nuclei. Examples already exist of fitted PESs in translationally and rotationally invariant coordinate systems,<sup>5</sup> though to our knowledge only with the aim of obtaining energies and gradients. We have implemented two neural network algorithms to fit the potential energy surface of the reaction  $\text{CH}_3\text{OH} + \text{H} \rightarrow \text{CH}_2\text{OH} + \text{H}_2$  using coordinates built on either internuclear distances or inverse internuclear distances. We compare the training time and accuracy in a reaction rate calculation between these networks and a network trained using normal coordinates.

- [1] T. B. Blank, S. D. Brown, A. W. Calhoun, and D. J. Doren, J. Chem. Phys **103**, 4129 (1995).
- [2] D. F. R. Brown, M. N. Gibbs, and D. C. Clary, J. Chem. Phys **105**, 7597 (1996).
- [3] K. T. No, B. H. Chang, S. Y. Kim, M. S. Jhon, and H. A. Scheraga, Chem. Phys. Lett. **271**, 152 (1997).
- [4] H. Gassner, M. Probst, A. Lauenstein, and K. Hermansson, J. Phys. Chem. A **102**, 4596 (1998).
- [5] J. Behler, Phys. Chem. Chem. Phys. **13**, 17930 (2011).

## Oxygen reduction reaction on a defective ZrO<sub>2</sub> surface

**Yoshiyuki Yamamoto, Shusuke Kasamatsu and Osamu Sugino**

*Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Chiba, Japan*

Polymer electrolyte fuel cell (PEFC) has attracted attention as an energy conversion device with high-energy density, zero emission and low operating temperature. Performance of PEFCs largely depends on the catalytic activity of the oxygen reduction reaction (ORR) that occurs at the cathode electrocatalyst. Pt-based materials are usually used as electrocatalysts to enhance the ORR activity, but they have low durability and cost problems, which hamper the widespread use of PEFCs.

Defective oxide electrocatalysts, such as Zr-based materials, are expected as promising alternatives to the Pt electrocatalysts due to their high durability and low cost [1]. Although pristine oxides are not active against the ORR, defects such as nitrogen atoms and oxygen vacancies make them active. The ORR activity has been improving year by year and some defective oxides are already comparable to Pt in a low current condition. Although experiments indicate that the ORR activity is correlated with the amount of oxygen vacancies, little is known about the microscopic mechanisms of the ORR, such as the active site, the reaction pathway and the rate-determining step.

The purpose of this study is to advance our understanding of the ORR mechanism on defective oxide surfaces. For this purpose, we model the defective tetragonal ZrO<sub>2</sub> (101) surface adsorbed with water molecules and calculate the free energies of the reaction intermediates [2]. Because there are various possible active sites, we firstly screen the active sites using the free energies of the latter part of the ORR and then calculate the free energy diagram of the entire reaction pathway for the screened active site.

The calculated free energies of ORR intermediates indicate the following. (1) Zr site has very low activity against the ORR due to too weak adsorptions of the intermediates even if defects exist around the Zr site. (2) Vo site can be the active site when nitrogen atoms are doped. This is because the doped nitrogen atoms make the oxygen vacancy stable. (3) The rate-determining step is the O<sub>2</sub> adsorption, which has at least 0.5 eV energy barrier. (4) Despite the weak adsorption of O<sub>2</sub> molecule, the four-electron reduction selectively occurs because the first reduction immediately cut the O-O bonding.

[1] K. Ota, Y. Ohgi, K. Matsuzawa, S. Mitsushima, A. Ishihara., ECS Transaction **45(2)**, 27 (2012).

[2] Y. Yamamoto, S. Kasamatsu, O. Sugino, in preparation.

## Computing Bulk Phase Infrared, Raman, VCD, and ROA Spectra from *ab initio* Molecular Dynamics

**Martin Brehm and Martin Thomas**

*Institut für Chemie - Theoretische Chemie, Martin-Luther-Universität Halle-Wittenberg,  
Von-Danckelmann-Platz 4, 06120 Halle (Saale), Germany.*

In this contribution, we present our newly developed methodology for computing Raman optical activity (ROA) spectra of liquid systems from *ab initio* molecular dynamics (AIMD) simulations [1]. The method is built upon our recent developments to obtain magnetic dipole moments from AIMD [2] and to integrate molecular properties by using radical Voronoi tessellation [3]. Large and complex periodic bulk phase systems can easily be treated, since only AIMD simulations are required as input, and no time-consuming perturbation theory is involved. The approach relies only on the total electron density in each time step and can readily be combined with a wide range of electronic structure methods. To the best of our knowledge, these are the first computed ROA spectra for a periodic bulk phase system. As an example, the experimental ROA spectrum of liquid (*R*)-propylene oxide is reproduced very well.

Together with our previous work on infrared, Raman, and VCD spectroscopy [2-4], the full set of vibrational spectra is routinely accessible for complex periodic bulk phase systems now. The methods are all implemented in our freely available open-source program package TRAVIS [5].

- [1] M. Brehm, M. Thomas, 2017, *submitted*.
- [2] M. Thomas, B. Kirchner, *J. Phys. Chem. Lett.* **7**, 2016, 509-513.
- [3] M. Thomas, M. Brehm, B. Kirchner, *Phys. Chem. Chem. Phys.* **17**, 2015, 3207-3213.
- [4] M. Thomas, M. Brehm, R. Fligg, P. Vöhringer, B. Kirchner, *Phys. Chem. Chem. Phys.* **15**, 2013, 6608-6622.
- [5] TRAVIS, see <http://www.travis-analyzer.de/>

## A theoretical mechanistic study on the reaction of a rhenium hydroxo complex toward methyl propiolate

Ramón López, Daniel Álvarez, M. Isabel Menéndez

*Departamento de Química Física y Analítica, Universidad de Oviedo,  
C/ Julián Clavería 8, 33006 Oviedo, Spain*

Experimental studies have shown that the complexes  $[\text{ReX}(\text{CO})_3(\text{N-N})]$  ( $\text{X}$  = nucleophilic ligand,  $\text{N-N}$  = bidentate ligand) have a rich reactivity against activated alkynes such as methyl propiolate (HMAD,  $\text{HC}\equiv\text{CCO}_2\text{Me}$ ) and dimethyl acetylenedicarboxylate (DMAD,  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ ) [1]. Three types of products have been reported depending on the nucleophilic ligand: a) C-C coupling between the acetylenic fragment and the bipy ligand ( $\text{X} = \text{PPh}_2$ , diphenylphosphanido), b) C-C coupling between the acetylenic fragment and a carbonyl ligand in *cis* disposition to the  $\text{X}$  ligand ( $\text{X} = \text{OH}$ , hydroxo;  $\text{NH}p\text{Tol}$  (*para*-tolylamido), and c) insertion of the acetylenic fragment into the  $\text{Re-X}$  bond ( $\text{X} = \text{OMe}$ , methoxo). A recent theoretical study on the reactions of HMAD with  $[\text{Re}(\text{PPh}_2)(\text{CO})_3(\text{N-N})]$  ( $\text{N-N} = \text{phen}$ , 1,10-phenanthroline; bipy, 2,2'-bipyridine) has revealed the existence of three reaction mechanisms leading to the products mentioned above [2]. They all have in common the formation of a zwitterion resulting from the attack of the phosphorus atom on the HMAD non-substituted carbon. Then, the system can evolve differently depending on whether the HMAD substituted carbon attacks the bidentate ligand, carbonyl ligand, or metal center. Since the product obtained with the hydroxo complex differs from that found with the phosphanido one, we want to know which are the factors governing the formation of one or another product. Therefore, we undertook a theoretical investigation on the mechanism of the reaction of  $[\text{Re}(\text{OH})(\text{CO})_3(\text{bipy})]$  toward HMAD whose main results are presented here.

[1] R. Arévalo, M. Espinal-Viguri, M.A. Huertos, J. Pérez, E. Hevia, J. Pérez, L. Riera, V. Riera, *Adv. Organomet. Chem.* **65**, 47 (2016).

[2] D. Álvarez, R. Mera-Adasme, L. Riera, G.I. Cárdenas-Jirón, J. Pérez, J. Díaz, M.I. Menéndez, R. López, *Inorg. Chem.* DOI: 10.1021/acs.inorgchem.7b00767, Publication Date (Web): May 18, (2017).

## A catalytic oxidation mechanism for the first C-H bond of organic molecules by MnO<sub>2</sub>

Meijuan Zhou<sup>1,2</sup>, Yi Dong<sup>2</sup>, Michael Springborg<sup>\*2,3</sup>

<sup>1</sup>*Institute of Atmospheric Sciences, Shanghai Key Laboratory of Atmospheric Particle Pollution & Prevention (LAP<sup>3</sup>), Department of Environmental Science & Engineering, Fudan University, Shanghai 200433, China*

<sup>2</sup>*Physical and Theoretical Chemistry, University of Saarland, 66123 Saarbrücken, Germany*

<sup>3</sup>*School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China*

\* Corresponding author: E-mail: [m.springborg@mx.uni-saarland.de](mailto:m.springborg@mx.uni-saarland.de)

The total oxidation process of benzene is very complex<sup>1</sup> but the cleavage of the first C-H bond is the initial step of the benzene oxidation, and is also the most vital step. DFT calculations were performed to investigate the catalytic oxidation mechanism for this step on the surfaces of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -MnO<sub>2</sub> based on experimental results. The catalytic abilities of MnO<sub>x</sub> in the total oxidation of benzene are related to the concentration of oxygen vacancies on the surfaces of the catalysts, and the existence of oxygen vacancies can enhance the adsorption and oxidation of benzene<sup>2-5</sup>. A fundamental question is whether benzene will react with oxygen co-adsorbed on the oxygen vacancies or with lattice oxygen on the surfaces of the catalysts. To study this, oxygen-deficient and oxygen-rich surface structures of the three MnO<sub>2</sub> crystal phases were considered in the theoretical calculations. Moreover, in order to study how general the conclusions are we also consider the adsorption of methane and formaldehyde. The nudged-elastic-band method was employed to calculate the energy barriers in the oxidation reaction processes of the first C-H bond on the different surfaces of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -MnO<sub>2</sub>, respectively. We demonstrate that oxygen-deficient MnO<sub>2</sub> surfaces facilitate the adsorption of oxygen molecules and benzene, and the first C-H bond of benzene is easier to be oxidized by the oxygen co-adsorbed on the oxygen vacancy than by the lattice oxygen.

These results of DFT calculations can be useful for a further understanding of the catalytic oxidation mechanism of organic molecules over the surfaces of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -MnO<sub>2</sub>, and the relationship between the catalytic performances and the surface structures.

[1] D. A. Bittker, *Combust. Sci. and Tech.* **79**, 49–72 (1991).

[2] T. Y. Li, A. J. Chiang, B. J. Liaw and Y. Z. Chen, *Appl. Catal. B: Environ.* **103**, 143–148 (2011).

[3] Z. Wang, G. Shen, J. Li, H. Liu, Q. Wang and Y. Chen, *Appl. Catal. B: Environ.* **138–139**, 253–259 (2013).

[4] W. Tang, X. Wu, D. Li, Z. Wang, G. Liu, H. Liu and Y. Chen, *J. Mater. Chem. A* **2**, 2544–2554 (2014).

[5] Z. Wang, Y. Deng, G. Shen, S. Akram, N. Han, Y. Chen and Q. Wang, *Chemistry Open* **5**, 495–504 (2016).



## Ionization potentials, electron affinities, and photoelectron spectra: Comparing various DFT and *GW* methods

L. Gallandi, T. Körzdörfer

*AG Computational Chemistry, University of Potsdam, Institute of Chemistry, Karl-Liebknecht Straße 24-25, D-14476 Potsdam-Golm*

The accurate prediction of molecular ionization potentials (IPs), electron affinities (EAs), and full valence photoelectron spectra (PES) has been, and still is, a challenging task for electronic structure theory. The most accurate wavefunction methods currently available, such as CCSD(T) or ADC3, suffer from their unfavorable scaling and high memory requirements, making them only available for small to medium sized molecules. In addition, such methods only provide straight-forward access to the highest (HOMO) IP and the lowest (LUMO) EA, but not the full PES and/or inverse PES. In both regards, DFT and many-body perturbation theory in the *GW* approximation are attractive alternatives.

To study and compare the performance of various DFT functionals, we calculated the IPs and EAs for 24 organic acceptor molecules [1, 2, 3, 4], both from a  $\Delta$ SCF approach as well as from the negative HOMO and LUMO eigenvalues, respectively. Our study includes various LDA, GGA, and meta-GGA functionals, as well as a number of global, range-separated, and double hybrid functionals. Basis set extrapolated CCSD(T) calculations [1] are used as a reference for those molecules. Not surprisingly, it is found that IP-tuned long range corrected hybrid functionals like LC- $\omega$ PBE and  $\omega$ B97 show the most accurate results. The quality of a one-shot correction of the DFT eigenvalues with the *GW* approach ( $G_0W_0$ ) depends heavily on the functional used in the DFT starting point. We demonstrate that calculations done on top of the IP-tuned LC- $\omega$ PBE calculations show even more accurate results compared to CCSD(T) [2].

The prediction of PES is an even more challenging task, as not only the HOMO, but also the other occupied orbitals are important. Furthermore the intensities and broadenings of the peaks are complicated to calculate. To allow for a better, direct comparison of the calculated PES with experiment, we developed a genetic algorithm which mimics the vibrational broadening and the different intensities to create a measureable value. The combination with the best  $G_0W_0$  calculations [2] and an alternate approach to the IP-tuning (the potential adjustment method [5]) yield very good PES in comparison with gas-phase experiments.

[1] R. M. Richard et al., *J. Chem. Theory Comput.* **12**, 595 (2016).

[2] L. Gallandi et al., *J. Chem. Theory Comput.* **12**, 605 (2016).

[3] J. W. Knight et al., *J. Chem. Theory Comput.* **12**, 615 (2016).

[4] O. Dolgounitcheva et al., *J. Chem. Theory Comput.* **12**, 627 (2016).

[5] A. Thierbach et al., *J. Chem. Theory Comput.* **submitted**.

## Dynamic Solvent Effects treated with a Quantum/Classical TDSCF Approach

Martin T. Peschel<sup>1</sup>, Julius P. P. Zauleck<sup>1</sup>, Florian Rott<sup>1</sup>, Sebastian Thallmair<sup>2</sup>,  
Regina de Vivie-Riedle<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Ludwig-Maximilians-Universität, Munich, Germany*

<sup>2</sup>*Groningen Biomolecular Sciences and Biotechnology Institute and The Zernicke Institute for Advanced Material, University of Groningen, The Netherlands*

Wavepacket dynamics on potential energy surfaces is a versatile tool to examine chemical reactions such as photodissociation or light-induced rearrangements. The course of these reactions can be substantially altered in solution, hence solvent effects have to be included in the simulations. In addition to electrostatic solvent effects, dynamic solvent effects, where the solvent redirects molecular motion of the solute, come into play when large geometrical changes in the molecular structure of the solute are involved [1].

A coupled quantum dynamics/molecular dynamics approach is presented that captures these effects in simulations of molecular wavepackets. It treats the solvent by classical molecular dynamics and couples it to the quantum solute using a time-dependent self-consistent field. This approach was tested on the photodissociation of ICN in liquid argon and then applied to the bond cleavage of the diphenylmethyltriphenylphosphonium cation in acetonitrile. In these simulations, the collision of the molecular wavepacket with the solvent cage and the resulting dissipative energy transfer from the quantum to the classical system is observed. Furthermore, an analysis in phase space reveals solvent induced decoherence (Figure 1).

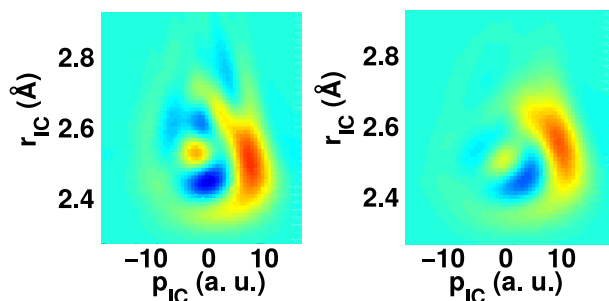


Figure 1: Wigner function of the photo dissociation of ICN after 348 fs in the gas phase (left) and in liquid Ar (right). The interference in solution is reduced due to decoherence.

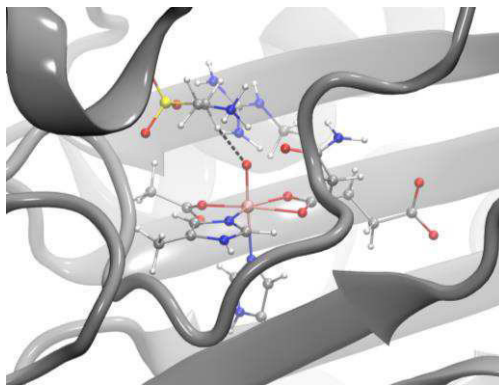
[1] S. Thallmair *et al.*, *J. Chem. Theory. Comput.* **11**, 1987–1995 (2015).

## QM/MM study of an atom tunneling in the hydroxylation process of taurine/ $\alpha$ -ketoglutarate dioxygenase (TauD)

Sonia Álvarez-Barcia<sup>1</sup>, Johannes Kästner<sup>1</sup>

<sup>1</sup>*Inst. for Theoretical Chemistry, University Stuttgart, Pfaffenwaldring 55, Stuttgart, Germany*

Enzymes of the class of  $\alpha$ -ketoglutarate dependent dioxygenases ( $\alpha$ KGDs) are vital in many biochemical and pharmacological processes, while details of their reaction mechanism remain poorly understood. This study focuses on one of the most studied  $\alpha$ KGDs: the Taurine/ $\alpha$ -ketoglutarate Dioxygenase (TauD).<sup>1</sup> More concretely, we are interested in clarifying one of the key steps in the catalytic cycle of the  $\alpha$ KGDs, the hydrogen atom transfer (HAT) process. We have studied the HAT process in TauD by QM/MM simulations (see Figure 1). Analysis of the charge and spin densities during the reaction demonstrates that a concerted mechanism takes place, where the H atom transfer happens simultaneously with the electron transfer from taurine to the Fe=O cofactor.<sup>4</sup> In addition, we have found that the reaction is significantly enhanced by atom tunneling, which increases the rate constant by a factor of 40 at 5 °C.<sup>4</sup> This causes a KIE of about 60, which is in excellent agreement with the experimental value of about 58.<sup>3</sup> These results influence our understanding of the whole class of  $\alpha$ KGDs.



**Figure 1:** Schematic representation of one reactant complex structure of the TauD enzyme.

- [1] B. K. Y. Mai, Y. Kim, *Inorg. Chem.* **55**, 3844 (2016). Godfrey, C. S. Porro, S. P. de Visser *J. Phys. Chem. A* **112**, 2464 (2008). See also refs. therein.
- [3] J. C. Price E. W. Barr, T. E. Glass, C Krebs C, J. M. Bollinger *J. Am. Chem. Soc.* **125**, 13008 (2003).
- [4] S. Álvarez-Barcia J. Kästner *J. Phys. Chem. B*, **121**, 5347 (2017).

## Replacing coarse-grained ligand on binding site by all-atom model

Tenfu Suzumura<sup>1</sup>, Hitoshi Goto<sup>1</sup>

<sup>1</sup> *Computer Science and Engineering, Toyohashi University of Technology,  
1-1 Hibarigaoka, Tempaku-cho, Toyohashi Aichi, 441-8580 Japan*

Techniques of multiscale/multiphysics simulation model have played an important role in analyzing larger systems such as biological macromolecules and polymer materials [1]. Especially, the coarse-grained model allows us to analyze large systems in nm -  $\mu$ m scale, so it is one of the most promising methodologies to investigate their dynamics of polymer's behaviors or its ligand complex formation in system. However, to simultaneously satisfy the advantages of high-speed calculation by the coarse-grained model and the high-precision energy evaluation by the all-atom model, more accurate transformation theory between both models is required [2]. In our laboratory, we have started the development of new fast docking method for protein-peptide complex by a coarse-grained model. In this study, various methods that can build the all-atom peptide geometry from the positions of the coarse-grained amino acid particles placed at the binding site of a protein determined by the docking method are examined. For the relatively shorter peptides (three or four residues) in a referenced protein-peptide complex, conformation database that is including all atom coordinates of all conformers and their MMFF94s energies in gas-phase has been constructed by using our efficient conformation search program CONFLEX [3]. The best fitting conformers in each coarse-grained model have been found from the conformation



Fig. 1 Superimpositions among the reference peptides (B&S) and the best fitting conformers in various coarse-grained models (wire).

database, and evaluated how fitting in all-atom model by superimposed RMS difference and the conformational distance (Fig. 1). Additionally, we compared our scheme for generating all-atomic coordinates from the coarse-grained particles with various coarse-grained models including the well-known definition as MARTINI [4].

[1] M. Karplus, *Angew. Chem.* **53**, 9992 (2014).

[2] S. Kmiecik, *et. al.*, *Chem. Rev.* **116**, 7898 (2016).

[3] H. Goto and E. Osawa, *J. Chem. Soc. Perkin Trans. 2*, **2**, 187 (1993).

[4] L. Monticelli, *et. al.*, *J. Chem.* **4**, 819 (2008).

## Theoretical investigation of organic ligands radiation stability

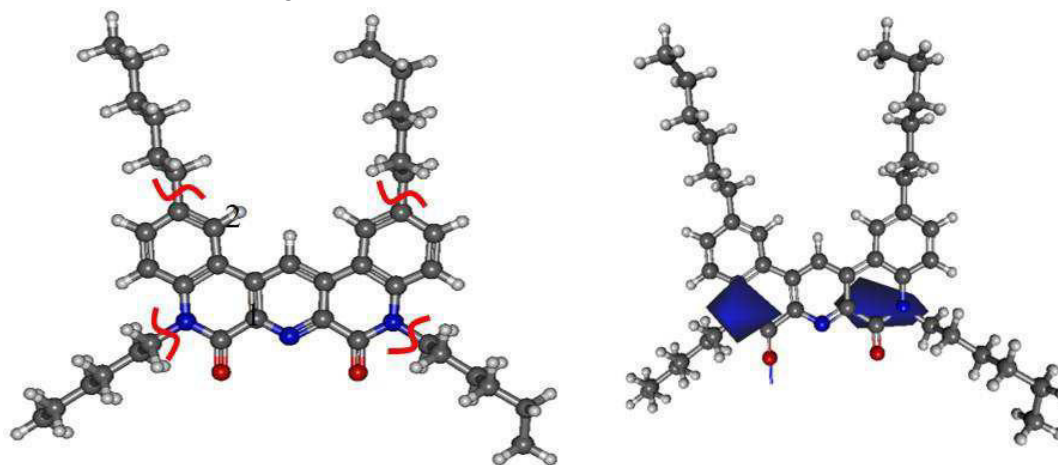
**Artem A. Mitrofanov<sup>1,2</sup>, Anastasia A. Smirnova<sup>1</sup>, Petr I. Matveev<sup>1</sup>, Vladimir G. Petrov<sup>1</sup>, Stepan N. Kalmykov<sup>1</sup>**

<sup>1</sup>*Department of chemistry, Moscow State University, Leninskie Gory 1-3, Moscow, Russia*

<sup>2</sup>*Faculty of Materials Science, Moscow State University, Leninskie Gory 1-73, Moscow, Russia*

Modern technologies for nuclear spent fuel reprocessing are based on liquid extraction, which allows us to recycle reagents in order to minimize an amount of nuclear waste. One of key questions of the reprocessing development is design of novel effective extractants and their radiation stability is one of main problems. Here we would like to introduce our results of our work on a topic of in silico design of such extractants and its radiation stability estimation using semiempirical and ab initio quantum chemistry methods.

We used two methods of electron structure analysis: Mayer bond order estimation and Fukui boundary orbitals theory. Combination of the methods allows us to take into account two main ways of ligands radiation destruction – direct homolytic bond break under irradiation and following radical reactions.



Pic.1 Proposed “weak bonds” (left) and radical Fukui surface (right)

Obtained results show good concurrence with experimental data either our or found in literature.

## Influence of Atom-Tunneling and Ice Surfaces on the Reaction Rates of Interstellar Water Formation

Jan Meisner<sup>1</sup>, Johannes Kästner<sup>1</sup>

<sup>1</sup>*Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany, meisner@theochem.uni-stuttgart.de*

Atom tunneling plays a crucial role in reactions in cryogenic environments like in the interstellar medium. Reactions are assumed to be catalyzed heterogeneously by surfaces coated with water ice. The reaction of  $\text{H}_2$  with the hydroxy radical is one of the most important routes of water formation in astrochemistry even though it possesses an activation energy of  $24 \text{ kJ mol}^{-1}$ . We calculated the gas-phase reaction rate constants using semiclassical instanton theory on a fitted potential energy surface [1]. The results are compared to harmonic transition state theory (HTST) to quantify the impact of atom tunneling [2]. We also present the influence of an ice surface on the reaction and propose a new approach of mimicking a surface by modifying the rotational partition function. To calculate the reaction on the ice surface a QM/MM setup with a thoroughly benchmarked QM region was used. The importance of ice surfaces for this reaction at the conditions in the interstellar medium is discussed [3].

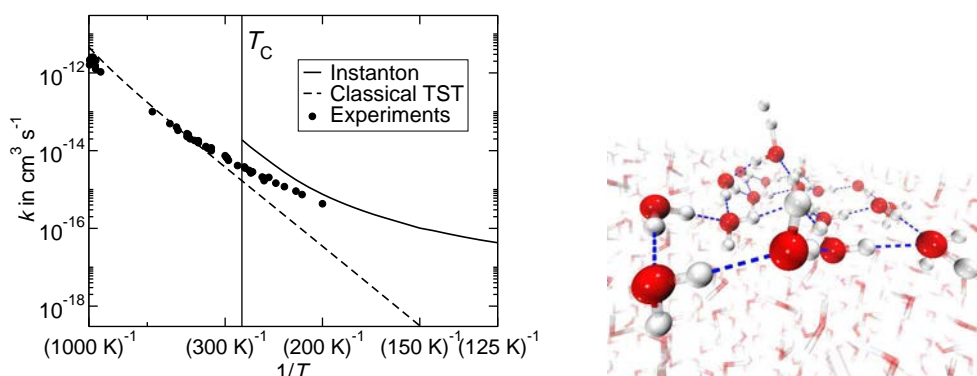


Figure 1: The reaction of  $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ . Left: Arrhenius plot of the gas phase reaction. Right: Transition structure of the reaction on an ice surface.

[1] J. Chen, X. Xu, X. Xu, and D. H. Zhang, *J. Chem. Phys.* **138**, 154301 (2013).

[2] J. Meisner and J. Kästner, *J. Chem. Phys.* **144**, 174303 (2016).

[3] J. Meisner, T. Lamberts, and J. Kästner, *submitted*

## A Quantum Chemical Definition of Electron-Nucleus Correlation Energy

Patrick Cassam-Chenaï<sup>1</sup>, Bingbing Suo<sup>2</sup>, Wenjian Liu<sup>3</sup>

<sup>1</sup>*Université Côte d’Azur, CNRS, LJAD, UMR 7351, 06100 Nice, France.*

<sup>2</sup>*Shaanxi Key Laboratory for Theoretical Physics Frontiers, Institute of Modern Physics, Northwest University, 229 Taibaibei Road, Xi’an 710069, Shaanxi, People’s Republic of China.*

<sup>3</sup>*Beijing National Laboratory for Molecular Sciences, Institute of Theoretical and Computational Chemistry, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, and Center for Computational Science and Engineering, Peking University, Beijing 100871, People’s Republic of China.*

We introduce a definition of electron-nucleus correlation energy by analogy with the quantum chemical definition of electronic correlation energy. The uncorrelated reference function is obtained by repeated electron-nucleus mean field configuration interaction steps until self-consistency is achieved. Electron-nucleus correlation and electronic correlation energies are compared on dihydrogen isotopologues.

[1] P. Cassam-Chenaï, B. Suo, W. Liu, *Theor. Chem. Account* **136**, 52 (2017)

[2] P. Cassam-Chenaï, B. Suo, W. Liu, *Phys. Rev. A* **92**, 012502 (2015)

## The incremental EOM-CCSD method and study of UV-Vis spectra in ThDP-dependent enzymes

Mirko Paulikat<sup>1</sup>, Ricardo A. Mata<sup>1</sup>

<sup>1</sup>*Institute of Physical Chemistry, University of Goettingen, Tammannstraße 6, D-37077 Göttingen, Germany*

*Ab initio* correlation methods suffer from their exponential scaling relative to the system size, allowing only the treatment of relatively small systems. In order to obtain significant savings in the computation time, incremental approaches can be applied to calculate the correlation energies of molecules. Here, the system is split into fragments, consisting of grouped valence orbitals. The energy is then computed in a many-body expansion. This approach was successfully applied for the calculation of the correlation energies of several molecules.[1]

The extension of this method to the calculation of excitation energies is not straightforward. A suitable reference for the basis of the expansion is missing opposed to ground state calculations, where usually localized Hartree-Fock orbitals are employed. Mata and Stoll proposed an incremental method for excited state energies with a mixed occupied orbital space, built from natural transition orbitals (NTOs) and localized molecular orbitals (LMOs).[2] Within this approach a main fragment could be defined containing the NTOs. Therefore, the excitation is well represented in all calculations of the many-body expansion. In order to refine this method, we tested different algorithms for the calculation of excitation energies of small to medium sized organic molecules. Furthermore, we applied the approach to reaction intermediates of thiamin diphosphate (ThDP) dependent enzymes. This has allowed us to explain measured UV-Vis spectra and identify on-pathway reaction intermediates.

[1] H. Stoll, *Chem. Phys. Lett.* **191**, 548 (1992).

[2] R. A. Mata, H. Stoll, *J. Chem. Phys.* **134**, 034122 (2011).



## Dynamic electron correlation for compact non-orthogonal orbital expansions of large active spaces

Sven Kähler<sup>1</sup>, Jeppe Olsen<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Aarhus University, Langelandsgade 140, 8000 Aarhus, Denmark*

A new computational approach is presented that calculates dynamic correlation terms in an efficient manner on top of compact non-orthogonal orbital-based wave function expansions and can give accurate results for systems that are too large to be treated with standard CASSCF and CASPT2. Non-orthogonal orbital-based expansions like spin-coupled valence bond have been shown to offer qualitatively correct descriptions even for challenging static correlation problems using far fewer CSFs than CASSCF expansions[1].

In the standard formulation, these smaller non-orthogonal expansions do not directly lead to computational savings, since for non-orthogonal orbitals all determinants interact with each other via the Hamiltonian instead of only those that differ in at most two occupied orbitals as for orthogonal orbitals. As a consequence non-orthogonal orbital-based normally scale quadratically in the number of active space configurations.

The new approach improves the scaling of dynamic correlation calculations from quadratic to linear. This is achieved via the use of biorthonormal orbital and CI expansions and efficient transformation algorithms[2] in an extension of the previous work on the improved scaling optimization of non-orthogonal orbitals[3]. With respect to non-orthogonal orbital-based multi-configurational perturbation theory for a spin-coupled valence bond reference, this constitutes an important improvement to the work of Chen and colleagues[4, 5]. Initial results including the chromium dimer are presented.

- [1] P. B. Karadakov, D. L. Cooper, B. J. Duke, J. Li, *J. Phys. Chem. A* **116**, 7238 (2012).
- [2] P.-Å. Malmqvist, *Int. J. Quantum Chem.* **30**, 479 (1986).
- [3] J. Olsen, *J. Chem. Phys.* **143**, 114102 (2015).
- [4] Z. Chen, J. Song, S. Shaik, P. C. Hiberty, W. Wu, *J. Phys. Chem. A* **113**, 11560 (2009).
- [5] Z. Chen, X. Chen, F. Ying, J. Gu, H. Zhang, W. Wu, *J. Chem. Phys.* **141**, 134118 (2014).

## Experimental and computational investigations on the enantioselective alkylation of $\alpha$ -ketoesters via copper catalysis

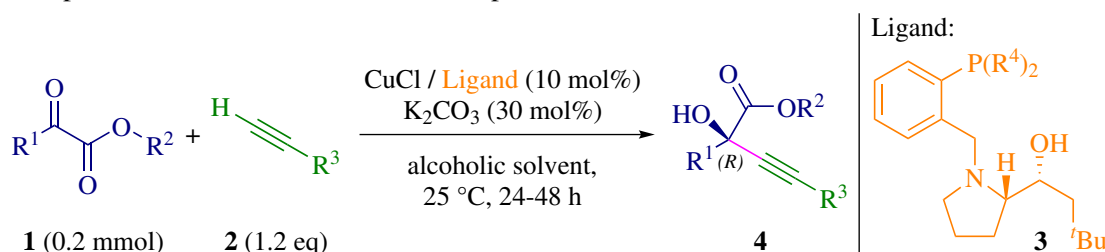
Martin Christoph Schwarzer<sup>1</sup>, Takaoki Ishii<sup>2</sup>, Akane Fujioka<sup>2</sup>, Hirohisa Ohmiya<sup>2</sup>, Masaya Sawamura<sup>2</sup>, Seiji Mori<sup>1</sup>

<sup>1</sup>College of Science, Ibaraki University, Mito 310-8512, Japan

<sup>2</sup>Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

Directionalized hydrogen bonds often play a key role in stabilizing not only intermediates, and products, but also transition states. Thus they are a very important element in developing new catalysts for asymmetric synthesis.

This study presents evidence for the enantioselectivity of the reaction of  $\alpha$ -ketoesters **1** with terminal alkynes **2**. The synthesis is controlled by copper catalysis utilizing hydroxy amine phosphine ligands **3** to selectively form the product **4** with the *R* stereo center. Reaction yields are up to 99% with enantiomeric excess up to 94%.



The stereo-selective bond formation is elucidated with a computational study employing density functional approximations, which have yielded good results in our previous studies.[1, 2] Gibbs activation energies are about 8 to 9 kcal mol<sup>-1</sup> for the most economic reaction pathways, which is a reasonable value at room temperature. The main product of the reaction is the *R*-alcohol. The *S* transition states are about 1 kcal mol<sup>-1</sup> higher in energy than the corresponding *R* states, because of disfavoured interactions between the phenyl moieties of the reactants.[3] Intramolecular O–H···O hydrogen bonding plays a key role into stabilizing the transition state conformations. A notable secondary interaction arises from a non-classical C–H···O hydrogen bond, which leads to a preference for only a few reaction pathways. This can be quantified with an analysis in terms of the quantum theory of atoms in molecules.

- [1] T. Ishii, R. Watanabe, T. Moriya, H. Ohmiya, S. Mori, M. Sawamura, *Chem. Eur. J.* **19**, 13547 (2013).
- [2] Gaussian 09, Rev. D01; Optimizations: DF-BP86/def2-SVP (imag. freq.  $i = [0, 1]$ , IRC confirmed); Energies: DF-BP86-D3(BJ)-PCM(*t*BuOH)/def2-TZVPP; Thermal corrections estimated at 298 K and 1 atm on optimized geometries.
- [3] M. C. Schwarzer, T. Ishii, A. Fujioka, H. Ohmiya, M. Sawamura, S. Mori, *in prepn.*

## Ultracold Chemistry: Theory of photoassociation processes of alkali metal clusters

Jan Schnabel<sup>1,2</sup>, Andreas Köhn<sup>1,2</sup>

<sup>1</sup>*Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany*

<sup>2</sup>*Center for Integrated Quantum Science and Technology IQ<sup>ST</sup>*

Chemistry in the sub-micro-Kelvin range provides the ability of studying molecular binding mechanisms on a fundamental level. In this respect rubidium became a vital species which can nowadays be routinely cooled and trapped. An important experimental method to create ultracold molecules is photoassociation. However, to generate higher associated clusters (e.g. Rb<sub>3</sub>) the intrinsic spontaneous decay in photoassociation has to be controlled. This can be done using an optical microcavity detecting the photon emitted during the decay process. Therewith non-destructive measurements as well as high resolution spectroscopy becomes possible (experiments are going to be performed by J. Hecker Denschlag et. al., Institute for Quantum Matter, University of Ulm).

From theoretical point of view we need to perform highly accurate computations of the expected states and transitions due to growing degrees of freedom. To achieve the required precision we have to find a well suited description of the electronic structure (i.e. correlation effects and spin-orbit coupling) and, depending on the measured accuracy, develop a method which explicitly treats the nuclei dynamics.

In this poster we investigate the applicability of an *ab initio* method with a large-core (i.e. only the 5s electron is treated as valence) effective core potential (ECP) and core polarization potential (CPP) [1] using a non-relativistic MRCI approach. For this purpose we constructed an even-tempered basis set from a given valence basis set [2]. In addition to the dimer molecule revealing some inherent problems coming with large-core ECPs we focus on the study of the rubidium trimer complex regarding possible configurations and coupling between several states. Thereby, following [3], we generated potential energy surfaces of spin-polarized trimers helping to understand the overall binding topology and giving hints for the experimental realization.

- [1] H. Silberbach, P. Schwerdtfeger, H. Stoll, H. Preuss. *J. Phys. B: At. Mol. Phys.* **19**, 501-510 (1986)
- [2] I.S. Lim, P. Schwerdtfeger, B. Metz, H. Stoll. *J. Chem. Phys.* **122**, 104103 (2005)
- [3] P. Soldán. *J. Chem. Phys.* **132**, 234308 (2010)

## Analysis of energy contributions to environmental effects on excited states

Heiner Schröder<sup>1</sup>, Tobias Schwabe<sup>1</sup>

<sup>1</sup>*Center for Bioinformatics, University of Hamburg, Bundesstraße 43, Hamburg, Germany*

An analysis of Schwabe[1] concluded that the spectral shift of an electronic excitation of a chromophore in an environment (with non-overlapping charge densities) may be separated into four distinct contributions. Three of these constitute differences between the ground state and the excited state of interest, namely (i) the Coulomb interaction, (ii) a classical induction effect and (iii) the London dispersion interaction. The fourth term is known as (iv) non-resonant excitonic coupling and depends on the transition moment of the respective excitation. This analysis is of importance for the construction of embedding approaches, which account for a mutual interaction of both subsystem. Contributions (ii) and (iv) were often seen as alternatives in such schemes and either one was neglected. Here, we analyze the importance of both contributions in the framework of polarizable embedding[2, 3]. Therefore we developed a state-specific correction for the induction effect (ii), which leaves London dispersion (iii) as the only missing contribution. We show that both contributions ((ii) and (iv)) may have a non-negligible effect depending on the nature of the excitation. Full QM reference data instead of experimental data is used to ensure direct comparability of (vertical) excitation energies.

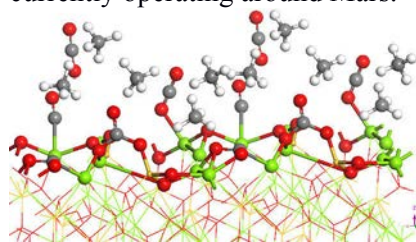
- [1] T. Schwabe, *J. Chem. Phys.* **145**, 154105 (2016).
- [2] J. M. Olsen, K. Aidas, J. Kongsted, *J. Chem. Theory Comput.* **6**, 3712 (2010).
- [3] K. Sneskov, T. Schwabe, J. Kongsted, O. Christiansen, *J. Chem. Phys.* **134**, 104108 (2011).

## Adsorption of CO<sub>2</sub> and methane onto olivine surfaces in Mars conditions

E. Escamilla-Roa<sup>1</sup>, J. Martin-Torres<sup>1,2</sup>, C.I. Sainz-Díaz<sup>1</sup>

<sup>1</sup>*Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Av. de las Palmeras 4, 18100 Granada, Spain.* <sup>2</sup>*Luleå University of Technology, 97187 Luleå, Sweden.*

Methane has been detected on all planets of our Solar System, and most of the larger moons, as well as in dwarf-planets like Pluto and Eric. Very recently has been reported the detection of methane on Mars after measurements from the rover Curiosity, which is operating on Mars since August 2012 [1]. The presence of this molecule in rocky planets is very interesting because its presence in the Earth's atmosphere is mainly related to biotic processes. Although the source of methane on Mars has not been determined, there is a good number of working, both abiotic and biotic, hypotheses trying to explain its presence on Mars. Space instrumentation in orbiters around Mars has detected olivine on the Martian soil and dust [2]. On the other hand the measurements of methane from the Curiosity rover show fluctuations between 0.69 ppbv to 7.2 ppbv in a short time span of 20-months [1]. The reasons of these fluctuations are unknown, and constitute a hot topic in planetary research. The goal of this study is investigate at atomic level the interaction processes of methane and other Mars atmospheric species (CO<sub>2</sub>, H<sub>2</sub>O) with two forsterite surfaces (100), through electronic structure calculations based on the Density Functional Theory (DFT). We propose two models to simulate the interaction of adsorbates with the surface of dust mineral, such as simultaneous mixtures (5CH<sub>4</sub>+5H<sub>2</sub>O/5CH<sub>4</sub>+5CO<sub>2</sub>) and as a clathrate adsorption. We have obtained interesting results of the adsorption process in the mixture 5CH<sub>4</sub>+5CO<sub>2</sub> (Fig. 1). As expected, the water molecules are chemisorbed through associative and dissociative processes. In all models, the methane molecules were only trapped and held by water or CO<sub>2</sub> molecules. In the dipolar surface; the CO<sub>2</sub> molecules had an interesting behaviour in the adsorption process, producing new species as the follow: one CO adsorbed (that came from dissociation of one CO<sub>2</sub> molecule), two CO<sub>2</sub> molecules chemisorbed to mineral surface where one of them formed carbonate group. May be that this effect can be catalyzed by methane presences. Our results suggest that CO<sub>2</sub> has a strong interaction with the mineral surface when is present the CH<sub>4</sub>. The new species formed have been corroborated with infrared frequencies that have a good agreement with experimental values. Our study also supports infrared spectroscopic observations on Mars, as those to be performed by instruments on the ESA's ExoMars Trace Gas Orbiter, currently operating around Mars.



**Fig. 1.** The adsorbed complexes of CO<sub>3</sub>, CO<sub>2</sub> and CO onto dipolar mineral surface in an amorphous mixture (5CH<sub>4</sub>:5CO<sub>2</sub>).

- [1] C. R Webster, et. al. *Science* **347**, 415 (2015).
- [2] D. F. Blake, et.al. *Science* **341**, 77 (2013).

## Modeling of nonlinear optical response

**Carolin Hühn, Marek Sierka**

*Otto Schott Institute of Materials Research, Friedrich Schiller University Jena,  
Löbdergraben 32, 07743 Jena, Germany*

One of the main challenges in the application of electronic structure methods for modeling of nonlinear optical phenomena is the proper description of the strong excitation limit. In case of the weak excitation limit, perturbation theories based on DFT are usually applied to predict properties of electronic excited states, such as linear-response time-dependent DFT (LR-TDDFT). However, fundamental understanding of nonlinear excited state dynamics at the femto- and sub-femtosecond time regimes requires going beyond the linear response. Unlike the weak excitation limit, where frequency-domain perturbative approaches suffice, the strong excitation regime is best captured with a real-time, real-space time-dependent DFT (RT-TDDFT). Here, the time evolution of the electron density is monitored directly, which provides access to the fundamental mechanisms of electronic excitations. Moreover, nonlinear spectroscopy experiments with short pulses can be directly simulated and fully nonlinear (beyond perturbation theory) spectral information is easily obtainable. Here, an implementation of RT-TDDFT within the TURBOMOLE program package [1-3] is presented using a first-order Magnus propagator and the predictor-corrector scheme. The performance and accuracy of the implementation is assessed using comparison with LR-TDDFT for small molecules interacting with weak electromagnetic fields (*cf.* Fig. 1).

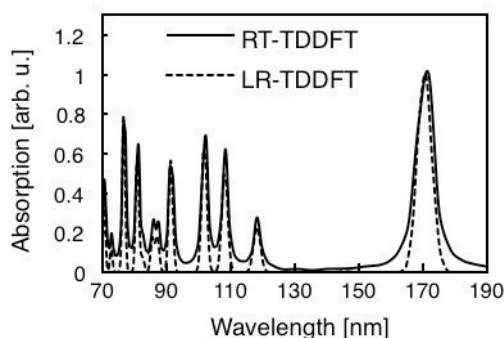


Figure 1: UV absorption spectrum of benzene calculated using LR-TDDFT and RT-TDDFT.

- [1] TURBOMOLE 7.1, a development of the University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>.
- [2] F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, F. Weigend, *WIREs Comput. Mol. Sci.* **4**, 91 (2014).
- [3] R. Łazarski, A. M. Burow, M. Sierka, *J. Chem. Theory Comput.* **11**, 3029 (2015).

## Bond Indicators from Relativistic and Multiconfigurational Calculations: Application to Astatine Species

**Cecilia Gomez Pech<sup>1,2</sup>, Dumitru-Claudiu Sergentu<sup>1,2</sup>, Julien Pilmé<sup>3</sup>, Nicolas Galland<sup>2</sup> and Rémi Maurice<sup>1</sup>**

<sup>1</sup>*SUBATECH, UMR 6457, IN2P3/IMT Atlantique/Université de Nantes, Nantes, France*

<sup>2</sup>*CEISAM, UMR 6230, Université de Nantes, Nantes, France*

<sup>3</sup>*LCT, UMR 7616, Sorbonne Universités, UPMC Université Paris 06, Paris, France*

Among the chemical bond descriptors that have been defined in the framework of multiconfigurational calculations, the Effective Bond Order (EBO) model, that can be considered as a generalization of the formal bond order concept, has been widely used during the last decade for studying chemical bonds in transition metal complexes and clusters, as well as in heavy-element systems [1]. Furthermore, two-step spin-orbit configuration interaction (SOC) methods enable to account for the influence of spin-orbit coupling (SOC) on this quantity [2, 3]. However, so far very little has been said about the reliability of reported EBO values. Since the set of natural orbitals produced by complete active space self-consistent field (CASSCF) calculations is not unique, different CI coefficients can be obtained, leading to arbitrary EBOs. In this work, we first show how rotations of the CASSCF active orbitals matter for the calculation of EBOs and then we also present the application of two different criteria to guide orbital rotations to define unbiased EBOs. Astatine compounds such as At<sub>2</sub>, AtI and AtBr are considered as our case studies where the role of SOC on the chemical bonds of these systems is highlighted. Additionally, our extension of Quantum Chemical Topology (QCT) analysis [4] to SOC calculations wavefunctions allows for the very first time the description of these bonds in terms of indicators coming from two different perspectives, *i.e.* molecular orbital theory and QCT, at this relativistic and multiconfigurational level.

- [1] B. O. Roos, A. C. Borin, L. Gagliardi, *Angew. Chem. Int. Ed.* **46**, 1469 (2007).
- [2] F. Gendron, B. Le Guennic, J. Autschbach, *Inorg. Chem.* **53**, 13174 (2014).
- [3] R. Maurice, F. Réal, A. S. P. Gomes, V. Vallet, G. Montavon, N. Galland, *J. Chem. Phys.* **142**, 094305 (2015).
- [4] J. Pilmé, E. Renault, F. Bassal, M. Amaouch, G. Montavon, N. Galland, *J. Chem. Theory Comput.* **10**, 4830 (2014).

## Tensor decomposition methods for correlated electron pairs

Airi Kawasaki<sup>1</sup>, Osamu Sugino<sup>1</sup>

<sup>1</sup>*The Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba, Japan*

The problem of strongly correlated electrons is one of the most challenging themes of computational science. It requires us to go beyond the perturbative approaches based on Hartree-Fock (HF) or conventional density functional theories, but our progress is far from satisfactory. As a step forward, we focus on the antisymmetrized geminal power (AGP) theory, which is closely related to the BCS theory of superconductors and the GCM theory of nuclear physics, and develop a computational method for treating interacting geminals as an extension of our previous work [1].

AGP is a mean field theory of electron pairs, or geminals, and is alternatively called as HF-Bogoliubov theory where intra-pair correlation is accurately treated. To treat the inter-pair correlation as well, we prepare several geminals of the form

$$\sum_{ab}^M F_{ab}[i] c_a^\dagger c_b^\dagger \equiv \hat{F}[i], \quad (1)$$

where  $M$  is the number of orbitals and  $F_{ab}[i]$  with  $i = 1, 2, \dots$  is an antisymmetric matrix, and construct the trial wave function by using a polynomial,  $p$ , of the geminals as

$$|\Psi\rangle = p(\hat{F}[1], \hat{F}[2], \dots) |0\rangle. \quad (2)$$

We then formulated successfully a variational method to obtain the total energy with use of formulae developed in the GCM theory and the tensor decomposition methods of mathematics, although the trial wave function has previously been considered numerically intractable. In this presentation, we will show how variationally accurate total energy can be obtained using different set of polynomials taking a simple Hubbard model and a single impurity Anderson model. We note that the method has so far been formulated without intentional approximation except for the form of the trial wave function: The calculation then scales exponentially with the system size, requiring us to develop methods of approximation.



## **Analytical Stress Tensor with Density Fitting and Continuous Fast Multipole Methods**

**Martin Becker, Marek Sierka**

*Otto Schott Institute of Materials Research, Friedrich Schiller University of Jena,  
Löbdergraben 32, 07743 Jena, Germany*

The stress tensor represents the derivatives of the energy of a periodic system with respect to the strain tensor components. It plays an essential role for structure optimisations and molecular dynamics simulations that involve both atomic positions and lattice parameters. Therefore its efficient evaluation is of particular interest. Our implementation of the analytical stress tensor is realized within the framework of Kohn-Sham density functional theory using Gaussian-type orbitals as basis functions. Its key component is the efficient calculation of the Coulomb contribution by combining density fitting approximation and continuous fast multipole method. [1] For the exchange-correlation part the hierarchical numerical integration scheme is adopted. [2] For various periodic model systems the computational efficiency and favorable scaling behavior of the stress tensor implementation are demonstrated. The overall computational effort of the stress tensor calculation is comparable to that of the Kohn-Sham matrix formation.

- [1] R. Lazarski, A.M. Burow, M. Sierka, *J. Chem. Theory Comput.* **36**, 3029 (2015).
- [2] A.M. Burow, M. Sierka, *J. Chem. Theory Comput.* **7**, 3097 (2011).

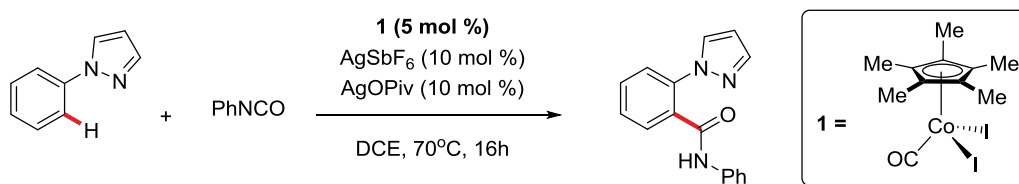
## Computational studies into the mechanism of cobalt-catalysed carboxylate-assisted C-H activation

Samuel. E. Neale\* and Stuart. A. Macgregor

*Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS*

Carboxylate assisted C-H activation has received considerable attention within the field of transition-metal catalysis.[1] Until relatively recently the dominant transition metals that facilitate these reactions have been restricted to Rh, Ir, Pd and Ru. Over the last few years there has been an increase in reports in which first row transition metals are successfully employed, and unlike the second/third row systems, mechanistic insight into these systems is less defined. One crucial property of first-row transition metal complexes that also presents a challenge in mechanistic investigations is the potential for accessibility of higher spin-states along the proposed catalytic pathway.

A cobalt-catalysed aryl and alkenyl aminocarbonylation developed by the Ackermann group was chosen for investigation by density functional theory.[2] In particular the proposed AMLA/CMD (ambiphilic metal-ligand activation / concerted metalation-deprotonation) mechanism was investigated with different levels of theory, including a range of different functionals and higher-level DLPNO-CCSD(T) calculations.[3]



**Scheme 1.** Co(III)-catalyzed aryl aminocarbonylation.[2]

A mechanism for the overall catalytic cycle was characterized and found to be in agreement with experiment, with reversible C-H activation and rate-determining nucleophilic attack on the bound isocyanate. The testing of various different functionals on the AMLA/CMD pathway across the three potentially viable spin states ( $^1[\text{Co}]$ ,  $^3[\text{Co}]$  and  $^5[\text{Co}]$ ) outlined a sensitivity of spin-state energetics, particularly dependent on the admixture of Hartree-Fock exchange, demonstrating the importance of careful consideration in selecting an appropriate computational method.

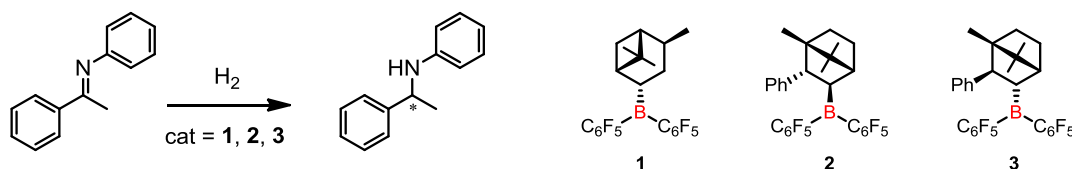
- [1] D. L. Davies, S. A. Macgregor, C. L. McMullin, *Chem. Rev.* (2015)
- [2] J. Li, L. Ackermann, *Angew. Chem., Int. Ed.* **54**, 8551 (2015).
- [3] M. Sparta, F. Neese, *Chem. Soc. Rev.* **43**, 5032 (2014).

## On the Origin of Stereoselectivity in FLP-Catalyzed Asymmetric Hydrogenation of Imines

Andrea Hamza, Imre Pápai

*Institute of Organic Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar tudósok körútja 2., 1117 Budapest, Hungary*

Enantioselective hydrogenation of imines with H<sub>2</sub> using frustrated Lewis pairs (FLPs) as catalysts is considered as a promising strategy to develop metal-free methods to synthesize chiral amines [1,2]. Most of the efforts along these lines have focused on design of chiral boranes [3,4,5], but tweezer-like aminoboranes have shown to be efficient catalysts as well [6,7]. With the aim at establishing a clear understanding of the enantioselectivity determining factors in these reactions, we initiated computational studies for reactions shown below.



Transition states of the stereoselectivity determining hydride-transfer step have been identified and analyzed [8]. We find that a “pocket-type” arrangement of the catalyst – that is different from the X-ray structure – provides multiple contacts ready for attractive interactions with the approaching iminium ion. The experimental enantioselectivity ratios are quantitatively reproduced by our computations. In addition, alterations to the boranes are proposed in order to improve the stereoselectivity.

- [1] X. Feng, H. Du, *Tetrahedron Letters* **55**, 6959 (2014)
- [2] L. Shi, Y.-G. Zhou, *ChemCatChem* **7**, 54 (2015)
- [3] D. Chen, Y. Wang, J. Klankermayer, *Angew. Chem. Int. Ed.* **49**, 9475 (2010)
- [4] G. Ghattas, D. Chen, F. Pan, J. Klankermayer, *Dalton Trans.* **41**, 9026 (2012)
- [5] Y. Liu, H. Du, *J. Am. Chem. Soc.* **135**, 6810 (2013)
- [6] V. Sumerin, K. Chernichenko, M. Nieger, M. Leskelä, B. Rieger, T. Repo, *Adv. Synth. Catal.* **353**, 2093 (2011)
- [7] M. Lindqvist, K. Borre, K. Axenov, B. Kótai, M. Nieger, M. Leskelä, I. Pápai, T. Repo, *J. Am. Chem. Soc.* **137**, 4038 (2015)
- [8] A. Hamza, I. Pápai, *Manuscript in preparation*

## Theoretical Investigation of a Cloke-Wilson Rearrangement of VCP with a Photoactive Fe-Nitrosyl-Catalyst

Florian Bauer<sup>1</sup>, Andreas Köhn<sup>1</sup>

<sup>1</sup>*Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany*

It is known that  $\text{Fe}[(\text{CO})_3\text{NO}]^-$  is catalytically active in the Cloke-Wilson rearrangement of a vinylcyclopropane derivative (VCP) forming a dihydro-vinylfuran derivative. The reaction occurs under thermal and photochemical conditions [1]. The mechanisms under thermal conditions were investigated by means of DFT [2].

In this work the mechanism of the photochemical reaction, where the catalyst is in its lowest triplet state is described. To this end different DFT-D3 methods were used. Also the conductor-like screening model (COSMO) was employed to account for the solvent, which is important for this anionic system. The photochemical reaction features  $\eta^2$ - and  $\eta^3$ -bonds between the iron center and the organic substrates, thereby lowering the activation energy of the reaction. In agreement with [2] natural population analysis shows that the iron center is neutrally charged for the excited catalyst species as well.

Different VCP-derivatives were considered - created by swapping one electron withdrawing group, methylating at the vinyl group or at the cyclopropane ring - and the reaction rates were calculated using transition state theory. The calculated results for both the thermal and the photochemical reaction partially agree with the experimental findings, although it seems the effect of additional methyl groups is overestimated by DFT.

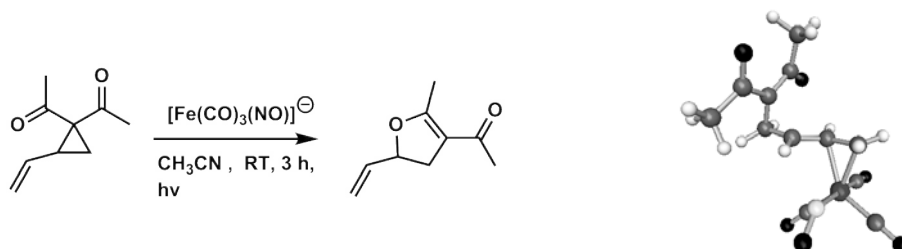


Figure 1: Overall reaction scheme (left) and ring opening transition state for the proposed triplet mechanism (right).

- [1] C. Lin, D. Pursley, J. E. M. N. Klein, J. Teske, J. A. Allen, F. Rami, A. Köhn, and B. Plietker, *Chem. Sci.* **6**, 7034 (2015).
- [2] J. E. M. N. Klein, G. Knizia, B. Miehl, J. Kästner, and B. Plietker, *Chem. Eur. J.* **20**, 7254 (2014).

## Quantum chemical conformational analyses unveil conformational flexibility of physiological (L-histidinato)(L-threoninato)copper(II) in aqueous solution

Michael Ramek<sup>1</sup>, Marijana Marković<sup>1,2</sup>, Claudia Loher<sup>1</sup>, Jasmina Sabolović<sup>2</sup>

<sup>1</sup>*Institute of Physical and Theoretical Chemistry, Graz University of Technology, Stremayrgasse 9, A-8010 Graz, Austria*

<sup>2</sup>*Institute for Medical Research and Occupational Health, Ksaverska cesta 2, P. O. Box 291, HR-10001 Zagreb, Croatia*

By now experimental studies for physiological ternary (L-histidinato)(L-threoninato)copper(II) complex in solutions did not report any firm structural information [1,2]. To complement experimental findings we performed conformational analyses for the ternary complex in the gas phase and in an implicitly modeled aqueous medium using the density functional theory (DFT) functional B3LYP [3]. 1728 initial structures, which cover the conformational space of the complex in three copper(II) coordination modes with *trans*- and *cis*-configuration, were used for geometry optimizations. The effects of intermolecular interactions on the complex properties are examined. Different energy landscapes in the gas phase and aqueous solution are obtained with much more possible aqueous conformers than vacuum conformers. Less strained structures are detected in aqueous solution than in the gas phase. While the *trans* conformers in glycine-like coordination are the most stable in vacuum, conformers in all coordination modes are predicted within 15 kJ mol<sup>-1</sup> in aqueous solution. The diversity of lowest-energy aqueous geometries with or without the intra- and inter-residual hydrogen bonds, and comparisons with the previously studied parent binary complexes bis(L-histidinato)copper(II) [4] and bis(L-threoninato)copper(II) [5] reveal a pronounced conformational flexibility of the title complex in aqueous solution. The flexibility explains previous experimental findings [1,2] on the lack of inter-residual strain and the abundance of the ternary over the parent complexes determined in aqueous solutions at physiological pH values.

Acknowledgment: This work has been supported by the Croatian Science Foundation under the project IP-2014-09-3500.

- [1] H. C. Freeman, R.-P. Martin, *J. Biol. Chem.* **24**, 4823 (1969).
- [2] O. Yamauchi, T. Sakurai, A. Nakahara, *J. Am. Chem. Soc.* **101**, 4164 (1979).
- [3] M. Ramek, M. Marković, C. Loher, J. Sabolović, *Polyhedron* (submitted).
- [4] M. Marković, M. Ramek, J. Sabolović, *Eur. J. Inorg. Chem.* 198 (2014).
- [5] M. Marković, M. Ramek, C. Loher, J. Sabolović, *Inorg. Chem.* **55**, 7694 (2016).

# Time-Dependent Quantum Description of Double Core Hole States Formation in Carbon Monoxide.

Solène Oberli<sup>1</sup>, Nicolas Sisourat<sup>1</sup>, Patricia Selles<sup>1</sup>, Stéphane Carniato<sup>1</sup>

<sup>1</sup>*Sorbonne Universités, UPMC Univ. Paris 06, CNRS, Laboratoire de Chimie Physique Matière et Rayonnement, 4 place Jussieu 75005, Paris, France*

The unprecedented radiation intensity of x-ray free electron lasers (XFELs) offers the opportunity to create double core hole (DCH) states via sequential absorption of two x-ray photons within a single pulse [1]. This x-ray two-photon process opens the way to a highly sensitive spectroscopy known as x-ray two-photon photoelectron spectroscopy (XTPPS). The theoretical description of XTPPS is challenging owing to the competition between photon absorption and electronic relaxation by Auger decay which occur at similar femtosecond timescales. In case of molecular targets, nuclear dynamics, which takes place in this timescale, complicates further the analysis. Previous studies are limited to classical rate-equation models for describing the time evolution in the different ionization channels [1,2]. In this work, we present for the first time a full quantum model to investigate DCH states formation through sequential one x-ray photon absorption. Our model includes explicitly the interaction with the pulse, the Auger decay and the nuclear dynamics. Absolute double core hole cross sections are provided using a time-dependent scheme within the local approximation [3]. The influence of the nuclear dynamics is assessed for the prototype CO molecule. Signature in double core hole photoelectron spectra of the competition between photon absorption and Auger decay is discussed. We show that DCH states formation can be actively triggered by varying the laser pulse characteristics.

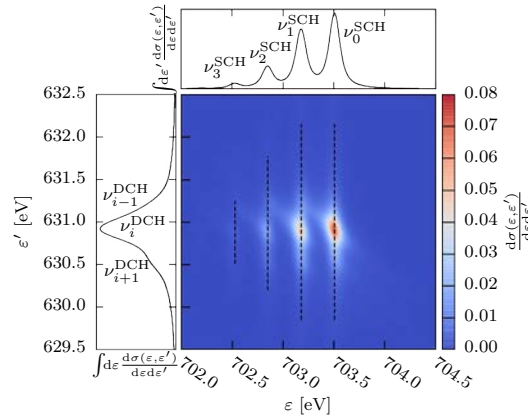


Figure 1: Photoelectron-photoelectron spectrum of the carbon single-site DCH state in CO.

- [1] R. Santra, N. V. Kryzhevoi and L. S. Cederbaum, *Phys. Rev. Lett.* **103**, 013002 (2009).
- [2] C. Buth, J.-C. Liu, M. H. Chen, J. P. Cryan, L. Fang, J. M. Glowina, M. Hoener, R. N. Coffee and N. Berrah, *J. Chem. Phys.* **136**, 214310 (2012).
- [3] E. Pahl, H.-D. Meyer and L. S. Cederbaum, *Z. Phys. D Atom. Mol. Cl.* **38**, 215 (1996).

## Characterization of PTCDA thin films and the electronic character: the dimer picture and beyond

Daniel Bellinger<sup>1</sup>, Volker Engel<sup>1</sup> and Bernd Engels<sup>1</sup>

<sup>1</sup> *Institut für Phys. und Theor. Chemie, Universität Würzburg, Emil-Fischer-Straße. 42, 97074 Würzburg, Germany*

Perylene based compounds are a promising class of materials for optoelectronic devices. The study of their optoelectronic properties by means of theoretical approaches allows gaining a deeper insight. The characteristics and the ongoing processes, which occur in thin film devices<sup>[1]</sup> are still under debate for this class of materials, especially for the PTCDA molecule.<sup>[2]</sup>

Within our approach, we use the dimer model<sup>[3]</sup> and go even beyond by inclusion of aggregate effects and by modelling the environment in the crystal surrounding using QM/MM and Continuum solvation approaches. Including different motifs and degrees of freedom in our studies, we are getting closer to the explanation of the absorption and emission spectra. In addition, polarization dependent experiments should be explainable within our calculations by a careful analysis of the coupling between different stacks within the crystal. Besides the description of the dimer on a very sophisticated level of theory (SCS-CC2) we were able to show that in fact TD-DFT ( $\omega$ B97xd) and semi-empirical computations (ZINDO) are reliable and can therefore be used to treat larger systems as well.<sup>[2b]</sup>

- [1] **a)** V. Settels, A. Schubert, M. Tafipolsky, W. Liu, V. Stehr, A. K. Topczak, J. Pflaum, C. Deibel, V. Engel, R. F. Fink, B. Engels, *Journal of the American Chemical Society* **2014**, *136*, 9327-9337; **b)** A. Schubert, V. Settels, W. Liu, F. Wuerthner, C. Meier, R. F. Fink, S. Schindlbeck, S. Lochbrunner, B. Engels, V. Engel, *Journal of Physical Chemistry Letters* **2013**, *4*, 792-796; **c)** W. Liu, V. Settels, P. H. P. Harbach, A. Dreuw, R. F. Fink, B. Engels, *Journal of Computational Chemistry* **2011**, *32*, 1971-1981.
- [2] **a)** D. Bellinger, V. Settels, W. Liu, R. F. Fink, B. Engels, *Journal of computational chemistry* **2016**, *37*, 1601-1610; **b)** D. Bellinger, J. Pflaum, C. Brüning, V. Engel, B. Engels, *Physical Chemistry Chemical Physics* **2017**, *19*, 2434-2448.
- [3] B. Engels, V. Engel, *Phys. Chem. Chem. Phys.* **2017**, *19*, 12604-12619.

## Broken-Symmetry Solutions and Magnetic Exchange Couplings from Subsystem DFT

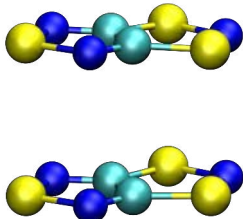
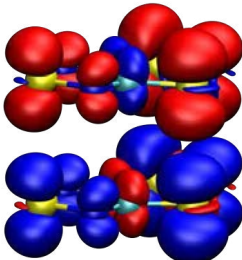
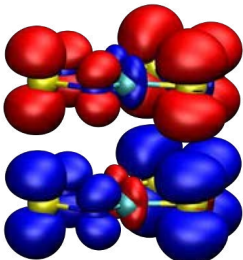
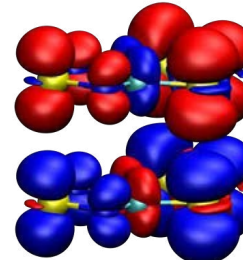
Anja Massolle<sup>1, 2</sup>, Johannes Neugebauer<sup>1, 3</sup>

<sup>1</sup>*Organisch-Chemisches Institut and Center for Multiscale Theory and Computation,  
Westfälische Wilhelms-Universität, Corrensstraße 40, Münster, Germany*

<sup>2</sup>*Email: a.massolle@uni-muenster.de*

<sup>3</sup>*Email: j.neugebauer@uni-muenster.de*

Modeling of macroscopic magnetism only from a solid-state structure is an error-prone task. Our group has recently developed a black-box approach [1] which is based on the so-called first-principles bottom-up approach [2] and qualitatively predicts and analyses the relation between a crystal structure and its magnetic properties. This method uses broken-symmetry (BS) Kohn–Sham density functional theory (KS-DFT) calculations for the prediction of magnetic coupling constants and was applied to various verdazyl radicals [1, 3].

KS-DFT Spin density		sDFT Spin density	
LDA/TZ2P	B3LYP/TZ2P	LDA/PW91k/TZ2P	B3LYP/PW91k/TZ2P
			

However, approximate KS-DFT has problems in describing polyradical systems due to the effects of the self-interaction error. Subsystem DFT (sDFT) is computationally less demanding than KS-DFT and allows to predefine the spin state for each subsystem. We demonstrate that sDFT is able to converge to BS-like states, even in cases where KS-DFT fails. We also illustrate that spin densities and exchange coupling constants calculated with sDFT are more robust than the ones obtained with BS KS-DFT, although the coupling constants appear to be systematically smaller.

- [1] T. Dresselhaus, S. Eusterwiemann, D. R. Matuschek, C. G. Daniliuc, O. Janka, R. Pöttgen, A. Studer, J. Neugebauer, *Phys. Chem. Chem. Phys.* **18**, 28262–28273 (2016).
- [2] M. Deumal, M. J. Bearpark, J. J. Novoa, M. A. Robb, *J. Phys. Chem. A* **106**, 1299–1315 (2002).
- [3] S. Eusterwiemann, T. Dresselhaus, C. Doerenkamp, O. Janka, O. Niehaus, A. Massolle, C. G. Daniliuc, H. Eckert, R. Pöttgen, J. Neugebauer, A. Studer, *Chem. Eur. J.* **23**, 6069–6082 (2017).



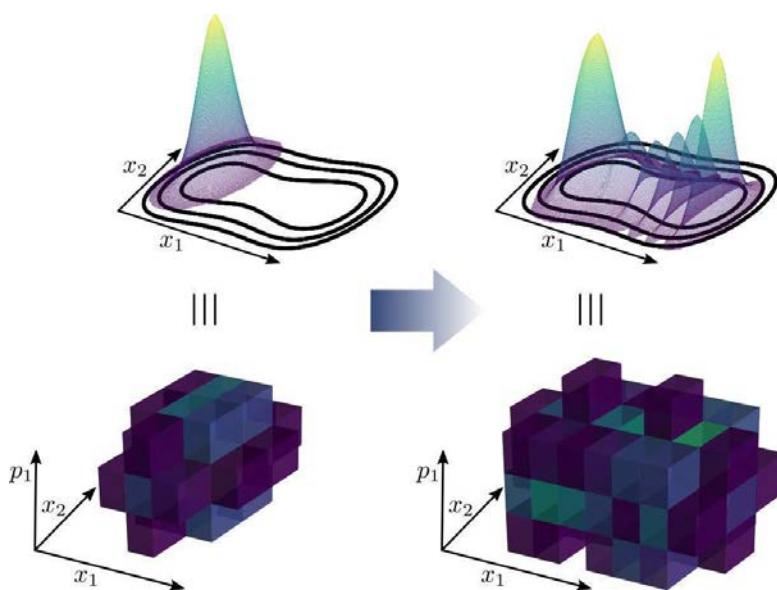
## Efficient approaches for multidimensional quantum dynamics: Dynamical pruning in phase, position and configuration space

Henrik R. Larsson<sup>1,2</sup>, Bernd Hartke<sup>1</sup>, David J. Tannor<sup>2</sup>

<sup>1</sup>*Institut für Physikalische Chemie, Christian-Albrechts-Universität, 24098 Kiel, Germany*

<sup>2</sup>*Department of Chemical Physics, Weizmann Institute of Science, 76100 Rehovot, Israel*

Widespread practical use of quantum dynamics is strongly hampered by exponential scaling with dimensionality. In part, this unfavourable scaling is due to employing many basis functions that are rarely or never used in the actual dynamics. Hence, by dynamically pruning (DP) the basis down to the actually used functions at each time step, substantial savings in computing time and memory are obtained [1, 2]. This idea has been combined with different types of basis functions [1, 3–6] in conventional quantum dynamics, resulting in speed-ups of up to 25 for nonadiabatic dynamics of six-dimensional pyrazine, without jeopardizing accuracy. Recently, DP has been combined with the multiconfiguration time-dependent Hartree method (MCTDH) [7, 8], and extended to both the primitive basis in which the single-particle functions (SPFs) are represented and the SPF configurations themselves [2]. As we illustrate for nonadiabatic 24-dimensional pyrazine, pruning the primitive basis allows for the propagation of higher-dimensional SPFs and partially lifts the sum-of-product-form requirement onto the structure of the Hamiltonian. Dynamical pruning the set of configurations (DP-MCTDH) yields significant speed-up factors between 5 and 50, making it competitive with the multilayer MCTDH method.



- [1] H. R. Larsson, B. Hartke, D. J. Tannor, *J. Chem. Phys.* **2016**, *145*, 204108.
- [2] H. R. Larsson, D. J. Tannor, arXiv:1705.02769, submitted to *J. Chem. Phys.*
- [3] A. Shimshovitz, D. J. Tannor, *Phys. Rev. Lett.* **2012**, *109*, 070402.
- [4] D. J. Tannor, N. Takemoto, A. Shimshovitz, *Adv. Chem. Phys.* **2014**, *156*, 1–34.
- [5] D. J. Tannor, S. Machnes, E. Assémat, H. R. Larsson, *Adv. Chem. Phys.* **2017**, in press.
- [6] B. Poirier, *J. Theor. Comp. Chem.* **2003**, *02*, 65–72.
- [7] M. H. Beck, A. Jäckle, G. A. Worth, H.-D. Meyer, *Phys. Rep.* **2000**, *324*, 1–105.
- [8] G. A. Worth, *J. Chem. Phys.* **2000**, *112*, 8322–8329.

## Simulation of Glycine Precursor Formation in the Interstellar Medium

Max Nepomuk Markmeyer<sup>1</sup>, Jan Meisner<sup>1</sup>, Thanja Lamberts<sup>1</sup>, Johannes Kästner<sup>1</sup>

<sup>1</sup>*Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, Stuttgart, Germany*

In the interstellar medium complex organic molecules can form even though the temperature and the density of molecules are very low. One such complex molecule is glycine, which is of special interest with respect to the origin of life.

In this project we simulated the formation of the HOCO radical, that Woon suggested as a precursor to Glycine [1]. In difference to Rimola, who investigated the HOCO formation by combination of CO and OH [2], we simulated its formation by hydrogen abstraction from formic acid (see figure 1). The reaction was simulated with different astrochemically relevant radicals (OH, NH<sub>2</sub>, hydrogen atoms).

Due to the low temperatures in the interstellar medium tunneling plays a major role for the reactions and the reaction rate constants were calculated with the instanton method.

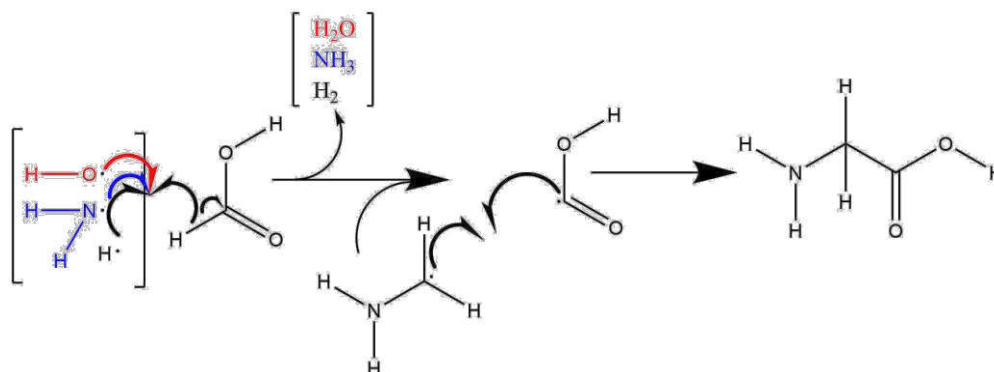


Figure 1: Reaction pathway towards glycine.

[1] D. E. Woon, *ApJ.*, **571**, 177 (2002)

[2] A. Rimola, M. Sodupe, P. Ugliengo, *ApJ.*, **754**, 24 (2012)

## Proton Loading Site in Cytochrome *c* Oxidase

Jovan Dragelj<sup>1</sup>, Ernst-Walter Knapp<sup>1</sup>

<sup>1</sup>*Department of Biology, Chemistry, Pharmacy / Institute of Chemistry and Biochemistry,  
Freie Universitaet Berlin, Fabeckstrasse 36a, Berlin, Germany*

Cytochrome *c* oxidase (CcO) is the final enzyme in the respiratory chain in mitochondria and also an integral part of the metabolism of many types of bacteria. CcO catalyzes the reduction of molecular oxygen to water and utilizes the resulting free energy to pump protons across the membrane thereby creating an electrochemical gradient. Despite intensive research, it is not understood how CcO achieves the unidirectional proton transport and avoids short circuit of the pump. Proton pumping is achieved via proton input channels, which can vary in number and role in different organisms. Here, we consider CcO from *R. sphaeroides*. [1–4]

The Proton Loading Site (PLS) in the center of CcO should have the ability to transiently store a pumped proton, by changing its pK<sub>A</sub> value depending on the redox-state of the enzyme. The identity of the PLS is still not clear. Several candidates are discussed: the propionates of heme *a*<sub>3</sub> (likely the D-propionate) [5,6] or histidine His334 coordinated to the Cu<sub>b</sub> [7] or an unspecified cluster of residues surrounding hemes. [8] The goal of this work is to provide more insight on the identity and function of PLS by focusing on the suggested candidates, by using quantum-chemical and electrostatic energy computations combined with MD simulations for estimating the corresponding pK<sub>A</sub> values.

- [1] P. Brzezinski, R.B. Gennis, *J. Bioenerg. Biomembr.*, **40**, 521–531 (2008).
- [2] V.R. Kaila, M.I. Verkhovsky, M. Wikström, *Chem. Rev.*, **110**, 7062–7081 (2010).
- [3] A.L. Woelke, G. Galstyan, E.-W. Knapp, *Biochim. Biophys. Acta - Bioenerg.*, **1837**, 1998–2003 (2014).
- [4] A.L. Woelke, G. Galstyan, A. Galstyan, T. Meyer, J. Heberle, E. Knapp, *J. Phys. Chem. B.*, **117**, 12432–12441 (2013).
- [5] V.R.I. Kaila, V. Sharma, M. Wikström, *Biochim. Biophys. Acta - Bioenerg.*, **1807**, 80–84 (2011).
- [6] M. Sezer, A.L. Woelke, E.W. Knapp, R. Schlesinger, M.A. Mroginiski, I.M. Weidinger, *Biochim. Biophys. Acta - Bioenerg.*, **1858**, 103–108 (2017).
- [7] D.M. Popovi, A.A. Stuchebrukhov, *J. Am. Chem. Soc.*, **126**, 1858–1871 (2004).
- [8] J. Lu, M.R. Gunner, *PNAS*, **111**, 12414–12419 (2014).

## TDDFT-Based Protocol with Local Hybrid Functionals for the Screening of Potential Singlet Fission Chromophores

Robin Grotjahn<sup>1</sup>, Toni M. Maier<sup>1</sup>, Josef Michl<sup>2,3</sup>, Martin Kaupp<sup>1</sup>

<sup>1</sup>*Institut für Chemie, Theoretische Chemie/Quantenchemie, Sekr. C7, Technische Universität Berlin, Straße des 17. Juni 135, D-10623, Berlin, Germany*

<sup>2</sup>*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, 16110 Prague 6, Czech Republic*

<sup>3</sup>*Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215, United States*

In the singlet fission process, parts of the excitation energy of a chromophore in its  $S_1$  state are transferred to a neighboring chromophore in its  $S_0$  ground state, yielding both chromophores in their  $T_1$  state. Exploitation of the singlet fission process allows in principle the design of dye-sensitized solar cells (DSSC) exhibiting an efficiency beyond the Shockley-Queisser limit of 32%. For that purpose, it is crucial that the chromophore exhibits specific requirements regarding the relative energies of its  $S_0$ ,  $S_1$ ,  $T_1$  (and  $T_2$ ,  $S_2$ ) electronic states.

Accurate quantum-chemical computations of the corresponding excitation energies are thus highly desirable. Due to its favorable cost-performance ratio, density functional theory (DFT) is the method of choice for the treatment of large systems. Here we use a set of potential singlet-fission chromophores [1] to evaluate a variety of DFT-based methods, with an emphasis on local hybrid functionals with position-dependent exact-exchange admixture.[2] New reference CC2/CBS vertical excitation energies for the test set have been calculated, which exhibit somewhat more uniform accuracy than the previous CASPT2-based data. The new reference data have been used to evaluate a wide range of functionals, comparing full linear response TDDFT, the Tamm-Dancoff approximation (TDA), and  $\Delta$ SCF calculations.

The overall best accuracy is provided by two simple two-parameter local hybrid functionals and the more empirical M06-2X global meta-GGA hybrid. Due to its lower empirism and wide applicability, the *Lh12ct*-SsifPW92 local hybrid [3] is employed in the suggested computational protocol for the prediction of the relevant excitation energies in singlet-fission chromophores. While full linear response TDDFT is used for the  $S_1$ ,  $S_2$ , and  $T_2$  excitations,  $\Delta$ SCF is preferred for  $T_1$  excitations. When some error compensation with suitable DFT-optimized structures is exploited, even the most critical  $T_1$  excitations can be brought close to the desired accuracy of 0.20 eV, while the other excitation energies are obtained even more accurately. This fully DFT-based protocol should become a useful tool in the field of singlet fission.

[1] J. Wen, Z. Havlas, J. Michl, *J. Am. Chem. Soc.* **137**, 165 (2015).

[2] J. Jaramillo, G. E. Scuseria, *J. Chem. Phys.* **118** 1068 (2003).

[3] A. V. Arbuznikov, M. Kaupp, *J. Chem. Phys.* **136** 014111 (2012).

## Protonation effects on the multi-photoelectron storage capacity of a series of novel black absorbers

**Philipp Traber<sup>1</sup>, Jean-François Lefebvre<sup>2,3</sup>, Stephan Kupfer<sup>1</sup>, Ying Zhang<sup>1,4</sup>, Benjamin Dietzek<sup>1,4</sup>, Murielle Chavarot-Kerlidou<sup>3</sup>, Stefanie Gräfe<sup>1</sup>**

<sup>1</sup>*Institute for Physical Chemistry and Abbe Center of Photonics, Friedrich Schiller University Jena, Germany*

<sup>2</sup>*Département de Molecular Pharmacochimie, University Grenoble Alpes, France*

<sup>3</sup>*Chemistry and Biology of Metals laboratory, University Grenoble Alpes, France*

<sup>4</sup>*Leibniz Institute of Photonic Technology Jena, Germany*

The need for sustainable and clean energy is more important than ever, for which sunlight is a very promising source. Therefore newly synthesized poly-*N*-heterocyclic Ruthenium dyes [1] (see figure 1), related to bent complexes by MacDonnell et al. [2, 3, 4], are investigated which shall harvest light efficiently in (dye-sensitized) solar cells. MacDonnell's bent structures are advantageous due to their reduction and electron storage properties. [4]



Figure 1: Synthesized Ruthenium complexes of Chavarot-Kerlidou et al. [1]

To gain insights on the ground state as well as the excited state properties upon (multi-)photo-activation (TD-)DFT, UV-vis and Resonance Raman studies have been performed. Alike, the pH-dependency of photo-induced intermediates has been studied by a spectro-electrochemical approach. The results show that the multi-charge transfer character is highly influenced by the substitution pattern.

- [1] J.-F. Lefebvre, D. Saadallah, P. Traber, S. Kupfer, S. Gräfe, B. Dietzek, I. Baussanne, J. de Winter, P. Gerbaux, C. Moucheron, M. Chavarot-Kerlidou, M. Demeunynck, *Dalton Trans.*, **45**, 16298 (2016)
- [2] R. Konduri, H. Ye, F. M. MacDonnell, S. Serroni, S. Campagna, K. Rajeshwar, *Angew. Chem. Int. Ed.* **41**, 3185 (2002).
- [3] K. L. Wouters, N. R. de Tacconi, R. Konduri, R. O. Lezna, F. M. MacDonnell, *Photosynth. Res.*, **87**, 41 (2006)
- [4] S. Singh, N. R. de Tacconi, N. Diaz, R. O. Lezna, J. M. Zuñiga, K. Abayan, F. M. MacDonnell, *Inorg. Chem.*, **50**, 9318 (2011)

## Metastability of the low-lying electronic states of $\text{CBr}^{2+}$ : A CASSCF/MRCI study

Igor Araújo Lins<sup>1</sup>, Antonio Ricardo Belinassi<sup>2</sup>, Fernando Rei Ornellas<sup>2</sup>, Tiago Vinicius Alves<sup>1</sup>

<sup>1</sup>*Departamento de Físico-Química, Instituto de Química, Universidade Federal da Bahia, Salvador, 40170-115, Brazil*

<sup>2</sup>*Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748, São Paulo, São Paulo, 05508-900, Brazil*

Spectroscopic data for the low-lying electronic states of the doubly ionized cation,  $\text{CBr}^{2+}$ , are scarce due to the inherent difficulties related to the preparation and detection of this highly reactive ion. To the best of our knowledge, the only experimental evidence of this dication was reported in 1982 by Proctor *et al.* [1], who demonstrated by charge stripping mass spectrometry the existence of this species. In this context, the aim of this work is to present a reliable characterization of the metastability, structure, and spectroscopy of the low-lying electronic states of  $\text{CBr}^{2+}$  thus extending our present knowledge of the halocarbon dications. For this purpose, the low-lying electronic states of  $\text{CBr}^{2+}$  correlating with the two lowest dissociation channels was investigated at a high level theoretical approach, SA-CASSCF/MRCI. Spin-orbit interaction changes substantially the profile of the potential energy curves, specially for the ground ( $X^2\Sigma^+$ ) and first excited ( $1^2\Pi$ ) states. The second adiabatic ionization energies are also determined and show an excellent agreement with the experimental derived values. Tunneling widths computed for the  $\Omega$  bound states show that the lowest vibrational levels of components  $1/2$  are stable against tunneling.

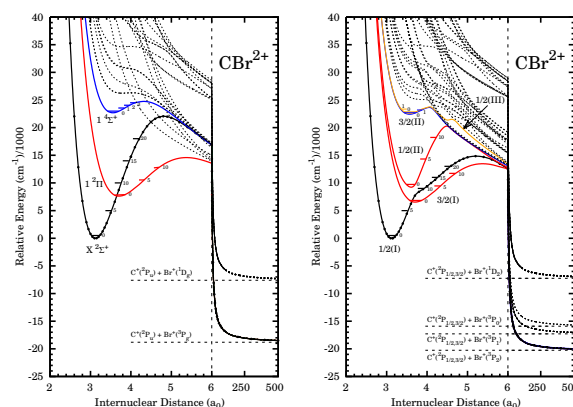


Figure 1: Potential energy curves for the lowest-lying doublet and quartet ( $\Lambda+S$  and  $\Omega$ ) states

[1] C. Proctor, C. Porter, T. Ast, J. Beynon *Int. J. Mass Spectrom.* **41**, 251 (1982).

## Treatment of molecular Feshbach resonances in equation-of-motion coupled-cluster theory

Thomas-Christian Jagau<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of Munich (LMU), D-81377 Munich, Germany*

Temporary anions play an important role in various areas of physics, chemistry, and biology as they can act as doorway states opening new reaction channels that are inaccessible in the corresponding neutral species [1]. The theoretical treatment of temporary anions is difficult since they are embedded in the continuum and cannot be associated with discrete eigenstates in the Hermitian domain of the Hamiltonian. An elegant treatment is, however, possible in non-Hermitian quantum mechanics in the form of electronic resonance states with complex energy, for example, using complex absorbing potentials (CAPs) [2].

Depending on their electronic structure, temporary anions can be classified as either shape or Feshbach resonances [1]. A shape resonance is located above its parent state and decays by a one-electron process. In contrast, a Feshbach resonance is located below its parent state but above another detachment threshold. Its decay is a two-electron process and governed by electron correlation.

Shape resonances can be described with good numerical accuracy using the CAP-augmented equation-of-motion coupled-cluster singles and doubles method (CAP-EOM-CCSD) [3]. However, similarly to doubly excited bound states, Feshbach resonances are placed several electron volts too high in energy, i.e., above their parent state, within the EOM-CCSD approximation and acquire spurious shape-resonance character.

In this study, several approaches that include triples excitations in an approximate manner in the EOM-CC ansatz are applied to molecular Feshbach resonances. We find that methods that correct the EOM-CCSD energies in an *ad hoc* manner do not improve upon EOM-CCSD and still place the resonance and its decay channels in the wrong energetic order. In contrast, the EOM-CCSD(T)(a)\* method [4] in which the similarity-transformed Hamiltonian is built up from CCSD amplitudes that have been corrected for triples excitations yields the correct energetic order. Our results indicate that CAP-EOM-CCSD(T)(a)\* describes Feshbach resonances of small molecules with excellent accuracy and may become the method of choice for such electronic states.

- [1] T.-C. Jagau, K.B. Bravaya, A.I. Krylov, *Annu. Rev. Phys. Chem.* **68**, 525 (2017).
- [2] U.V. Riss, H.-D. Meyer, *J. Phys. B* **26**, 4503 (1993).
- [3] D. Zuev, T.-C. Jagau, K.B. Bravaya, E. Epifanovsky, Y. Shao, E. Sundstrom, M. Head-Gordon, A.I. Krylov, *J. Chem. Phys.* **141**, 024102 (2014).
- [4] D.A. Matthews, J.F. Stanton, *J. Chem. Phys.* **145**, 124102 (2016).

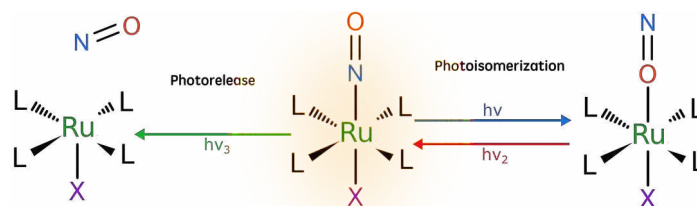
## AB INITIO INVESTIGATION OF $\text{trans-}[\text{RuCl}(\text{NO})(\text{py})_4]^{2+}$ PHOTOCHEMISTRY

**Francesco Talotta,<sup>1,2</sup> Leticia Gonzalez<sup>2</sup>, Martial Boggio-Pasqua<sup>1</sup>**

<sup>1</sup>*Laboratoire de Chimie et Physique Quantiques, Université Paul Sabatier – Bât. 3R1b4  
118 route de Narbonne, 31400 Toulouse, France*

<sup>2</sup>*Istitut für Chemie, Universität Wien, Währinger tr. 17, 1090 Vienna, Austria*

Ruthenium nitrosyl complexes have found utility in a variety of applications, such as optical switches, data storage, and medicine. Depending on the ancillary ligands, environment, and irradiation wavelength, these complexes can undergo either intramolecular NO linkage photoisomerization or NO photorelease (Figure 1). In the last two years, DFT studies of both the NO linkage photoisomerization and photorelease process in the  $\text{trans-}[\text{RuCl}(\text{NO})(\text{py})_4]^{2+}$  complex revealed a complex two-step photoisomerization mechanism involving a sequential two-photon absorption.[1,2] This mechanistic picture has been confirmed experimentally recently.[3] The DFT study was based on the exploration of the lowest singlet and triplet potential energy surfaces, assuming efficient decay via intersystem crossing (ISC) from the first singlet excited state to the lowest triplet state. It would therefore be desirable to verify this hypothesis by determining the possible pathways for ISC along with the spin-orbit couplings responsible for such radiationless transitions. In addition, the role of other excited states has not been investigated so far and it is interesting to know what are their potential roles in the photoisomerization mechanism. It is important to verify that a single-configuration-based method such as DFT can be reliable to describe complex photochemical mechanisms such as the ones studied here.[4] Thus, in my poster I will present the results of accurate ab initio calculations using MS-CASPT2 methods on the  $\text{trans-}[\text{RuCl}(\text{NO})(\text{py})_4]^{2+}$  complex that describe i) the absorption spectra of the involved isomers ii) the main ISC pathway after initial photoexcitation iii) the photoisomerization pathways. A critical assessment of the DFT and TD-DFT results will be made.



- [1] J. S. García *et al.*, *J. Mol. Model.* **11**, 284 (2016).
- [2] J. S. García *et al.*, *Inorg. Chem.* **54**, 8310 (2015).
- [3] L. Khadeeva *et al.*, *Inorg. Chem.* **55**, 4117 (2016).
- [4] M. G. Delcey *et al.*, *J. Chem. Phys.* **140**, 174103 (2014).

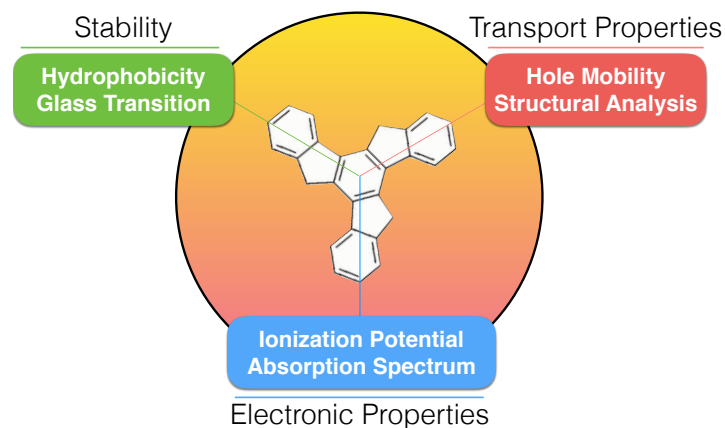


## A Rising Star: Truxene as a Promising Hole Transport Material in Perovskite Solar Cells

Kun-Han Lin, Antonio Prlj and Clémence Corminboeuf

*Laboratory for Computational Molecular Design, Institute of Chemical Sciences and Engineering, Ecole polytechnique fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.*

Within only five years, the power conversion efficiency of perovskite solar cell (PSC) has soared to 22.1% [1]. Among recently proposed high-performance PSCs, hole transport layers are proved to be essential components for the devices [2]. Truxene and its derivatives have been extensively employed for various applications and are considered to be promising dopant-free hole transport materials (HTMs) in perovskite solar cells [3]. Yet, a systematic exploration of their performance for this specific application remain lacking. In our work, multiscale simulations are used to investigate the key structure-property relationships of truxene derivatives featuring distinct variations to the parent core. Specifically, the role of heteroatoms, alkyl chains, and substitution site on the most relevant electronic, transport, and stability properties to high performing PSCs are assessed. Our findings demonstrate that each of the considered truxenes are potential alternatives to the current state-of-the-art HTM Spiro-OMeTAD.



- [1] <http://www.nrel.gov>, accessed: June, 2017.
- [2] E. J. Juarez-Perez, M. Wußler, F. Fabregat-Santiago, K. Lakus-Wollny, E. Mankel, T. Mayer, W. Jaegermann and I. Mora-Sero, *J. Phys. Chem. Lett.*, **5**, 2014.
- [3] F. Goubard and F. Dumur, *RSC Adv.*, **5**, 2015.

## Analytical first derivatives for DLPNO-MP2

Peter Pinski, Frank Neese

*Max Planck Institute for Chemical Energy Conversion,  
Stiftstr. 34-36, 45470 Mülheim an der Ruhr, Germany*

Conventional electron correlation approaches exhibit a steep increase of the computational effort with the number of electrons and basis functions involved in the calculation. In order to reduce the scaling of these accurate methods with system size, local correlation approaches have been developed over the past few decades.[1] More recently, the concepts of pair natural orbitals (PNOs)[2,3] were combined with the domain approximation and pair screening criteria. With the resulting Domain Local Pair Natural Orbital (DLPNO) methodology, linear scaling implementations of methods such as Coupled Cluster or MP2 could be developed.[4,5] They permit energy calculations on systems containing up to several hundred atoms to be performed using conventional cluster hardware, while reproducing energy differences of their respective canonical parent methods to within chemical accuracy.

Analytical gradients were implemented in the past for domain-based local correlation methods.[6] Taking derivatives of PNO-based methods demands additional scrutiny, not only because they lack invariance to unitary transformations among occupied orbitals, but also because the response of PNOs to external perturbations needs to be considered beyond the relaxation of MOs. We present the implementation and performance of exact analytical first derivatives for the DLPNO-MP2 method. Even though the relaxation of PNOs accounts for a moderate contribution to the overall computational cost, we also investigate the accuracy of more approximate schemes, which neglect derivative contributions.

- [1] P. Pulay, *Chem. Phys. Lett.* **100**, 151 (1983).
- [2] W. Meyer, *J. Chem. Phys.* **58**, 1017 (1973).
- [3] F. Neese, F. Wennmohs, A. Hansen, *J. Chem. Phys.* **130**, 114108 (2009).
- [4] C. Riplinger, F. Neese, *J. Chem. Phys.* **138**, 034106 (2013).
- [5] P. Pinski, C. Riplinger, E.F. Valeev, F. Neese, *J. Chem. Phys.* **143**, 034108 (2015).
- [6] A. El Azhary, G. Rauhut, P. Pulay, H.-J. Werner, *J. Chem. Phys.* **108**, 5185 (1998).



**Multiconfigurational ab initio and DFT study of metal-metal bonded diruthenium mixed valence complexes.**

**Luís Henrique F. de Moraes, Guilherme Menegon Arantes, Denise de Oliveira Silva.**

*Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748, 05508-000, São Paulo, Brazil*

Metal-metal multiply bonded diruthenium compounds bearing a mixed valence  $\text{Ru}_2^{5+}$  core tetracoordinated to carboxylates have received much attention because of their unique electronic, magnetic and biological properties [1-3]. The compounds have a typical  $[\text{Ru}_2(\text{O}_2\text{CR})_4]$  paddlewheel geometrical arrangement in which the four equatorially bridged carboxylate ligands stabilize the Ru-Ru bonds. The axial positions are available for either an anion or a neutral molecule [1]. Although the electronic structure of this class of complexes has been studied [1], to our knowledge they have not yet been the subject of high level calculations. To gain newer insights we have employed here CASSCF and CASPT2 methods with the MOLCAS code in model complexes  $[\text{Ru}_2(\text{O}_2\text{CH})_4]^+$  and  $[\text{Ru}_2(\text{O}_2\text{CH})_4\text{Cl}_2]^-$ . The results revealed that the electronic structure shows significant multiconfigurational behavior and the quartet state has lower energy than the doublet state in both compounds. The electronic spin density is equally delocalized between the two ruthenium centers, in agreement with the mixed valence character seen in electron spin resonance (ESR) experimental data [4]. The configuration with  $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*1}$  molecular orbital occupation dominates the ground state wavefunction with approximately 80% weight. The CASPT2 results were compared with the energetics of several density functionals in order to find an efficient description of the structure and reactivity of diruthenium complexes.

- [1] M. A. S. Aquino, *Coord Chem Rev.* **248**, 1025 (2004).
- [2] L. Messori, T. Marzo, R. N. F. Sanches, Hanif Ur Rehman, D. de Oliveira Silva, and A. Merlino, *Angew. Chem. Int. Ed. Engl.* **53**, 6172 (2014).
- [3] D. de Oliveira Silva, *Anticancer. Agents Med. Chem.* **10**, 312 (2010).
- [4] F. A. Cotton, E. Pedersen, *Inorg. Chem.* **14**, 383 (1975).

## Nonadiabatic dynamics of intramolecular singlet fission in covalently linked pentacene dimers

**S. Rajagopala Reddy, Pedro B. Coto, Michael Thoss**

*Institut für Theoretische Physik und Interdisziplinäres Zentrum für Molekulare Materialien,  
Friedrich-Alexander-Universität Erlangen-Nürnberg, Staudtstraße 7/B2, Erlangen, 91058,  
Germany*

*E-mail:rajagopala.seelam@fau.de*

Singlet fission is a photophysical process that converts one singlet exciton to two triplet excitons, via formation of a singlet multiexcitonic state [1]. It has received great interest recently to increase the efficiency of photovoltaic cells beyond the Shockley-Queisser limit [2, 3]. In this contribution, we present a quantum dynamical study of intramolecular singlet fission in a series of modified pentacene dimers covalently bonded to a phenylene spacer in ortho-, meta-, and para- conformations [4]. The study employs a methodology that combines both electronic structure theory and quantum dynamical simulations. The results show that the population of the multiexcitonic state is facilitated by the existence of higher lying charge transfer states which participate in a superexchange-like way [5]. The key roles played by molecular vibrations and stacking interactions between the chromophores in the process are also discussed [5].

- [1] M. B. Smith and J. Michl, *Chem. Rev.* **110**, 6891 (2010).
- [2] M. C. Hanna and A. J. Nozik, *J. Appl. Phys.* **100**, 074510 (2006).
- [3] W. Shockley and H. J. Queisser, *J. Appl. Phys.* **32**, 510 (1961).
- [4] J. Zirzmeier, D. Lehnherr, P. B. Coto, E. T. Chernick, R. Casillas, B. Basel, M. Thoss, R. R. Tykwinski, D. M. Guldi, *Proc. Natl. Acad. Sci. (USA)* **112**, 5325 (2015).
- [5] S. R. Reddy, P. B. Coto, D. M. Guldi and M. Thoss, (Manuscript in preparation).

## Recent Developments on Local Hybrid Functionals

**Toni M. Maier<sup>1</sup>, Matthias Haasler<sup>1</sup>, Hilke Bahmann<sup>1</sup>, Alexei V. Arbuznikov<sup>1</sup>,  
Martin Kaupp<sup>1</sup>**

<sup>1</sup>*Institut für Chemie, Theoretische Chemie/Quantenchemie, Sekr. C7, Technische Universität  
Berlin, Straße des 17. Juni 135, D-10623 Berlin, Germany*

Local hybrid functionals constitute a relatively recent class of exchange-correlation (XC) functionals, which features a variable amount of exact exchange in different molecular regions regulated by the so-called local mixing function (LMF). Despite the ambiguity arising due to the local exact-exchange admixture, known as gauge problem,[1] local hybrids early showed large potential for the description of ground-state properties, such as atomization energies and barrier heights.[2] However, a reduced computational efficiency in comparison to conventional global hybrid functionals in first implementations[3] limited their wide applicability.

Here, we present some of our recent developments in the field of local hybrid functionals, with a special emphasis on new approaches to overcome the above-mentioned issues. First, we discuss the first TDDFT implementation of local hybrid functionals into the common quantum-chemical program TURBOMOLE.[4] Besides a detailed first examination of their performance for vertical excitation energies,[5] especially concerning difficult excitation classes such as charge-transfer, Rydberg and core excitations, and the application to an extended polymer model system, we highlight the high computational efficiency in comparison to a conventional global hybrid implementation, achieved by using a semi-numerical integration scheme. Besides established local hybrid functionals, we also evaluate the performance of a new local hybrid employing a novel empirical LMF based on the reduced density Hessian. Furthermore, a universal scheme to derive semi-local and thus computationally tractable calibration (gauge) functions based on semi-local exchange functionals is presented.[1] Together with a new calibration scheme based on potential-energy curves of noble-gas dimers, we show that the influence of the gauge problem can be effectively mitigated with these new partial-integration gauge (pig) calibration functions.

- [1] T. M. Maier, M. Haasler, A. V. Arbuznikov, and M. Kaupp, *Phys. Chem. Chem. Phys.* **18**, 21133 (2016).
- [2] M. Kaupp, H. Bahmann, and A. V. Arbuznikov, *J. Chem. Phys.* **127**, 194102 (2007).
- [3] A. V. Arbuznikov, M. Kaupp, and H. Bahmann, *J. Chem. Phys.* **124**, 204102 (2006).
- [4] T. M. Maier, H. Bahmann, and M. Kaupp, *J. Chem. Theory Comput.* **11**, 4226 (2015).
- [5] T. M. Maier, H. Bahmann, A. V. Arbuznikov, and M. Kaupp, *J. Chem. Phys.* **144**, 074106 (2016).

## Lessons from the spin-polarization/spin-contamination dilemma of transition-metal hyperfine couplings for the construction of new functionals.

Caspar J. Schattenberg<sup>1</sup>, Toni M. Maier<sup>1</sup>, Martin Kaupp<sup>1</sup>

<sup>1</sup>*Institut für Chemie, Theoretische Chemie/Quantenchemie, Technische Universität Berlin  
Sekt. C7, Straße des 17. Juni 135, D-10623, Berlin, Germany*

Local hybrid functionals (LH) are a new and promising approach within the density functional framework, defined by its position-dependent admixture of exact exchange, which is governed by a local mixing function (LMF).[1] The increased flexibility was already shown to provide improved performance in the calculation of thermochemical and kinetic data,[2, 3] while ongoing research aims on further validation and development of the LH scheme, e.g. for the calculation of a variety of molecular properties.[4] The calculation of hyperfine coupling constants (HFCCs) in the non-relativistic limit hereof constitutes a promising model, as (i) HFCCs are known to be extremely sensitive to the admixture of exact exchange and may thus strongly benefit from the improved flexibility of LHs and (ii) the calculation of such first order properties provides a quick assessment of the (parameter specific) quality of the simulated electronic structure (since such first order properties are directly accessible via a simple eigenvalue equation).[5, 6] Here, the performance of different density functional approaches, including newly implemented LMFs, is compared in the calculation of metal HFCCs for different 3d transition metal complexes. Furthermore, the potential of the LH approach will be outlined in further detail by optimization of empirical LMF parameters for selected model complexes.

- [1] K. Burke, F. G. Cruz and K.-C. Lam, *J. Chem. Phys.* **109**, 8161 (1998).
- [2] A. V. Arbuznikov, H. Bahmann and M. Kaupp, *J. Chem. Phys.* **127**, 194102 (2007).
- [3] K. Theilacker, A. V. Arbuznikov, H. Bahmann and M. Kaupp, *J. Chem. Phys. A* **115**, 8890 (2011).
- [4] A. V. Arbuznikov and M. Kaupp, *J. Chem. Theory Comput.* **5**, 2985 (2009).
- [5] M. L. Munzarová and M. Kaupp, *J. Phys. Chem. A* **103**, 9966 (1999).
- [6] M. L. Munzarová and M. Kaupp, *J. Am. Chem. Soc.* **122**, 11900 (2000).

# Reactive intermediates involving group IV and VI metal centers.

## Joint UV-PES - DFT studies.

S. Labat,<sup>1</sup> E-D. Sosa-Carrizo,<sup>1</sup> K. Parker,<sup>2</sup> M. Etienne,<sup>2</sup> J.-M. Sotiropoulos,<sup>1</sup>  
K. Miqueu<sup>1</sup>

<sup>1</sup>IPREM UMR CNRS 5254, UNIV PAU & PAYS ADOUR. Hélioparc, 2 avenue P. Angot 64053 Pau Cedex 09 (France). <sup>2</sup> LCC, UPR 824 –205 route de Narbonne, BP 44099, F-31077, Toulouse (France)

Provide information on transient species involved in mechanisms remains a challenge for the chemists. Direct observation of reaction intermediates, although highly valuable, is rare because of their intrinsically low life. This is especially true for unsaturated transition metal complexes involved in C-H bond cleavage. Common approach to study reactions in solution includes kinetic studies or chemically trapping reaction intermediates. In gas phase, UV-Photoelectron Spectroscopy (UV-PES) and mass spectroscopy (MS) coupled with Flash Vacuum Thermolysis (FVT) are appropriate techniques for the generation and identification of transient species. Joint with DFT studies, UV-PES gives further insight on the electronic structure of new compounds. Thanks to this approach, we recently characterized, by their ionization potentials, two transient terminal electrophilic phosphinidene complexes  $[RP=W(CO)_5]$  (with R= Me, Ph), from thermolysis of the corresponding 7-phosphonornbornadiene complexes after loss of dimethyl 4,5-dimethylphthalate at 160°C.[1]

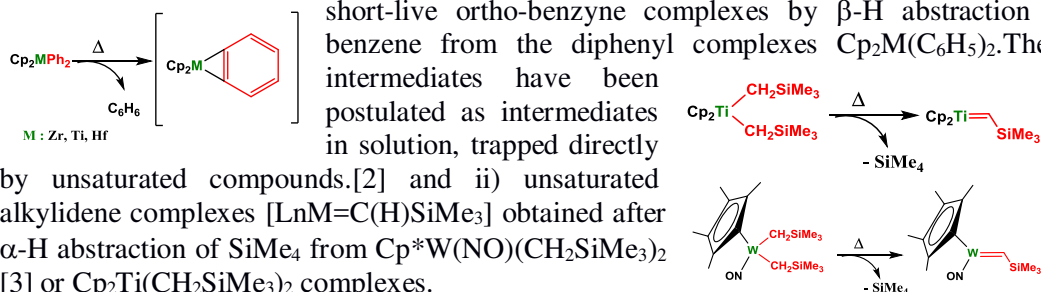
We took advantage of this original approach to characterize *in situ* in gas phase: i) short-live ortho-benzyne complexes by  $\beta$ -H abstraction of benzene from the diphenyl complexes  $Cp_2M(C_6H_5)_2$ . These intermediates have been postulated as intermediates in solution, trapped directly by unsaturated compounds.[2] and ii) unsaturated alkylidene complexes  $[LnM=C(H)SiMe_3]$  obtained after  $\alpha$ -H abstraction of  $SiMe_4$  from  $Cp^*W(NO)(CH_2SiMe_3)_2$  [3] or  $Cp_2Ti(CH_2SiMe_3)_2$  complexes.

DFT calculations allowed us : i) to confirm the formation of these transient species; ii) to assign the different ionizations on the photoelectronic spectra, which are real electronic "fingerprints" and iii) to give further insight on their electronic structure and describe the mechanism of the thermal decomposition. These results will be presented in this poster.

[1] S. Labat, K. Miqueu, J.-M. Sotiropoulos, P. Baylère, G. Pfister-Guillouzo, N-H. Tran Huy, F. Mathey, *Eur. J. Inorg. Chem.* 1694 (2014).

[2] See for example: C. B. Pamplin, P. Legzdins, *Acc. Chem. Res.*, **36**, 223 (2003).

[3] the thermal decomposition of analogue complex  $[Cp^*W(NO)(CH_2tBu)_2]$  was also study in solution and the corresponding alkylidene complex  $[Cp^*W(NO)=CHtBu]$  was postulated as intermediate and immediately chemically trapped, G. Erker, *J. Organomet. Chem.*, **134**, 189, (1977).





## Calculating Protein-Ligand Binding Affinities with the Quantum-mechanical GFN-xTB Method

Katja Ostermeir<sup>1</sup>, Andreas H. Göller<sup>2</sup>, Stefan Grimme<sup>1</sup>

<sup>1</sup>*Mulliken Center for Theoretical Chemistry, Institute for Physical and Theoretical Chemistry, University of Bonn, Bonn, 53115, Germany*

<sup>2</sup>*Bayer AG, Drug Discovery – Chemical Research, Wuppertal, 42096, Germany*

Predicting the effect of chemical modification of ligands on binding affinities is of central importance for efficient drug design and in silico improvement of ligands. The accuracy of common molecular mechanics methods depends on the underlying classical force fields with all their limitations regarding non-classical binding effects. Recently it has been shown, that QM methods are an accurate tool to calculate absolute binding free energies of supra-molecular complexes with 300-400 atoms [1]. This single structure approach has proven successful to calculate absolute binding free energies of pharmaceutically relevant systems as the blood coagulation factor Xa that had been (co-)crystallized with rivaroxaban [2]. IC<sub>50</sub> data are available for a set of 25 ligands, that share the same diversely substituted scaffold. QM calculations with protein cutouts of the binding pocket with about 1000 atoms result in absolute binding affinities, that deviate by less than 1.5 kcal/mol from experiment for 14 out of 25 ligands [3]. Here we show, that the highly efficient semi-empirical GFN-xTB method [4] represents a computationally efficient alternative to calculate relative binding affinities. It drastically speeds up calculations compared to dispersion corrected DFT, includes an implicit solvation model, provides reasonable vibrational free energy contributions, and includes all major quantum electronic effects which are absent in force fields.

[1] S. Grimme, *Chem. Eur. J.* **18**, 9955-9964 (2012).

[2] S. Roehrig, A. Straub, J. Pohlmann, T. Lampe, J. Pernerstorfer, K-H. Schlemmer, P. Reinemer, E. Perzborn, *J. Med. Chem.* **48**, 5900-5908 (2005).

[3] S. Ehrlich, A. H. Göller, S. Grimme, *ChemPhysChem.* **18**, 865-979 (2017).

[4] S. Grimme, C. Bannwarth, P. Shushkov, *J. Chem. Theory Comput.* **13**, 1989-2009 (2017).

## **Explicit description of solvent is important to predict the electronic properties of phthalocyanines derivatives?**

**Felipe C. T. Antonio<sup>1</sup>, Mateus Zanotto<sup>1</sup>, Paula Homem-de-Mello<sup>1</sup>**

*Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Av. dos Estados, 5001, Santo André, São Paulo, Brazil*

The study of electronic properties of photosensitizing compounds, in which the derivatives of porphyrins, phthalocyanines and naphthalocyanines are focused here, has attracted the interest of the academic community recently thanks to the wide range of applications as, e.g., in energy conversion for solar cells or in photodynamic therapy (PDT), the main objective of the present work. [1,2]

Computational studies of Zn(II)-Phthalocyanines (ZnPc) and Zn(II)-Naphthalocyanines (ZnNc) were carried out in order to obtain electronic properties, aiming their use as photosensitizers in PDT. For such application, electronic transition may occur in the region between 600 and 800 nm.[2,3]

An usual tool to obtain the electronic absorption spectra including solvent effects is use a continuum model. However, depending on the solvent, one or two molecules could coordinate to the central ionic metal of the macrocycles studied. Thus, we have evaluated the coordination of four different solvents: acetone, DMF (connected by nitrogen and oxygen), THF and DMSO (sulfur and oxygen bonded to the Zn(II)), to ZnPc and ZnNc, as well their derivatives tetrasubstituted with tert-butyl groups. The different coordinated systems were optimized with BLYP / 6-311G (d) and D3BJ dispersion correction.

When the solvent is explicitly described, it is possible to observe in the electronic transitions, especially for compounds coordinated to DMSO, the increasing participation of inner occupied orbitals and outermost unoccupied orbitals as well as changes in energy in which some transitions occur. Such results may indicate, albeit preliminarily, a more adequate way to describe the solvent effect in such systems.

[1] Liao, M. S.; Scheiner, S., *Journal of Computational Chemistry* 23, 15 (2002).

[2] Dougherty, T. J., *Photochemistry and Photobiology* 58, 6 (1993).

[3] Dolmans, D. E. J. G. J., Fukumura, D., Jain, R. K., *Nature Rev. Cancer* 3, 380-387 (2003).

## Oligothiophene molecules on a metal substrate: electronic response to supramolecular packing

**L. K. Scarbath-Evers<sup>1</sup>, E. Schreck<sup>2</sup>, R. Hammer<sup>2</sup>, W. Widdra<sup>2</sup>, D. Sebastiani<sup>1</sup>**

<sup>1</sup>*Institute of Chemistry, Martin Luther University Halle-Wittenberg, von-Danckelmann Platz 4, Halle, Germany*

<sup>2</sup>*Institute of Physics, Martin Luther University Halle-Wittenberg, von-Danckelmann Platz 3, Halle, Germany*

We investigate the layer-wise growth of  $\alpha$ -sexithiophene ( $\alpha$ -6T) on Au(100) combining QM/MM calculations and STM measurements. Our main focus lies on the impact of the layer morphology on the electronic properties of the  $\alpha$ -6T molecules.  $\alpha$ -6T is an organic semiconductor and serves as a model system for polythiophene which has already found application in electronic devices. An optimization of the device performance requires a fundamental understanding of the interplay between packing structure and electronic structure of the molecules. So far, research was mainly concentrated on the adsorption structure of single molecules of  $\alpha$ -6T up to one monolayer on different gold surfaces [1] and the bulk structure of  $\alpha$ -6T [2]. The packing structure of several  $\alpha$ -6T layers on gold, however, has not been investigated.

We observe a flat adsorption for the first monolayer of  $\alpha$ -6T on gold, whereas the molecules in the second layer are horizontally shifted and slightly tilted around their long molecular axis. Both, the tilt angle as well as the horizontal shift significantly alter the electronic properties of the  $\alpha$ -6T layers.

[1] M. Kiel et. al., *Phys. Rev. B* **75**, 195439 (2007).

[2] G. Horowitz et. al. *Chemistry of Materials* **7**, 1337 (1995).

## **A Materials Genome Approach to Catalysis: Transforming Waste CO<sub>2</sub> to Value-Added Products like Methanol**

**Andrew Harris<sup>1</sup>, Martin Green<sup>1</sup>**

*<sup>1</sup>Materials Measurement Lab, National Institute of Standard and Technology, 100 Bureau Drive, Gaithersburg, MD, USA*

Earth abundant metals are sought which will catalyze the reduction of carbon dioxide and carbon monoxide to simple alcohols for capture and extraction to produce value added chemicals from waste streams. First density functional theory is being used to identify potential metal catalysts (both monometallic and bimetallic) based on surface binding energies for further experimental study. Then powders of these metal catalysts will be produced by tube furnace reduction and studied by differential scanning nanocalorimetry. Using the enthalpy of desorption, binding energies can be calculated and compared to theoretical predictions. The catalytic activity will also be measured in a fixed bed catalytic reactor to elucidate correlation between binding energy and catalytic activity. All data generated will be deposited into a repository for data curation and further future study.

## Insights of the Photoredox Catalysis from a Computational Point of View

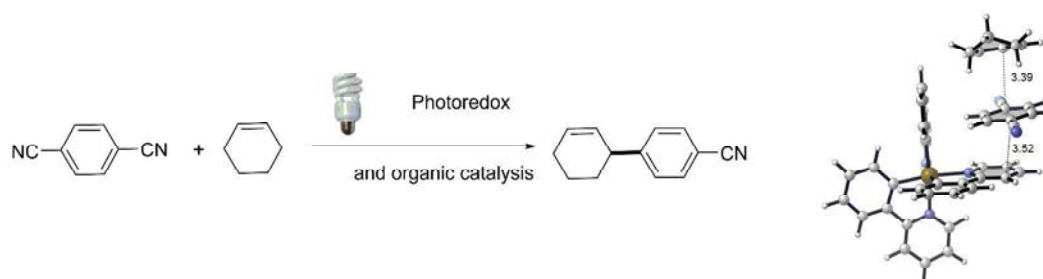
Miquel Torrent-Sucarrat,<sup>1,2,3</sup> Mikel Odriozola-Gimeno,<sup>1</sup> Ivan Rivilla,<sup>1</sup>  
Fernando P. Cossío<sup>1,2</sup>

<sup>1</sup> Department of Organic Chemistry I, Universidad del País Vasco - Euskal Herriko Unibertsitatea (UPV/EHU), Manuel Lardizabal Ibilbidea 3, 20018 Donostia, Spain.

<sup>2</sup> Donostia International Physics Center, Manuel Lardizabal Ibilbidea 4, Donostia, Spain.

<sup>3</sup> Ikerbasque, María Díaz de Haro, 3, 6º, 48013 Bilbao, Spain.

Over the last decade, visible-light-mediated photoredox catalysis has emerged as a valuable tool to generate single-electron transfer (SET) processes with organic substrates. This general strategy has also opened up a wide array of new synthetic methodologies.<sup>1</sup> For instance, MacMillan and co-workers established an elegant dual photoredox-organocatalytic platform to enable the functionalization of unactivated sp<sup>3</sup> C-H bonds.<sup>2</sup> With the aim of bringing more understanding about the crucial factors involved in these reactions, we have studied by means of DFT and TD-DFT calculations the arylation of the allylic sp<sup>3</sup> C-H bond.<sup>2c</sup> Three different reaction mechanisms associated with the electron transfer process have been considered: a) outer-sphere; b) inner-sphere; c) inside-out-sphere. From our results we conclude that the former and the latter reaction mechanisms are both feasible and complementary. Nevertheless, the inside-out-sphere scheme presents the advantage that avoids the formation of the reactive anionic radical intermediates.<sup>3</sup>



[1] a) C. K. Prier, D. A. Rankic, D. W. C. MacMillan *Chem. Rev.* **113**, 5322 (2013); b) M. H. Shaw, J. Twilton, D. W. C. MacMillan *J. Org. Chem.* **81**, 6898 (2016).

[2] a) K. Qvortrup, D. A. Rankic, D. W. C. MacMillan *J. Am. Chem. Soc.* **136**, 626 (2014); D. Hager, D. W. C. MacMillan *J. Am. Chem. Soc.* **136**, 16986 (2014); J. D. Cuthbertson, D. W. C. MacMillan *Nature* **519**, 74 (2015).

[3] M. Odriozola-Gimeno, I. Rivilla, F. P. Cossío, M. Torrent-Sucarrat *submitted*.

## Effects of relativity on the structure of metal complexed crown ethers

Meagan Oakley<sup>1</sup>, Shakiba Azimi<sup>1</sup>, Mariusz Klobukowski<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of Alberta, 11227 Saskatchewan Drive, Edmonton, Alberta, Canada*

Instruments for the detection of heavy metal ions are generally costly and require extensive sample preparation. Recent advancements in fluorescence spectroscopy resulted in sensitive detection and determination of metal ions, as well as simplicity and low-cost instrumentation. A preliminary computational study in our group offered insight into findings by Kim et al.[1] in 2008, where they found that a BODIPY appended thiacycrown ether (shown in Figure 1) showed highly selective chelation enhanced fluorescence (CHEF) in response to mercury (II). The efficiency of the crown ether as a positive fluorescent sensor for the  $\text{Hg}^{2+}$  metal ion was studied by considering other crown ether formulas with varying numbers of carbon and sulphur atoms, as well as other metal ions. Calculated absorption and emission wavelengths were done at a low-level of theory and were significantly underestimated when compared with experiment. This

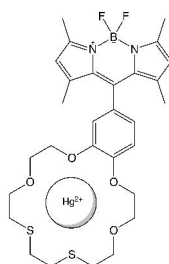


Figure 1: BODIPY appended thiacycrown ether complexed with  $\text{Hg}^{2+}$  investigated by Kim et al in 2008.

study expands previous work to include more metal cations, and choose two crown-ethers (18-crown-6 ether and thiacycrown ether). We also perform calculations at a higher-level of theory (DFT, TD-DFT for excited states) to determine why mercury (II) was preferred, and attempt to design highly selective chemosensors. For a more realistic modelling of the experimental environment, we will include solvent (COSMO) and relativistic effects (ZORA) using the Amsterdam Density Functional program. The computed energies of complexation will include thermal corrections. Excited state calculations will also be done to determine absorption and emission wavelengths.

- [1] H. J. Kim, S. H. Kim, J. H. Kim, E. Lee, K. Kim, J. S. Kim, *Bull. Korean Chem. Soc.* **29**, 1831 (2008).

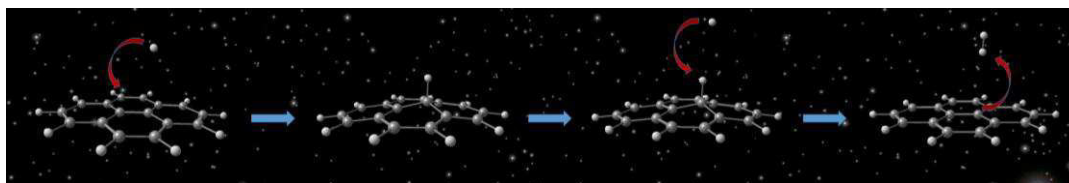
## Molecular Hydrogen formation onto PAH surface analyzed by Reaction Force and Activation Strain Model

César Barrales-Martínez<sup>1</sup>, Diego Cortés-Arriagada<sup>2</sup>, Soledad Gutiérrez-Oliva<sup>1</sup>

<sup>1</sup> *Laboratorio de Química Teórica Computacional (QTC), Departamento de Química-Física, Facultad de Química, Pontificia Universidad Católica de Chile, Av. Vicuña Mackenna 4860, Macul, Santiago, Chile.*

<sup>2</sup> *Programa Institucional de Fomento a la Investigación, Desarrollo e Innovación. Universidad Tecnológica Metropolitana. Ignacio Valdivieso 2409, P.O. Box 8940577, San Joaquín, Santiago, Chile.*

H<sub>2</sub> is the most abundant molecule in the interstellar medium (ISM) [1] however its formation process is not well characterized yet [2]. We present a DFT study of the H<sub>2</sub> formation on a polycyclic aromatic hydrocarbon (PAH) molecule via Eley-Rideal mechanism, such as see in Fig. 1. The results show that H atom adsorbs on a PAH surface overcoming an activation energy, which is different in each possible site of its surface. Moreover, the abstraction of the H adsorbed on pyrene by another H atom occurs barrierless in all sites of it, confirming that PAHs are able to act as a catalyst in the H<sub>2</sub> formation in the ISM.



**Figure 1.** H<sub>2</sub> formation on a PAH surface via Eley-Rideal mechanism.

According to perform a deep analysis of the reaction mechanism, two methodologies were used, the reaction force analysis (RFA) [3], which has been used in a related work[4], and the activation strain model [5] (ASM). From the RFA it has been found that the activation of the H chemisorption process is mainly governed by structural changes of the reactants (~70% of energy barriers) related to the H approach to surface and the distortion of it. Moreover, ASM shows that the energy barriers are dominated mostly by a repulsive interaction between reactants. On the other hand, the H abstraction by an incoming H atom, which leads to H<sub>2</sub> formation, is a barrierless process due to a high attractive interactions that begin to act at the beginning of the reaction.

**Acknowledgments:** This work was supported by FONDECYT #1141098.

### References

- [1] Herbst E. *Chem. Soc. Rev.* **30**, 168 (2001).
- [2] Vidali G. *Chem. Rev.* **113**, 8762 (2013).
- [3] Toro-Labbé A. *J. Phys. Chem. A*. **103**, 4398 (1999).
- [4] Cortés-Arriagada D. et al. *J. Chem. Phys.* **141**(13), 134701 (2014).
- [5] Bickelhaupt F. M. *J. Comput. Chem.* **20**, 114 (1999).

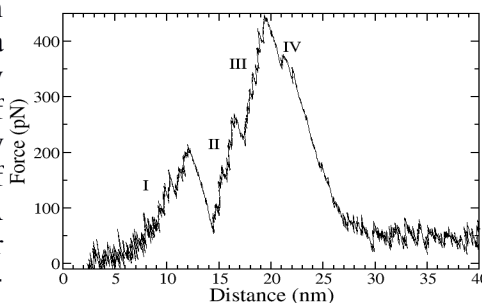
## Atomic Force Spectroscopy of Streptomycin Binding Aptamer: An Out-of-Equilibrium Molecular Dynamics Study

**Luis A. Baptista and Paulo A. Netz**

*Theoretical Chemistry Group, Physical Chemistry Department,  
Chemistry Institute, Universidade Federal do Rio Grande do Sul,  
Porto Alegre, Brazil*

One of the major goals in molecular biology is to understand the role of RNA when interacting with small molecules. Streptomycin, an aminoglycoside antibiotics, is known to target bacterial complex RNA structural domains. Several techniques have been used to understand how streptomycin is able to bind to specific RNA folding topologies. Recently, Nick and coworkers<sup>1</sup> used computer simulations and single-molecule force spectroscopy (SMFS) to study the interactions in a specific streptomycin-binding RNA (aptamer) and found that streptomycin stabilizes the RNA structure due to the formation of strong and long-lived hydrogen bonds. The purpose of this work is to investigate the interaction between RNA and streptomycin, using Langevin out-of-equilibrium (pulling) computer simulations, in order to simulate the SMFS experiment and thus obtain dynamic information about the events involved in the force-induced aptamer rupture.

After careful tuning of the Langevin simulation parameters using atomistic molecular dynamics simulations as targets, several pulling simulations were carried out for the aptamer with and without streptomycin. Figure 1 shows a typical force-extension curve (FEC) obtained by pulling simulations for shear geometry of RNA/streptomycin complex. One should identify four distinct regions: I) Exponential increase of force with the increase of end-to-end (ee) RNA distance; II and III) After a force-jump, a linear increase of force with ee distance, with a force-jump between regions II and III; and IV) A linear decrease in the force with increase of ee distance.



*Figure 1: Force-extension curve for  
RNA/streptomycin end-to-end pulling*

The microscopic events involved in the detailed regions could be clearly identified with the simulations and are: I partial elongation of the RNA molecule, maintaining the binding pocket, followed by a large force-jump (disruption of the tertiary structure); II straightening of the strands; III sliding of the strands, followed by the final (IV) rupture, where streptomycin acts like a bridge between the two strands.

The use of out-of-equilibrium computational simulations of stretching of RNA/streptomycin complex allowed us to understand the details of RNA interactions with streptomycin, showing a well defined hierarchical process, where the structures are first elongated, with subsequently lost of the aptamer tertiary structure around streptomycin and total straightening.

References:

1. Thomas A. Nick et al. *J. Phys. Chem. B* **120**, 6479 (2016)



## Modeling of oligosaccharides within glycoproteins from free-energy landscapes

Aysegül Turupcu<sup>1</sup>, Chris Oostenbrink<sup>1</sup>

<sup>1</sup>*Institute of Molecular Modeling and Simulation, University of Natural Resources and Life Sciences, Muthgasse 18, 1190 Vienna, Austria*

Glycosylation occurs on more than 50 % of the eukaryotic proteins and it is crucial to understand its effect since those macromolecules control most of the processes in living cells [1]. However, the conformations of glycans in conjugation with glycoproteins form a challenge both for experimental and theoretical methods. Their complexity is the result of the variety of possible monomeric units which are linked in a branched way and have differently populated conformational states. There is a pronounced lack of spatial information about them causing an obstacle to grasp the whole picture about their biological functions.

In this context, the solution conformations of all disaccharides constituting biologically relevant N- and O-linked glycan units are studied using the local elevation umbrella sampling method (LEUS). The first phase of this method relies on building up a memory-based biasing potential energy term which penalizes the revisiting of previously sampled conformational space [2]. A subsequent umbrella sampling phase uses this biasing potential for production simulation. The adaptable nature of the LEUS method allows modeling of the carbohydrate moiety of the glycoproteins by using biasing potentials for glycosidic linkages of all disaccharide fragments in the glycan unit and enhancing the sampling in the production phase. We first reduced the glycan complexity to the disaccharide level and identified their free-energy landscapes via their glycosidic angles ( $\phi$ ,  $\psi$ ) which possess all the relevant information about their structural properties. Then, we increased the complexity level by one and analyzed them as trisaccharides to see the effect of the consecutive linkage on the free-energy landscape of a particular glycosidic linkage. This analysis gave us the opportunity to build the whole glycan tree from their disaccharide units according to their conformational preferences. This bottom up approach allowed us to use several efficient methods to model the glycoprotein in the absence of any experimental data.

[1] A. Varki, *Glycobiology* **27**, (2017).

[2] H. S. Hansen, and P. H. Hünenberger, *J. Comput. Chem.* **31**, (2010).

## Superatomic states in nickel clusters: revising the prospects for transition metal based superatoms

James Gilmour<sup>1</sup>, Julia Schacht<sup>2</sup>, Lukas Hammerschmidt<sup>1</sup>, Nicola Gaston<sup>1</sup>

<sup>1</sup>*MacDiarmid Institute for Advanced Materials and Nanotechnology, The Department of Physics, The University of Auckland, Private Bag 92019, Auckland 1142, New Zealand*

<sup>2</sup>*School of Chemical and Physical Sciences, Victoria University of Wellington, P.O. Box 600, Wellington 6412, New Zealand*

Certain clusters of metal and metalloid atoms have attracted significant interest due to the presence of a degenerate global shell structure akin to that seen in an individual atom. Upon closure of one of these electronic subshells there is an increase in the thermodynamic stability of the clusters, which has led to the term superatom.[1, 2, 3, 4, 5]

The role that transition metals play in the existing superatom framework is not fully understood, especially when considering highly degenerate systems with large numbers of *d*-electrons. Utilising Density Functional Theory Methods we have elucidated the structure of the  $\text{Ni}_x^y$  ( $x = 5-10$ )( $y=0,\pm 1,\pm 2$ ) clusters and explored their electronic structure. From this it is shown that the local and global electronic structure of these clusters cannot be treated as if they were independent and that the effect of adding an electron to a superatomic system is more heavily contextualised than it would be for non-transition metal clusters.

- [1] W.A. De Heer, *Rev. Mod. Phys.* **65**, 611 (1993).
- [2] W.D. Knight, K. Clemenger, W.A. Deheer, W.A. Saunders, M.Y. Chou, and M.L. Cohen, *Phys. Rev. Lett.* **52**, 2141-2143 (1984).
- [3] A.W. Castleman, S.N. Khanna, A. Sen, A.C. Reber, M. Qian, K.M. Davis, S.J. Pepper-nick, A. Ugrinov and M.D. Merritt, *Nano Lett.* **7**, 2734-2741 (2007).
- [4] A.W. Castleman and S.N. Khanna, *J. Phys. Chem. C* **113**, 2664-2675 (2009).
- [5] H. Watanabe and T. Inoshita, *Optoelectron. Devices Technol* **1**, 33-39 (1986).

## **Towards a Theoretical Description of Solid State Materials Made From Superatoms and Fullerenes as Building Blocks**

**Lukas Hammerschmidt<sup>1</sup>, Nicola Gaston<sup>1</sup>**

<sup>1</sup>*MacDiarmid Institute for Advanced Materials and Nanotechnology, Department of Physics,  
University of Auckland, Auckland, New Zealand*

A major challenge in the production of nanomaterials is the control over product sizes and reproducibility. A way to circumvent these two problems could be to synthesize materials directly from nano-sized building blocks, of which so-called superatoms are one example [1, 2]. Superatoms are metal clusters of specific sizes that show an exceptional thermodynamic stability and, in a way, mimic the electronic behaviour of normal atoms. Those two features can often be explained within a simple shell model of delocalized valence electrons in an effective potential [3, 4]. Then, the striving for shell closing promotes superatoms to act as bonding partners in molecules or solid state compounds. The variety of possible structures opens a broad field of new materials with a high potential for intriguing physical properties.

Here, we present a theoretical approach towards the description of solid state compounds made from superatomic metal clusters and fullerenes. Starting from density functional theory, we work towards an effective model to obtain various physical properties. The latter can be interesting in future applications. For validity we compare to experiment where possible [5]. Hereby, the focus always lies on the applicability of the superatomic concept within solid state superatomic materials. The latter would allow to a certain extent to apply a chemical intuition for determining new materials.

- [1] X. Roy, C.-H. Lee, A. C. Crowther, C. L. Schenck, T. Besara, R. A. Lalancette, T. Siegrist, P. W. Stephens, L.E. Brus, P. Kim, M.L. Steigerwald, and C. Nuckolls, *Science* **341**, 157-160 (2013).
- [2] M. Schulz-Dobrick and M. Jansen, *Angew. Chem. Int. Ed.* **47**, 2256-2259 (2008).
- [3] W. A. deHeer, *Rev. Mod. Phys.* **65**, 611-675 (1993).
- [4] W. D. Knight, K. Clemenger, W. A. deHeer, W. A. Saunders, M. Y. Chou, and M. L. Cohen, *Phys. Rev. Lett.* **52**, 2141-2143 (1984).
- [5] L. Hammerschmidt, J. Schacht, and N. Gaston, *Phys. Chem. Chem. Phys.* **18**, 32541-32550 (2016).

## **Electronic properties of DNA: description of weak interactions and reactivity of TATA box models**

**Jorge Gutiérrez-Flores<sup>1</sup>, Estrella Ramos<sup>1</sup>, Carlos I. Mendoza<sup>1</sup>, Enrique Hernández-Lemus<sup>2</sup>**

<sup>1</sup>*Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior s/n, Ciudad Universitaria, Coyoacán, 04510, Mexico City, Mexico*

<sup>2</sup>*Computational Genomics, National Institute of Genomics Medicine, Mexico City, Mexico*

DNA is one of the most important biomolecules since it contains all the genetic information about an organism. Under normal conditions, DNA frequently adopts a B-DNA conformation whose structure and stability is mainly determined by the number and type of weak interactions. There are different kinds of weak interactions, nevertheless, it is believed that hydrogen bonds (between nitrogenous bases) and pi stacking (between base pairs) are the most relevant in DNA stability [1]. Due to its importance, several theoretical works have been made to describe these interactions, however, most of them often consider only the presence of two nitrogenous bases, having a limited overview of the participation of these in B-DNA stabilization. Therefore, in this project we describe these interactions considering the effect of length chain on the energy related to both hydrogen bonds and pi stacking, using as model TATA-box-like chains with N base pairs (with N=1 to 14) and taking into consideration two different models: ideal B-DNA and relaxed B-DNA. We found that there are more changes in hydrogen bond energies associated with the length chain than in the case of pi stacking interactions, consequently the effect of neighbors' presence is more important for hydrogen bonds. Furthermore, with our results, we estimate that hydrogen bonds participate more significantly in the DNA stabilization, nevertheless, the contribution of pi stacking is not negligible.

In addition, we are interested in the reactivity properties of DNA to explain proteins selectivity. Hence, using the information provided by Fukui functions, we make a first approximation of TATA binding protein (TBP) selectivity to TATA box, obtaining results in agreement with those reported experimentally.

The study was realized under the framework of DFT using the code DMol3 (M06-L/DN) implemented in Materials Studio.

[1] E. T. Kool, *Annu. Rev. Biophys. Biomol. Struct.* **30**, 1 (2001).

## Hydrogen adsorption and spillover mechanisms on metal-doped carbon nanohorn: Insights from DFT calculations

Chompoonut Rungnim<sup>1</sup> and Supawadee Namuangruk<sup>1</sup>

<sup>1</sup>National Nanotechnology Center, National Science and Technology Development Agency,  
Khlong Luang, Pathumthani, Thailand

The potential use of hydrogen gas as an alternative green energy has been in spotlight for many years. The challenge of this research field is to develop safe and efficient hydrogen storage for the use of hydrogen with fuel cells. Carbon nanohorn (CNH) is one of porous materials with promising hydrogen storage capability. It has been suggested that high hydrogen adsorption efficiency of the porous material relates to the migration of hydrogen atoms from metal catalyst onto the porous support called spillover mechanism.[1-4] For hydrogen adsorption on metal-doped carbon nanohorn (M-CNH), the spillover mechanism has not been clearly understood. For that reason, the aim of this work is to explore hydrogen adsorption mechanism onto M-CNH by using density functional theory calculations. The focused model in this work is platinum doped CNH or Pt-CNH. The results show that the hydrogen adsorption mechanism on Pt-CNH supports the concept of spillover mechanism. The Pt metals acts as active sites for hydrogen dissociation and then the hydrogen atoms migrate to carbon atoms of the CNH. The reactivity of carbon atoms on the CNH tip facilitates the hydrogen spillover reaction indicated by its low energy barrier and thermodynamics favorable.

[1] G.M. Psofogiannakis, G.E. Froudakis, *Chem. Commun.* **47**, 7933 (2011).

[2] D.S. Pyle, E.M. Gray, C.J. Webb, *Int. J. Hydrogen Energy*. **41**, 19098 (2016).

[3] R. Juarez-Mosqueda, A. Mavrandonakis, A.B. Kuc, L.G.M. Pettersson, T. Heine, *Front. Chem.* **3**, 1 (2015).

[4] I. López-Corral, S. Piriz, R. Faccio, A. Juan, M. Avena, *Appl. Surf. Sci.* **382**, 80 (2016).

## Using Frontier Molecular Orbital Analysis for Prediction of Regioselectivity of 1,4,5-Trisubstituted 1,2,3-Triazoles Synthesis

Nawarat Saksumolrat<sup>a</sup>, Waraporn Parasuk<sup>b</sup>, and Vudhichai Parasuk<sup>a\*</sup>

<sup>a</sup>Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

<sup>b</sup>Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand

Huisgen cycloaddition is one of the most interesting 1,3-dipolar cycloaddition that has been studied for century. Thomas *et.al.* [1] have shown that regioisomers of the product of 1,3-dipolar cycloaddition can be controlled with the regio excess (re) of 99 %. Here, we have shown that the 1,3-dipolar cycloaddition reaction could perfectly be explained by the Frontier Molecular Orbital (FMO) theory. The Klopman-Salem equation that based on FMO was used to predict the regioselectivity of seventeen 1,3-dipolar cycloaddition reactions of three reactants (aldehyde, nitroalkane, and azide), which yield 1,4,5-trisubstituted 1,2,3-triazoles according to the experiments of Thomas *et.al.* [1]. The schematic drawing of the reaction was shown in Fig.1. The calculations showed excellent agreement with the experiments and revealed insight on the regioselectivity of this 1,3 dipolar cycloaddition reaction.

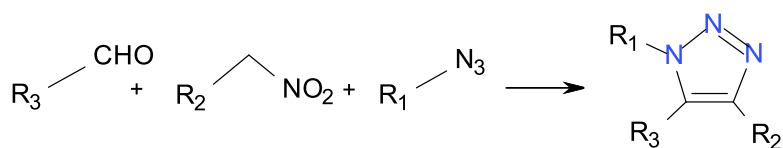


Fig. 1 Schematic drawing represents the reaction for 1,4,5-trisubstituted 1,2,3-triazoles synthesis from aldehyde, nitroalkane, and azide

[1] J. Thomas, J. John, N. Parekh, W. Dehaen *Angew. Chem. Int. Ed.* **43**, 10155-10159 (2014).

## Density-Functional Tight-Binding Parameterization for Metal-Organic Frameworks

Chien-Pin Chou<sup>1</sup>, Hiromi Nakai<sup>1-4</sup>

<sup>1</sup>*Research Institute for Science and Engineering, Waseda University, 3-4-1, Okubo, Shinjuku-ku, Tokyo 169-8555, Japan*

<sup>2</sup>*Department of Chemistry and Biochemistry, Waseda University, 3-4-1, Okubo, Shinjuku-ku, Tokyo 169-8555, Japan*

<sup>3</sup>*CREST, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan*

<sup>4</sup>*ESICB, Kyoto University, Kyotodaigaku-Katsura, Kyoto 615-8520, Japan*

Metal-organic frameworks (MOFs) are a class of crystalline materials that exhibit high potential for the carbon capture and storage (CCS) applications. MOF crystals have coordination networks consisting of the metal-containing subunits, *aka* the secondary building units (SBU), connected by organic ligand linkers. The density-functional tight-binding (DFTB) method is an approximated DFT method with careful approximations. The parameters for the DFTB method are pre-computed either directly from DFT or optimized from reference *ab initio* or DFT calculations, and stored in files, which makes the DFTB method in general three orders of magnitude faster than average DFT methods. Incorporating the divide-and-conquer (DC) technique, the time-complexity with respect to the number of atoms in DFTB can be reduced from cubic to be nearly linear[1]. The most widely used DFTB parameterization set *3ob*[2] for organic and bio-organic systems has been extensively tested and successfully applied to many applications. Recently, the *3ob* set has been extended to cover several metal elements. However, the metal parameterization in the set were not parameterized for the MOFs. Benchmarks of those parameters on the geometry of DFT-optimized MOF structures are showing significant deviations and may not be suitable for MOF-related application. The aim of this study is to create a new DFTB parameterization set, which not only refines the existing parameters in the *3ob* parameterization set, but also extends it to the other common metals in MOFs, such as Cd and Al. The automatized DFTB parameterization toolkit named ADPT[3] has been employed for the refining processes, in which extra reference data of several SBUs obtained from DFT have been included in the optimizing procedure for better metal repulsive potentials. We expect that the new parameterization for MOFs will benefit the further studies on applications involving MOFs.

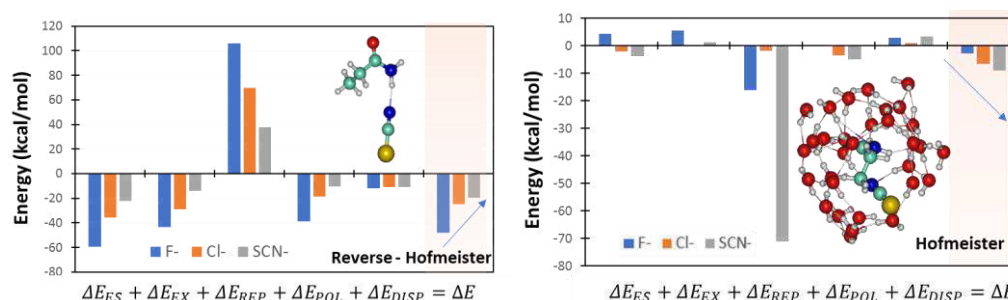
- [1] H. Nishizawa, Y. Nishimura, M. Kobayashi, S. Irle, and H. Nakai, *J. Comput. Chem.* **37**, 1983 (2016).
- [2] M. Gaus, A. Goez, and M. Elstner, *J. Chem. Theory Comput.* **9**, 338 (2013).
- [3] C.-P. Chou, Y. Nishimura, C.-C. Fan, G. Mazur, S. Irle, and H. A. Witek, *J. Chem. Theory Comput.* **12**, 53 (2016).

## Decomposing the Origin of Hofmeister Effects.

Kasimir Gregory<sup>1</sup>, Grant B. Webber<sup>1</sup>, Erica Wanless<sup>1</sup>, Alister J. Page<sup>1</sup>

<sup>1</sup>Newcastle Institute for Energy and Resources, The University of Newcastle, Callaghan, Australia

The Hofmeister series,<sup>1</sup> established in 1888, is a specific ordering of ions in terms of their effects on various biological, polymer, and electrochemical systems. It characterises cations and anions as either kosmotropic (which bring order to the solution) or chaotropic (which disrupt order in the solution). Though there has been substantial research into the effects of these salts on various protein and polymer systems, no quantitative explanation of the Hofmeister series has been proposed to date.<sup>2</sup> Here, we combine a stochastic search algorithm (Kick<sup>3</sup>), DFTB3<sup>4</sup>/DFT calculations and energy decomposition analysis (EDA)<sup>5</sup> to investigate the energetic origins of the Hofmeister series. We show, for the first time, that Hofmeister effects arise in the absence of a solvent. The interaction strength between cations/anions and unsolvated substrates, including poly(N-isopropylacrylamide) and amino acids, correlates precisely with the “reverse” Hofmeister series. Accounting for the energy penalty of partially desolvating the ion and the substrate gives rise to the Hofmeister series itself. While it has been suggested that dispersion interactions between the ion and substrate underpin the Hofmeister effect,<sup>6</sup> our results show that dispersion interactions are secondary to other interactions, such as polarisation.



**Figure 1.** EDA analysis of substrate-ion interactions without (left) and with (right) a solvent environment reveal reverse-Hofmeister and Hofmeister series, respectively.

- [1] Hofmeister, F., *Arch. Pharmacol.* **1888**, 24, 247. [2] Mazzini, V.; Craig, V. S. J., *Curr. Opin. Colloid Interface Sci.* **2016**, 23, 82-93. [3] Addicoat, M. A.; Fukuoka, S.; Page, A. J.; Irle, S., *J. Comput. Chem.* **2013**, 34, 2591-2600. [4] Gaus, M.; Cui, Q.; Elstner, M., *J. Chem. Theory Comput.* **2012**, 7, 931-948. [5] Su, P.; Li, H., *J. Chem. Phys.* **2009**, 131, 014102. [6] Ninham, B. W.; Yaminsky, V., *Langmuir* **1997**, 13, 2097-2108.



## Configuration interaction singles and doubles using exact exchange Kohn Sham orbital in real-space grid method.

Jaechang Lim<sup>1</sup>, Sunghwan Choi<sup>1</sup>, Jaewook Kim<sup>1</sup>, and Woo Youn Kim<sup>1\*</sup>

<sup>1</sup>*Department of Chemistry, 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea*

To assess the performance of multi-configuration method combined with real space grid method and exact exchange Kohn Sham (KS) orbitals, we implemented configuration interaction singles and doubles (CISD) in real space grid code. Exact exchange KS orbitals were calculated based on Krieger-Li-Iafrate (KLI) approximation. Consequently, KLI-CISD showed better performance than Hartree-Fock (HF) CISD for small molecules in both computational costs and accuracy. KLI-CISD converges much faster with respect to size of simulation box and active space than HF-CISD. Also, KLI-CISD provides more accurate excitation energy even with a few number of dominant configurations than HF-CISD, with many more configurations. For instance, the excitation energy of form amide  $1^1A''$  state obtained from KLI-CISD with 9316 number of configurations (5.85 eV) is closer to the reference excitation energy (5.63 eV) than that of HF-CISD with 340201 number of configurations (7.47 eV). This outstanding performance of KLI-CISD comes from distinct feature of KLI orbitals such as bound virtual orbitals with compact shape and similar orbital energy gap compared to vertical excitation energy. We expect that multi-configuration method combined with exact exchange KS orbital and real space grid method where systematic control of basis error is straightforward can be a new promising way of calculating accurate electronic structure

[1] S. Choi, K. Hong, J. Kim and W. Y. Kim, *J. Chem. Phys.* **142**, 094116 (2015).

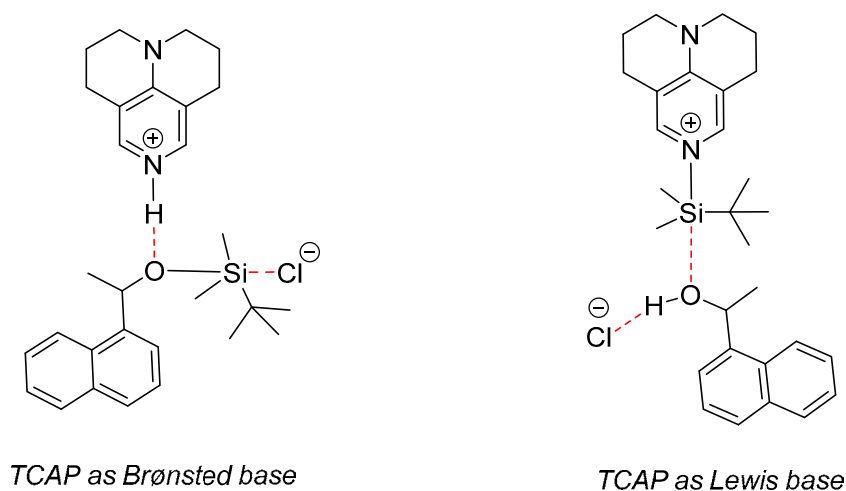
[2] J. Kim, K. Hong, S. Choi, S. Hwang, W. Y. Kim, *Phys Chem. Chem. Phys.* **17**, 31434 (2015).

## Base catalyst role on the silylation of secondary alcohols

Marta Marin-Luna<sup>1</sup>, Pascal Patschinski<sup>1</sup>, Hendrik Zipse<sup>1</sup>

<sup>1</sup> Chemistry Department, Ludwig-Maximilians-Universität Muenchen, Butenandtstrasse 5-13, Munich, Germany

Silylation reactions are one of the most useful strategies in protecting group chemistry, in particular for alcohol functions [1]. Recently, we reported quantitative studies on the response of absolute rate constants of alcohol silylation processes to experimental variables such as solvent, temperature, additives and type of reagent [2-3]. As far as we know, 9-azajulolidine (TCAP) has been shown to be the best catalyst in this kind of reactions. With the goal of shedding light on the TCAP role in this process we carried out a mechanistic study of this reaction by theoretical methods. Taking the silylation of 1-(1-naphthyl)ethanol as substrate model two mechanistic pathways have been conceived depending on how TCAP is taking part either as Brønsted or Lewis base (Figure 1). Our study shows that both mechanism are highly competitive and the dual base function of TCAP is completely plausible in terms of computed results.



**Figure 1.** Proposed transition structures for the silylation reaction of 1-(1-naphthyl)ethanol with TCAP as a Brønsted (left) and a Lewis (right) base.

- [1] P. J. Kocienski, *Protecting Groups*, 3rd ed.; Thieme: Stuttgart, (2005).
- [2] P. Patschinski; C. Zhang; H. Zipse, *J. Org. Chem.* **79**, 8348 (2014).
- [3] P. Patschinski; H. Zipse, *Org. Lett.* **17**, 1010 (2015).

**Electronic excitation spectra calculation of large systems (> 1000 atoms) with a tight-binding based simplified Tamm-Dancoff approximation (sTDA-xTB).****Jakob Seibert<sup>1</sup>, Christoph Bannwarth<sup>1</sup>, Stefan Grimme<sup>1</sup>**<sup>1</sup>*MCTC, University of Bonn, Berlingstr. 4, Bonn, Germany*

The computation of electronic absorption or circular dichroism (CD) spectra of molecules with a system size of 1000 atoms or more is challenging. However, CD spectroscopy is an important tool for structure elucidation of biomolecular systems or characterization of transition metal complexes. We previously developed the simplified variants of Tamm-Dancoff approximated (sTDA)[1] and time-dependent (sTD)[2] density functional theory which are based on a regular ground state Kohn-Sham determinant (obtained with hybrid or range-separated hybrid functionals[3]). This approach enables the computation of electronic spectra with TD-DFT accuracy for molecules up to a few hundred atoms. The computation of the ground state is the computational bottleneck. Our recently developed tight-binding method using an extended AO basis set (xTB)[4] solves this problem and enables the ultra-fast computation of electronic spectra by sTDA-xTB. Computed spectra for biomolecular systems (> 1000 atoms), e.g, for entire exemplary proteins and DNA fragments, as well as large transition metal complexes are presented.

[1] S. Grimme, *J. Chem. Phys.* **138**, 244104 (2013).

[2] C. Bannwarth, S. Grimme, *Comput. Theor. Chem.* **45**, 10401041, (2014).

[3] T. Risthaus, A. Hansen, S. Grimme, *Phys. Chem. Chem. Phys.* **16**, 14408 (2014).

[4] S. Grimme, C. Bannwarth *J. Chem. Phys.* **145**, 054103 (2016).

## Molecular Dynamics Simulations of Different Prion Variants

Ayşenaz Tavşanlı<sup>1</sup>, Fulya Ecem Keskin<sup>1</sup>, Bülent Balta<sup>1</sup>

<sup>1</sup>Graduate School of Science, Molecular Biology-Genetics and Biotechnology  
Department, Istanbul Technical University, Ayazaga Campus, Istanbul, Turkey

Transmissible spongiform encephalopathies (TSEs) are progressive neurodegenerative disorders [1] affecting both humans and animals [2]. They are characterized by long incubation periods, spongiform changes in the brain along with neuronal loss [1]. A protein called prion is believed to be the reason of TSEs [3].

Prion proteins are found most abundantly in the brain. The correctly folded protein is composed of two short  $\beta$ -strands (S1 and S2), three  $\alpha$ -helices (H1–H3), a disulfide bridge connecting H2 and H3, but abnormal folding of the protein leads to extensive  $\beta$ -sheet formation which causes the signs and symptoms of the disease [4].

In sheep, there is a polymorphism consisting of differences at positions 136, 154 and 171. TSE susceptibility according to these differences can be classified as follows [1]:

- the most resistant allele, ARR (A136, R154, R171)
- the allele with high resistance, ARQ (A136, R154, Q171)
- the most susceptible allele, VRQ (V136, R154, Q171)

Misfolding pathways of prion have been analyzed with implicit solvent molecular dynamic simulations which have been undertaken as follows:

- ARR, ARQ and VRQ have been simulated at 310 K for about 1000 ns to analyze whether valine/alanine variation at position 136 or arginine/glutamine variation at position 171 makes a difference to destabilize the structure and facilitate misfolding
- ARR, ARQ and VRQ simulations at 330 K have been conducted to accelerate possible misfolding processes

Alanine and valine are both hydrophobic amino acids but differ in their size. When the smaller amino acid alanine is found at position 136, it can be located at hydrophobic regions or exposed to solvent. On the other hand, when the larger amino acid valine is at position 136, it can be involved in unfavorable steric interactions.

Another observation in this study is that, during simulations at 310 K, the original  $\beta$ -sheet shifts compared to the crystallographic structure.

At 330 K, because of the high temperature, the C-terminus is more mobile and is likely to affect possible misfolding pathways.

[1] G.M. Cosseddu, U. Agrimi, J. Pinto and A.A. Schudel, *Rev. Sci. Tech. Off. Int. Epiz.*, **26** (3), 657-668 (2007).

[2] K. Pan, M. Baldwin, J. Nguyen, M. Gasset, A. Serban, D. Groth, I. Mehlhorn, Z. Huang, R. J. Fletterick, F. E. Cohen, and S. B. Prusiner, *Proc. Natl. Acad. Sci. USA*, **90**, 10962-10966 (1993).

[3] X. Lu, P. L. Wintrode, and W. K. Surewicz, *PNAS*, **104**, 5 (2007).

[4] M. Adrove, K. Pauwels, S. P. Cesira de Chiara, Z. Xu, C. Chapuis, A. Pastore, and H. Rezaei, *The Journal of Biological Chemistry*, **285** (27), 21004–21012 (2010).

## An additive QM/MM approach for the calculation of molecular crystals

Thorsten Teuteberg<sup>1</sup>, Ricardo A. Mata<sup>1</sup>

<sup>1</sup>*Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Tammanstraße 6,  
37077 Göttingen, Germany*

An additive QM/MM model for the investigation of molecular crystals is presented. It builds upon the original Chemshell[1] implementation of Bjornsson and Bühl[2] allowing for the convenient combination of various QM and MM program systems.

On the one-body level, a single molecule is chosen as the QM region. The MM region around consists of a finite cluster of explicit MM atoms, represented by point charges and non-bonding potentials, and additional background charges to include periodic boundary conditions. Cluster charges are QM-derived and calculated self-consistently, the non-bonding potentials are force field pair potentials. The QM calculation includes electrostatic embedding from the surrounding lattice.

Two-body corrections are considered for all molecules within a cutoff distance from the cluster origin. The contributing molecules are added to the one-body QM region one at a time, leaving the rest of the cluster unchanged. Two-body energy and gradient contributions are analytically composed from single and pair molecule energies and gradients.

The scheme allows for the calculation of molecular properties as well as full optimisation of the molecular geometry and cell parameters with respect to the lattice energy. Crystal symmetry is not considered explicitly, but symmetry relations between equivalent molecules of the unit cell are used in order to limit the size of the QM region to one single molecule. All structure parameters are solved self-consistently, with no restraints applied.

Application to the C21 set[3] of molecular crystals indicates that overall internal geometries and cell parameters in reasonable agreement with crystal structure data are obtainable already at the one-body level, while partially lattice energies are overestimated. Significant improvement is observed upon the inclusion of two-body corrections.

[1] ChemShell, a Computational Chemistry Shell, see [www.chemshell.org](http://www.chemshell.org).

[2] R. Bjornsson, M. Bühl, *J. Chem. Theory Comput.* **8**, 498 (2012).

[3] A. Otero-de-la-Roza, E. R. Johnson *J. Chem. Phys.* **137**, 054103 (2012).

## Electronic couplings for molecular charge transfer: the case of antiferromagnetically coupled systems

Adam Kubas

*Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224  
Warsaw, Poland*

We have recently introduced two databases, HAB11 and HAB7-, for electronic coupling matrix elements ( $H_{ab}$ ) for electron transfer in  $\pi$ -cojugated organic homo-dimers [1]. The reference data were obtained with high-level *ab initio* data at the multireference configuration interaction MRCI+Q level of theory, *n*-electron valence state perturbation theory NEVPT2, and (spin-component scaled) approximate coupled cluster model (SCS)-CC2. We found that the constrained density functional theory (CDFT) approach in combination with a modified PBE functional containing 50% Hartree-Fock exchange gives best results for absolute  $H_{ab}$  values and exponential distance decay constants  $\beta$ . The error of more approximate fragment orbital-based methods was somehow larger but systematic. General trends in accuracy of the tested methods are expected to be similar for comparable systems. However, typical biological electron transfer chains contain molecules that feature intrinsic antiferromagnetic coupling, e.g. iron-sulfur clusters in [FeFe]-hydrogenases. Molecules of such complicated electronic structure were not covered by our previous studies and literature lacks reliable benchmark data although some effective coupling approaches were recently demonstrated with semi-empirical and density functional theory methods [2]. To cover this class of donor-acceptor systems we performed a series of calculations on organic biradicals using CASSCF/MRCI+Q method. Interestingly, direct electronic couplings were found to be smaller than in the case of ferromagnetic coupling. High density of final states raised questions how to calculate effective  $H_{ab}$  values. As in the case of degenerated frontier orbitals of organic polycyclic molecules (coronene or C20) we will present various approaches to obtain effective electronic couplings. Moreover, the presentation will cover first DMRG calculations on the electronic coupling matrix elements in biologically-relevant  $[\text{Fe}_2\text{S}_2](\text{Cys})_4^{2-/3-}$  dimers.

- [1] (a) A. Kubas, F. Hoffmann, A. Heck, et al. *J. Chem. Phys.* **140**, 104105 (2014);  
(b) A. Kubas, F. Gajdos, A. Heck, et. al. *Phys. Chem. Chem. Phys.* **17**, 14342 (2015).  
[2] (a) A. Petrenko, M. Stein, *Int. J. Mol. Sci.* **18**, 100 (2017); (b) T. Hayashi, A. A. Stuchebrukhov, *PNAS* **107**, 19157 (2010).

Support from the National Science Centre, Poland grant 2015/17/D/ST4/00112 is gratefully acknowledged.

## Fulvenes as a new class of triplet ground state biradicals stabilized by Baird aromaticity

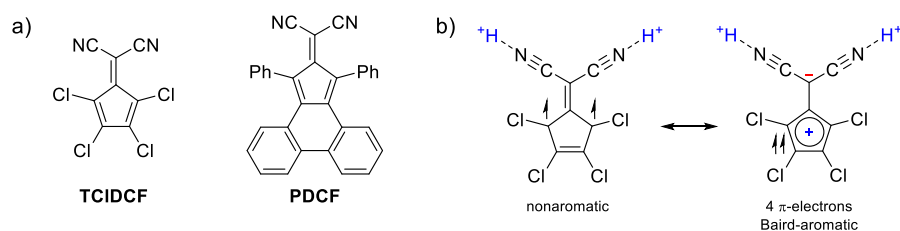
Saithalavi Anas,<sup>1,2</sup> Raffaello Papadakis,<sup>1,3</sup> Kjell Jorner,<sup>1,3</sup> Burkhard O. Jahn,<sup>1</sup> Ouissam El Bakouri,<sup>5</sup> Ferran Feixas,<sup>5</sup> Juan Casado,<sup>\*,4</sup> Miquel Solà,<sup>\*,5</sup> Ping Huang<sup>\*,3</sup> and Henrik Ottosson<sup>\*,1,3</sup>

<sup>1</sup> Department of Chemistry – BMC, Uppsala University, Box 576, 751 23 Uppsala, Sweden.

<sup>2</sup> Advanced Molecular Materials Research Centre, Mahatma Gandhi University, Kottayam, 686 560, Kerala, India. <sup>3</sup> Department of Chemistry – Ångström Laboratory, Uppsala University, Box 523, 751 20 Uppsala, Sweden. <sup>4</sup> Department of Physical Chemistry, University of Málaga, Campus de Teatinos s/n, 29071 Málaga, Spain. <sup>5</sup> Institut de Química Computacional i Catàlisi (IQCC) and Departament de Química, Universitat de Girona, Campus de Montilivi s/n, 17003 Girona, Catalonia, Spain.

Organic molecules with open-shell triplet ground states are rare and often unstable. Yet, if stable, they could form the basis for high-spin materials such as organic ferromagnets [1]. We report the formation of a new type of triplet ground state biradicals by coordination of two dicyanofulvenes with either protons or silyl cations (Figure 1a). The biradicals formed are stable to ambient air at room temperature for at least a week and for months at 77 K.

Quantum-chemical calculations reveal that the inverted singlet-triplet energy gap is strongly correlated with the aromatic character of the central five-membered ring (Baird aromaticity) [2,3]. This triplet state aromatic character can be understood based on a simple valence bond model in which this ring resembles the cyclopentadienyl cation, a well-established aromatic triplet ground state biradical (Figure 1b). Coordination of strong Lewis acids such as protons enhance this character by increasing the electron-withdrawing character of the cyano groups, ultimately giving a triplet ground state.



**Figure 1:** (a) Dicyanofulvenes (DCFs) which give triplet ground state biradicals upon coordination of protons or silyl cations (b) Valence bond model that explains the aromatic character of the DCFs in the triplet state.

[1] R. Breslow, *Pure Appl. Chem.*, **54**, 927 (1982). [2] N. C. Baird, *J. Am. Chem. Soc.*, **94**, 4941 (1972). [3] M. Rosenberg, C. Dahlstrand, K. Kilså, H. Ottosson, *Chem. Rev.* **114**, 5379 (2014).

## Partial Hessian Techniques in Vibrational Circular Dichroism

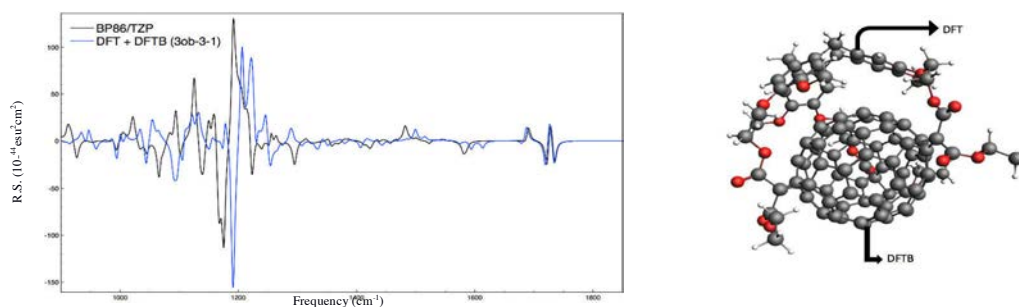
T.Q. Teodoro,<sup>1,2</sup> M. Koenis,<sup>3</sup> P.V. Nicu,<sup>3</sup> W.J. Buma,<sup>3</sup> S.E. Galembeck,<sup>2</sup>  
L. Visscher<sup>1</sup>

<sup>1</sup>*Faculty of Sciences, Vrije Universiteit Amsterdam, The Netherlands*

<sup>2</sup>*FFCLRP, Universidade de São Paulo, Ribeirão Preto, Brazil*

<sup>3</sup>*Faculteit der Natuurwetenschappen, Universiteit van Amsterdam, The Netherlands*

Vibrational Circular Dichroism (VCD), the differential absorption of left and right circularly polarized light in a vibrational transition  $\Delta\alpha(\omega) = \alpha L(\omega) - \alpha R(\omega)$ , is one of the most powerful techniques to determine the absolute configuration of a molecule. The intensities are given by the rotational strength associated to that transition, which can be written as a function of atomic polar (APT) and axial (AAT) tensors, and the eigenvalues and eigenvectors of the matrix of second energy-derivatives - the Hessian.<sup>1</sup> Obtaining the latter is usually the most demanding step in a computation of vibrational properties. In the present study, we divide the Hessian in sub-blocks as some parts of a given system, e.g., non-chiral chains with apolar bonds, have little effect on the VCD spectra. For these “approximate” regions we use Density-Functional based Tight-Binding (DFTB) theory, which is orders of magnitude faster than Density Functional Theory (DFT) that is applied for the “active” sub-system. In the example below it is shown the fingerprint region of the VCD spectra for the complex  $C_{105}H_{48}O_{18}$  as obtained by such “combined” method (blue line). Most displacements in the Buckyball were treated at the SCC-DFTB-3ob-3-1 level while the remaining ones were obtained in a BP86/TZP calculation. The spectrum agrees well with data from a full DFT calculation (black line). In our presentation, we will explore further the use of DFTB and partial techniques for speeding up VCD calculations that require addressing hundreds of conformers for a proper comparison with experimental data.



**Figure 1.** Theoretical VCD spectra for the complex on the right side as obtained by a full DFT calculation (black line) and a combined Hessian technique (blue line).

[1] V.P. Nicu, J. Neugenbauer, S.K. Wolff, E.J. Baerends, *Theor. Chem. Acc.* **119**, 245 (2008).

### Acknowledgements





## Selenium in GPx biochemistry: Insights from DFT studies on model chalcogenides

Marco Bortoli <sup>1</sup>, Laura Orian <sup>1</sup>, F. Matthias Bickelhaupt <sup>2, 3</sup>

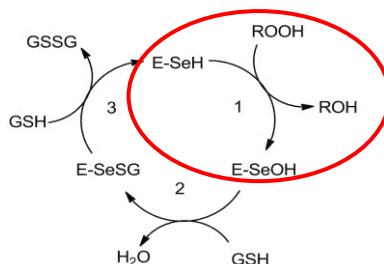
<sup>1</sup> *Dipartimento di Scienze Chimiche, Università degli Studi di Padova, Via Marzolo 1, 35131 Padova, Italy*

<sup>2</sup> *Department of Theoretical Chemistry and Amsterdam Center for Multiscale Modeling (ACMM), Vrije Universiteit Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands*

<sup>3</sup> *Institute for Molecules and Materials (IMM), Radboud University, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands*

In the human body, selenium is found in the modified amino acid selenocysteine (Sec), present in 25 proteins. On one hand, the insertion of Sec proceeds via a significantly more complicated mechanism than that of standard amino acids but, on the other hand, its presence enhances the functioning of the proteins involved. [1] For example, in the glutathione peroxidase (GPx) class of enzymes, substitution of Sec with a cysteine (Cys) residue results in a considerable loss of activity. Thus, GPx enzymes are a paradigmatic system for the investigation of the peculiar role of selenium as compared to sulfur. The ubiquitous GPx enzymes catalyze the reduction of organic hydroperoxides by glutathione via a three-step mechanism. [2]

These elementary reactions (Scheme 1) can be individually studied in model organochalcogenides *in silico*, leading to interesting outcomes for the rationalization of GPx activity as well as for the design of GPx mimics to be used as anti-oxidant drugs and more in general to understand fundamental aspects of the chemistry of chalcogens. [3] We present results on the oxidation of a chalcogen center by H<sub>2</sub>O<sub>2</sub> (step 1) in model diselenides and in cysteine/selenocysteine/tellurocysteine in a cluster resembling the catalytic pocket of GPx. State of the art DFT methods and activation strain analysis are employed to clarify the mechanism and energetics of these oxidations. [4]



Scheme 1. Catalytic mechanism of GPX enzyme (E).

[1] R. J. Hondal, E. L. Ruggles *Amino Acids*. **41**, 73 (2011).

[2] L. Orian, P. Mauri, A. Roveri, S. Toppo, L. Benazzi, V. Bosello-Travain, A. De Palma, M. Maiorino, G. Miotto, M. Zaccarin, A. Polimeno, L. Flohé, F. Ursini *Free Radical Biol. Med.* **87**, 1 (2015)

[3] L. Orian, S. Toppo, *Free Radicals Biol. Med.* **66**, 65 (2014).

[4] F. M. Bickelhaupt, K. N. Houk, *Angew. Chem., Int. Ed.*, DOI: 10.1002/anie.201701486

## Linear-scaling generation of potential energy surfaces for anharmonic vibrational spectra calculations

Carolin König<sup>1</sup>, Diana Madsen<sup>2</sup>, Ove Christiansen<sup>2</sup>

<sup>1</sup>*KTH Stockholm, Division of Theoretical Chemistry & Biology,  
Roslagstullsbacken 15, S-106 91 Stockholm, Sweden, carolink@kth.se*

<sup>2</sup>*Aarhus University, Department of Chemistry,  
Langelandsgade 140, DK-8000 Aarhus C, Denmark*

Accurate calculations of vibrational spectra using vibrational wave function techniques require accurate representations of multi-dimensional potential energy surfaces (PESs). Unfortunately, the construction of multi-dimensional PESs suffers from steep computational scaling with increasing system size. Recently, we have shown that molecular fragmentation schemes in combination with matching semi-local vibrational coordinates[1] allow for generation of PESs in a very cost-efficient manner. By introducing an additional transformation step, concerning only a fraction of the vibrational degrees of freedom, this scheme achieves linear scaling of the *accumulated cost* of the all electronic energy calculations required in the PES generation.[2]

In this contribution, I will (i) outline the principles behind our cost-efficient scheme to generate multi-dimensional PESs, (ii) show the fast convergence of the molecular fragmentation scheme in PES generations for oligo-phenyl examples, and (iii) provide comparison to experiment for smaller organic molecules, namely methylfurfural and dicyclopropenyl ketone.[3] I will further (iv) discuss the implication of this work for future applications to sizable and covalently bound systems.

- [1] C. König, M.B. Hansen, I.H. Godtliebsen, and O. Christiansen *J. Chem. Phys.* **2016**, *144*, 074108.
- [2] C. König and O. Christiansen *J. Chem. Phys.* **2016**, *145*, 064105.
- [3] D. Madsen, O. Christiansen, and C. König *in preparation* **2017**.

## Hybrid QM/MM Molecular Dynamics with AMOEBA Polarizable Embedding

**Daniele Loco<sup>1</sup>, Louis Lagardère<sup>2</sup>, Stefano Caprasecca<sup>1</sup>, Filippo Lipparini<sup>3</sup>,  
Jean-Philip Piquemal<sup>4</sup>, Benedetta Mennucci<sup>1</sup>**

<sup>1</sup>*Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via G. Moruzzi 13,  
I-56124 Pisa, Italy*

<sup>2</sup>*UPMC Univ. Paris 06, Institut des Sciences du Calcul et des Données, F-75005, Paris, France*

<sup>3</sup>*Institut für Physikalische Chemie, Universität Mainz, Duesbergweg 10-14, D-55128 Mainz,  
Germany*

<sup>4</sup>*UPMC Univ. Paris 06, UMR7616, Laboratoire de Chimie Théorique, F-75005, Paris, France*

In recent years lots of efforts have been devoted in the field of Classical Molecular Dynamics (MD) for the development of force fields that explicitly account for polarization, but still efficient for the study of large systems. They include many-body effects, improving, in principle, flexibility and accuracy. Such improvement is still not enough for the description of many important phenomena in molecular science, such as chemical reactivity and photoinduced processes, due to their intrinsic quantum nature. In that respect, Hybrid Quantum Mechanics/Classical methods represents a very promising strategy as they combines the computational efficiency of a classical model with the required quantum description of the subsystem of interest.

In this contribution We will present the implementation of a Born-Oppenheimer (BO) hybrid QM/MM MD strategy, based on the coupling[1] of Density Functional Theory (DFT) and the polarizable AMOEBA[2] force field. This approach involves the interplay between the Gaussian and Tinker suite of programs through a variational formalism allowing for a self-consistent relaxation of both the AMOEBA induced dipoles and the DFT electronic density at each MD step. Furthermore we take advantage of an Extended Lagrangian formulation (XL-BOMD)[3], improving the initial guess for the SCF equations, using the information that is available along the trajectory.

Test cases will be presented as benchmark for the performances of the code and examples of applications of embedded systems in different environments, with particular emphasis on the role of mutual polarization effects.

- [1] D. Loco, E. Polack, S. Caprasecca, L. Lagardère, F. Lipparini, J.-P. Piquemal, B. Mennucci, *J. Chem. Theory Comput.* **12**, 3654 (2016).
- [2] J. W. Ponder, C. Wu, P. Ren, V. S. Pande, J. D. Chodera, M. J. Schnieders, I. Haque, D. L. Mobley, D. S. Lambrecht, R. A. DiStasio Jr, M. Head-Gordon, G. N. I. Clark, M. E. Johnson, T. Head-Gordon, *J. Phys. Chem. B* **114**, 2549 (2010).
- [3] A. M. N. Niklasson, P. Steneteg, A. Odell, N. Bock, M. Challacombe, C. J. Tymczak, E. Holmström, G. Zheng, V. Weber, *J. Chem. Phys.* **130**, 214109 (2009).

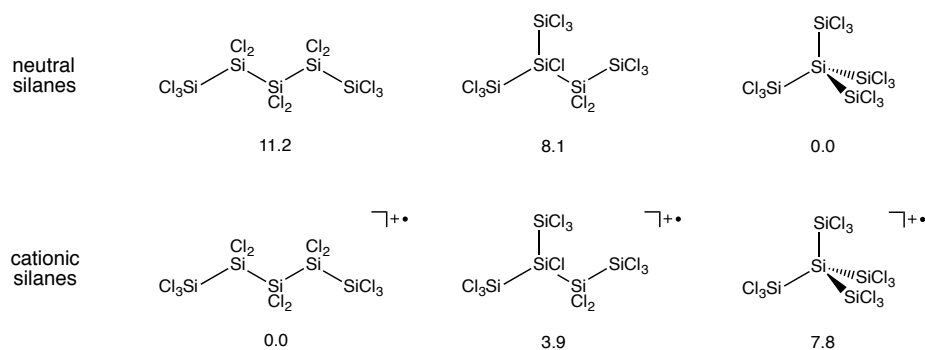
## A Mechanistic Exploration of the Plasma Formation of Perchlorosilanes

J. I. Schweizer<sup>1</sup>, M. Menche<sup>1</sup>, M. C. Holthausen<sup>1</sup>

<sup>1</sup>*Institut für Anorganische und Analytische Chemie, Goethe-Universität,  
Max-von-Laue-Str. 7, 60438 Frankfurt am Main, Germany*

The amine-induced formation of *neo*-Si<sub>5</sub>Cl<sub>12</sub> from Si<sub>2</sub>Cl<sub>6</sub> represents one of the few preparatively efficient synthetic routes to defined perchlorinated oligosilanes known to date.[1] Akin to the relative stabilities of hydrocarbon isomers – and in line with experimental findings – quantum-chemical calculations show that formation of branched silanes is thermodynamically favored over formation of the corresponding *n*-isomers. The plasma-assisted synthesis developed recently in our laboratory provides a unique route to perchlorinated oligosilanes. The latter are formed from SiCl<sub>4</sub> and H<sub>2</sub> by SiCl<sub>4</sub> polymerization and HCl elimination in a radiofrequency-assisted non-thermal plasma. Surprisingly, the reaction product is composed exclusively of unbranched silanes; plasma synthesis hence provides efficient access to a contra-thermodynamic product.

Here, a detailed quantum-chemical study on the reaction mechanism underlying the plasma-assisted formation of perchlorosilanes is reported. Preliminary results pointed at the involvement of radical cationic species in the reaction course.[2] The initial reaction between H<sub>2</sub> and SiCl<sub>4</sub><sup>++</sup> leads to formation of SiCl<sub>2</sub><sup>++</sup> as key reactive species that undergoes adduct formation with neutral silanes to yield higher oligosilanes. The proposed reaction mechanism explains the predominant formation of unbranched silanes. Alternative reaction of neutral SiCl<sub>4</sub> and H<sub>2</sub> as well as the involvement of other reactive species such as SiCl<sub>3</sub><sup>+</sup> are excluded as irrelevant.



**Figure 1.** Relative isomer stabilities for neutral Si<sub>5</sub>Cl<sub>12</sub> (top) and radical cationic Si<sub>5</sub>Cl<sub>12</sub><sup>++</sup> (bottom,  $\Delta H^{298}$  in kcal mol<sup>-1</sup>).

[1] G. Urry, *Acc. Chem. Res.* **3**, 306 (1970).

[2] E. M. L. Fink, A. Schießer, R. Berger, M. C. Holthausen, *Int. J. Mass Spectrom.* **354–355**, 378 (2013).

## QM/MM study of the reaction mechanism of the box H/ACA pseudouridine synthase catalysed uridine isomerisation

D. J. Kiss<sup>1,3</sup>, J. Oláh<sup>2</sup>, G. Tóth<sup>1</sup>, D. K. Menyhárd<sup>1</sup>, G. G. Ferenczy<sup>3</sup>

<sup>1</sup> Institute of Chemistry, Eötvös Loránd University, Pázmány P. s. 1/A, H-1117 Budapest, Hungary

<sup>2</sup> Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Gellért tér 4, H-1111 Budapest, Hungary

<sup>3</sup> Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar tudósok krt. 2. H-1117, Budapest, Hungary

Uridine isomerisation to pseudouridine is one of the most significant post-transcriptional modifications in RNAs, and the malfunctioning of H/ACA pseudouridine synthase, which is responsible for this chemical modification, is connected to serious diseases, like dyskeratosis congenital and various types of cancer. Four protein chains, a guide RNA and the substrate RNA form the active complex. (Figure 1a)

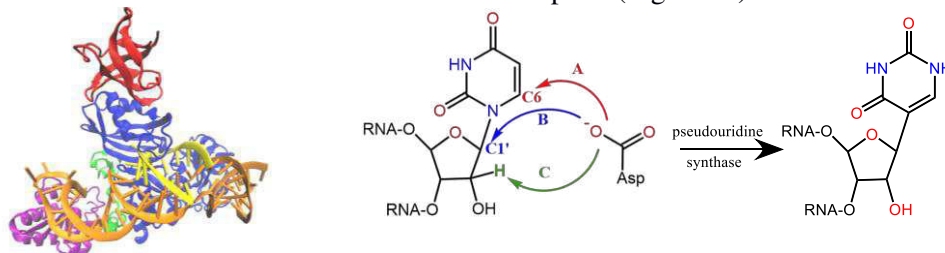


Figure 1: a) Structure of the enzyme complex b) Uridine isomerisation to pseudouridine

The crucial role of an aspartate residue in the catalysis has been experimentally validated; however, the atomistic details are still unclear. Three possible enzyme catalysed pathways were proposed in the literature (Figure 1b).[1] According to the Michael-addition scheme (A), the first step is the nucleophilic attack of the aspartate residue on the C6 of the uridine. The acylal scheme (B) starts with an attack on the C1' of the ribose by the aspartate, which causes the breaking of the C-N bond between the base and the ribose. In the glycal scheme (C) the aspartate deprotonates the C2' of the ribose.

Calculations show that the first step of the Michael-addition scheme did not lead to a stable intermediate in small model systems; a shallow minimum on the PES was observed using a larger QM model, however the QM/MM calculations estimated high barriers. The acylal scheme was ruled out because of the unfavourable orientation of the catalytic Asp for an S<sub>N</sub>2 reaction. The glycal scheme is in accordance with new experimental results[2] and reasonable QM/MM energies were calculated for the first steps of the reaction.

[1] F. Spenkuch, Y. Motorin, M. Helm, *RNA Biology* **11**, 1540 (2014).

[2] G.R. Veerareddygar, S.K. Singh, E.G. Mueller *J. Am. Chem. Soc.* **138**, 7852 (2016)

Acknowledgements: The authors are grateful for the financial support from the Hungarian Scientific Research Fund (OTKA, Grant No. 111862, 116305) and MedInProt Program. J. Olah was supported by a Bolyai Janos Research Scholarship and NKFIH Grant (PD115503).

## vdW-DF+ $U$ Description of Solid Oxygen

Shusuke Kasamatsu<sup>1</sup>, Takeo Kato<sup>1</sup>, Osamu Sugino<sup>1</sup>

<sup>1</sup>*The Institute for Solid State Physics, the University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa-shi, Chiba 277-8581, Japan*

Oxygen solidifies at low temperature into the paramagnetic cubic  $\gamma$  phase under 54 K, rhombohedral frustrated magnet  $\beta$  phase under 44 K, and the monoclinic antiferromagnetic  $\alpha$  phase under 24 K [1]. There is an unusually complicated coupling of the magnetic and lattice structures in those phase transitions, which results from a subtle balance of the van der Waals and spin-spin interactions between  $\text{O}_2$  molecules with spin  $S = 1$ . Conventional semilocal density functional approximations have proved to be quite unsatisfactory, and recently developed vdW-DF functionals solve the problem only partially; due to inaccurate description of the exchange interaction, the predicted lattice parameters of the  $\alpha$  phase are still off by as large as 15% compared to experiment [2]. Moreover, semiempirical tuning of spin-spin interaction in the vdW-DF energy functional (vdW-DF-SGC [2]) has also yielded sub-par results. Here, we consider applying the DFT+ $U$  approach [3] in combination with vdW-DF, which is implemented in VASP code [5], to describe the ground state  $\alpha$  phase of solid oxygen [4]. It is found that by combining DFT+ $U$  with vdW-DF-optB86b, virtually all lattice parameters improve up to  $U_{\text{eff}} = 12$  eV. This is explained by the correction of the overbinding between  $\text{O}_2$  molecules with opposite spin due to the on-site  $U$  interaction applied on the O  $2p$  orbitals.

- [1] Y. A. Freiman and H. J. Jodl, *Phys. Rep.* **401**, 1 (2004).
- [2] M. Obata *et al.*, *Phys. Procedia* **75**, 771 (2015).
- [3] S. L. Dudarev *et al.*, *Phys. Rev. B* **57**, 1505 (1998).
- [4] Kasamatsu *et al.*, *Phys. Rev. B*, in print; arXiv:1606.08568 [cond-mat.mtrl-sci].
- [5] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).

**Bonding of carbonyl groups to the dipentalene dititanium system  
relating to products from CO<sub>2</sub> activation**

**Luana F. Radu<sup>1</sup>, Amr A. A. Attia<sup>1</sup>, Alexandru Lupan<sup>1</sup>, R. Bruce King<sup>2</sup>**

<sup>1</sup>*Department of Chemistry, Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, Arany János 11, Cluj-Napoca, Romania*

<sup>2</sup>*Department of Chemistry and Center for Computational Quantum Chemistry, The University of Georgia, Athens, GA, United States*

The pentalene dianion [C<sub>8</sub>H<sub>6</sub>]<sup>2-</sup> (Pn<sup>2-</sup>) exhibits a variety of coordination modes, of interest being the ability to form bis-pentalene complexes – where two metals are located between pentalene ligands (the so-called “double sandwich” complexes). The structure of dipentalene dititanium, Pn<sub>2</sub>Ti<sub>2</sub> is relatively open so the titanium orbitals are accessible to small molecules. Therefore, dipentalene dititanium in presence of one or two equivalents of CO affords mono- and di-carbonyl compounds [1, 2]. With excess of CO, the tri-carbonyl complex is generated [3].

We have performed DFT calculations on Pn<sub>2</sub>Ti<sub>2</sub>(CO)<sub>n</sub> systems, where n = 1 – 4. The experimentally reported structures are shown to be the global minima for these systems.

[1] A. F. R. Kilpatrick, J. C. Green, F. G. N. Cloke, *Organometallics* **34**, 4830 (2015)

[2] A. F. R. Kilpatrick, J. C. Green, F. G. N. Cloke, *Organometallics* **34**, 4816 (2015)

[3] A. F. R. Kilpatrick, F. G. N. Cloke, *Chem. Commun.* **50**, 2769 (2014)

## Big Data Analysis of the NDDO Approximation to *ab initio* Molecular Electronic Integrals

Xin Wu, Pavlo O. Dral, Axel Koslowski, Walter Thiel

*Max-Planck-Institut für Kohlenforschung,  
Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany*

Modern valence-electron semi-empirical quantum chemical (SQC) methods [1] are based on the neglect of diatomic differential overlap (NDDO) approximation to *ab initio* molecular electronic integrals [2], which limits the *intrinsic* accuracy of an SQC method during the parameterization. In order to improve the SQC OMx methods [3] in a systematic manner, we performed comprehensive examinations of all kinds of *ab initio* molecular integrals in the non-orthogonal atomic basis and the symmetrically orthogonalized basis for 32 representative molecules, which cover simple saturated, unsaturated, and aromatic hydrocarbons as well as several  $\alpha$ -amino acids and entail over 1.4 million one-electron integrals and 168.8 million two-electron integrals in total. First of all, this exhaustive analysis provides quantitative measures of the errors caused by the neglect of various molecular integrals in the NDDO approximation. We confirm some previous qualitative conclusions about the behavior of NDDO two-electron integrals and about orthogonalization effects on the one-electron core Hamiltonian and support them by massive numerical evidence. The connections between certain one- and two-electron integrals, notably the resonance integrals and the relevant two-center hybrid electron repulsion integrals, are discussed in detail. Finally some plausible means for enhancing the OMx methods are proposed.

- [1] W. Thiel, *WIREs Comput. Mol. Sci.* **4**, 145 (2014).
- [2] J. A. Pople, D. P. Santry, G. A. Segal, *J. Chem. Phys.* **43**, S129 (1965).
- [3] P. O. Dral, X. Wu, L. Spörkel, A. Koslowski, W. Weber, R. Steiger, M. Scholten, W. Thiel, *J. Chem. Theory Comput.* **12**, 1082 (2016).



## Analytical nuclear excited-state gradients using frozen-density embedding to investigate molecular response in an explicit environment

**Johannes Heuser<sup>1</sup>, Sebastian Höfener<sup>1</sup>**

<sup>1</sup>*Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), P.O. Box 6980,  
D-76049 Karlsruhe, Germany*

The approximate second-order coupled cluster singles and doubles model (RICC2) can treat molecules containing tens of atoms with good precision including excited states exhibiting charge-transfer or double excitation character. However, the RICC2 method is limited by its quintic scaling, especially when excited-state geometries are to be optimized. Larger systems can be treated with density-functional theory (DFT), but the scaling of the method is still non-linear with system size.

A reduced scaling can be accomplished via subsystem approaches which partition the supersystem into subsystems. In the uncoupled frozen-density embedding (FDEu) scheme [1, 2], each subsystem can be treated individually with an appropriate quantum chemistry method while the interaction of the subsystems is described using DFT. For example, analytical nuclear gradients employing FDEu allow for geometry optimizations of a target molecule in an explicit molecular environment which enables the direct study of subsystem properties [3, 5, 6].

We present the derivation of analytical nuclear excited-state gradients for both the Tamm-Dancoff approximation (TDA) and RICC2 together with the implementation thereof in the KOALA program [4, 5, 6]. Orbital contributions from the environment molecules are neglected for both the energy and the gradient, resulting in an efficient treatment in the spirit of FDEu [5]. Excited-state geometries of a target molecule are investigated while being embedded in a molecular environment described at DFT level of theory, i.e., TDA-in-DFT and RICC2-in-DFT [6]. The accuracy of the subsystem-based approach is assessed in several case studies by comparison to supermolecular calculations.

- [1] T. A. Wesółowski, A. Warshel, *J. Phys. Chem.* **97**, 8050 (1993).
- [2] J. Neugebauer, *J. Chem. Phys.* **126**, 134116 (2007).
- [3] A. Kovyrshin, J. Neugebauer, *Phys. Chem. Chem. Phys.* **18**, 20955 (2016).
- [4] S. Höfener, *J. Comput. Chem.* **35** 1716 (2014).
- [5] J. Heuser, S. Höfener, *J. Comput. Chem.* **37**, 1092 (2016).
- [6] J. Heuser, S. Höfener, *submitted for publication*.

## Semiempirical quantum mechanical scoring functions for computer aided drug design

Jindřich Fanfrlík,<sup>1</sup> Jan Řezáč,<sup>1</sup> Martin Lepšík,<sup>1</sup> Adam Pecina,<sup>1</sup> Pavel Hobza<sup>1</sup>

<sup>1</sup> *Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Flemingovo nam. 2, 16610 Prague 6, Czech Republic.*

A reliable prediction of protein-ligand binding affinities is a very difficult task, which, among others, critically depends on a reliable description of noncovalent interactions. The general solution to the accurate description of noncovalent interactions is the use of quantum mechanics (QM). However, the price for the QM description are high computational requirements which can be overcome by various fragmentation techniques or by using linear-scaling semiempirical QM (SQM) methods. The quality of original SQM methods was low and thus we use corrected PM6-D3H4X or DFTB3-D3H4X methods which give highly accurate description of noncovalent interactions, comparable with the very demanding “golden standard” QM methods. PM6-D3H4X formed the core of SQM-based scoring function (SF)<sup>1</sup> which was successfully used for series of halogen bonded inhibitors of oxidoreductases.<sup>2</sup>

For its possible use in virtual screening, we have recently simplified and accelerated the SQM-based scoring function by employing only the dominant terms and neglecting expensive SQM optimization.<sup>3</sup> This novel scheme is called the SQM/COSMO scoring function and outperformed standard scoring functions (e.g. Glide, GOLD) in the ability to identify native binding pose which is a critical prerequisite for affinity estimation in physics-based scoring.<sup>3</sup>

[1] J. Fanfrlík, A. K. Bronowska, J. Řezáč, O. Přenosil, J. Konvalinka, P. Hobza, *J. Phys. Chem. B* **114**, 12666 (2010); M. Lepšík, J. Řezáč, M. Kolar, A. Pecina, P. Hobza, J. Fanfrlík, *ChemPlusChem* **78**, 921 (2013).

[2] J. Fanfrlík, M. Kolar, M. Kamlar, D. Hurny, F. X. Ruiz, A. Cousido-Siah, et al., *ACS Chem. Biol.* **8**, 2484 (2013); J. Fanfrlík, F. X. Ruiz, A. Kadlcikova, J. Řezáč, A. Cousido-Siah, A. Mitschler, et al., *ACS Chem. Biol.* **10**, 1637 (2015); A. Cousido-Siah, F. X. Ruiz, J. Fanfrlík, J. Gemenez-Deoz, A. Mitschler, M. Kamlar, *ACS Chem. Biol.* **11**, 2693 (2016).

[3] A. Pecina, R. Meier, J. Fanfrlík, M. Lepšík, J. Řezáč, P. Hobza, et al. *Chem. Comm.* **52**, 3312 (2016); A. Pecina, S. Haldar, J. Fanfrlík, R. Meier, J. Řezáč, M. Lepšík, P. Hobza, *J. Chem. Inf. Model.*, **57**, 127 (2017).

## Simulating osmotic equilibria: A new tool to calculate activities in concentrated solution

Michael Bley<sup>1</sup>, Magali Duvail<sup>1</sup>, Philippe Guilbaud<sup>2</sup>, Jean-François Dufrêche<sup>1</sup>

<sup>1</sup>*Institute for Separation Chemistry in Marcoule (ICSM), UMR 5257 CEA - Université Montpellier - CNRS - ENSCM, BP 17171, 30207 Bagnols-sur-Cèze, France*

<sup>2</sup>*CEA, Nuclear Energy Division, Research Department on Mining and Fuel Recycling Processes (SPDS/LILA), BP 17171, F-30207 Bagnols sur Cèze, France*

A new theoretical method is presented for predicting osmotic equilibria and activities[1], where a bulk liquid and its corresponding vapor phase are simulated by means of molecular dynamics using explicit polarization [2, 3]. Calculated time-averaged number density profiles provide the vapor phase densities. The activity of the solvent and the corresponding osmotic coefficient are determined by the vapor density at different solute concentrations with respect to the reference vapor density of the pure solvent. With the extended Debye-Hückel equation for the activity coefficient and the corresponding Gibbs-Duhem relation in addition the activity coefficients of the solutes are calculated by fitting the osmotic coefficients. A simple model based on the combination of Poisson processes and Maxwell-Boltzmann velocity distributions is introduced to interpret statistical phenomena observed during the simulations, which are related to evaporation and recondensation. This method is applied on various systems such as concentrated aqueous solutions of rare earth nitrates, mixtures of water and alcohols, and organic phases. The simulated activities, osmotic coefficients, and activity coefficients are in good agreement with the experimental findings for the aqueous solutions of the rare earth nitrates [4].

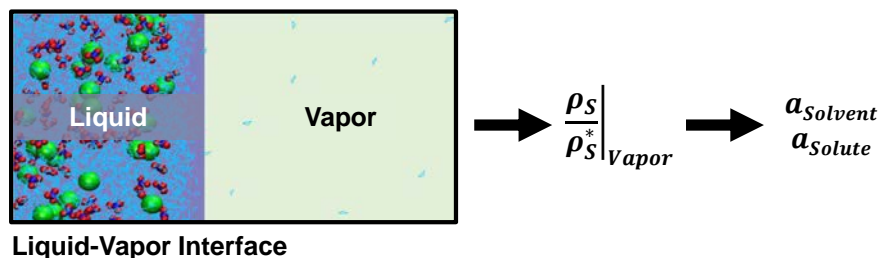


Figure 1: Schematic representation of molecular dynamics at a liquid-vapor interface. The vapor phase densities  $\rho_S^*$  for the pure solvent and  $\rho_S$  for a mixture directly provide the activities of the binary mixture. The liquid phase consists of water as solvent (blue), dysprosium  $\text{Dy}^{3+}$  (green), and nitrate  $\text{NO}_3^+$  ions (red).

- [1] M. Bley, M. Duvail, P. Guilbaud, J.-F. Dufrêche, *submitted to J. Phys. Chem. B*
- [2] J. W. Caldwell, P. A. Kollman, *J. Phys. Chem.* **100** 11460-11470 (1996)
- [3] M. Duvail, A. Ruas, L. Venault, P. Moisy, P. Guilbaud, *Inorg. Chem.* **49**, 519-530 (2010)
- [4] J. A. Rard, F. H. Spedding, *J. Chem. Eng. Data* **26**, 391-395 (1981)

## A perturbation-based Super-CI approach for the orbital optimization of a CASSCF wave function

Christian Kollmar<sup>1</sup>, Frank Neese<sup>1</sup>

<sup>1</sup>*Max Planck Institute for Chemical Energy Conversion, Stiftstraße 34-36, D-45470 Mülheim an der Ruhr*

A perturbation theory-based algorithm for the iterative orbital update in CASSCF calculations is presented. Following Angeli et al.[1], the first-order contribution of singly excited configurations to the CASSCF wave function is evaluated using the Dyall Hamiltonian as a zeroth-order Hamiltonian. Whereas these authors employ an iterative diagonalization of the first-order density matrix including the first-order correction arising from single excitations, the present approach uses the single excitation amplitudes directly for the construction of an anti-Hermitian matrix the exponential of which results in a unitary matrix which can be used for the orbital update. At convergence, the single excitation amplitudes vanish as a consequence of the generalized Brillouin's theorem. It is shown that this approach in combination with DIIS leads to very rapid convergence of the CASSCF iteration procedure.

- [1] C. Angeli, S. Evangelisti, R. Cimiraglia, and D. Maynau, *J. Chem. Phys.* **117**, 10525 (2002).

## Baird's rule under the umbrella of Clar's rule: A means for tuning the triplet state energies

**Rabia Ayub<sup>1</sup>, Ouissam El Bakouri<sup>2</sup>, Kjell Jorner<sup>1</sup>, Miquel Solà<sup>2\*</sup>,  
and Henrik Ottosson<sup>1\*</sup>**

<sup>1</sup>Department of Chemistry - Ångström Laboratory, Uppsala University, Box 523, SE-751 20 Uppsala, Sweden.

<sup>2</sup>Institut de Química Computacional i Catàlisi (IQCC), Universitat de Girona, c/ Maria Aurèlia Capmany 6, 17003 Girona, Catalonia, Spain.

**Abstract:** Aromaticity is a core concept in chemistry bridging organic chemistry with theoretical chemistry. The rule for aromaticity in the first triplet state ( $T_1$ ) was given by Baird in 1972.[1] This rule is now known as Baird's rule and it is the opposite to Hückel's rule. Thus, it tells that  $4n$  rings in their  $T_1$  states show aromaticity while  $4n+2$  rings display antiaromaticity.[2]

We combined Baird's rule with Clar's rule [3] to study the electronic properties of polycyclic conjugated hydrocarbons (PCH's) composed of one central  $[4n]$  unit fused with  $[4n+2]$  units, leading to  $4n\pi$ -electron perimeters (Figure 1). Three compound classes having three different central units were considered; cyclobutadiene (CBD; class A), cyclooctatetraene (COT; class B), and pentalene (PEN; class C). Within each isomeric series of PCHs, a decrease in the  $T_1$  energies is observed when going from linear to *cis*- and *trans*-bent connectivity. At the same time, the  $T_1$  state aromaticity of the central  $4n\pi$ -electron unit increases. In conclusion, the lowest triplet energy is observed for that isomer among a set of isomeric PCHs which in its  $T_1$  state hosts the largest number of aromatic cycles, *i.e.*, Clar  $\pi$ -sextets and Baird  $\pi$ -quartets/octets combined.[4]

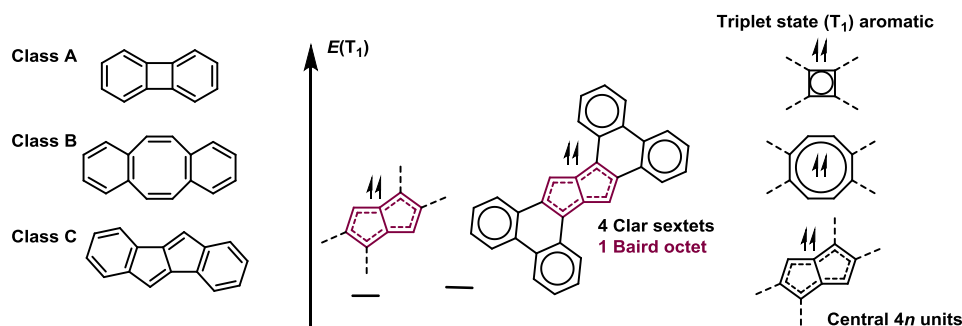


Figure 1: The compound classes and the three central  $4n\pi$ -electron units considered.

## References

- [1] (a) N. C. Baird, *J. Am. Chem. Soc.* **94**, 4941 (1972). (b) H. Ottosson, *Nat. Chem.* **4**, 969 (2012).  
[2] M. Rosenberg, C. Dahlstrand, K. Kilså, H. Ottosson, *Chem. Rev.* **114**, 5379 (2014). [3] E. Clar, *The Aromatic Sextet*, Wiley, New York, (1972). [4] R. Ayub, O. El Bakouri, K. Jorner, M. Solà, H. Ottosson, *J. Org. Chem.* (2017), DOI: 10.1021/acs.joc.7b00906.

## Allosteric Control of the DNA-RNA Translocation in Telomerase

Aydm ÖZMALDAR<sup>1,2</sup>, Bülent BALTA<sup>1,2</sup>

<sup>1</sup> *Istanbul Technical University, Dr. Orhan Ocalgiray Molecular Biology, Biotechnology and Genetics Research Center (ITU MOBGAM), Maslak, Istanbul, Turkey.*

<sup>2</sup> *Department of Molecular Biology & Genetics, Faculty of Science & Letters, Istanbul Technical University, Maslak, Istanbul, Turkey.*

The stabilization of the DNA-RNA duplex at the active site of telomerase during nucleotide incorporation and the mechanism of RNA-DNA translocation after the formation of the phosphodiester bond are not fully understood. To address these questions, *Tribolium castaneum* telomerase catalytic subunit TERT and the associated RNA-DNA hybrid have been simulated using Amber14 program with the ff14SB force field.

To investigate the structural changes along the functional cycle of telomerase, three different states have been modelled (without dNTP in the active site, with dNTP and after the incorporation of a nucleotide into the growing DNA chain). Each state can be considered as a step in the substrate recognition and translocation cycle.

In the crystal structure [1], dA23 of DNA is coordinated to RNA via Hoogsteen type hydrogen bonds. Such an interaction in telomerase is not expected, therefore all these three states have been investigated also by changing the conformation of this adenine in order to form a *canonical Watson-Crick* pair.

The analysis of these states has shown that before the formation of the phosphodiester bond between dNTP and DNA primer, TERT exhibits a closed conformation whereas after the formation of the phosphodiester bond, the fingers subdomain displays an opening movement. This opening movement is necessary for DNA-RNA translocation to allow further nucleotide addition. Some amino acid residues have critical roles in the allosteric control of opening. Therefore, they are mutated to alanine for testing their effect on the enzyme stabilization and allosteric regulation.

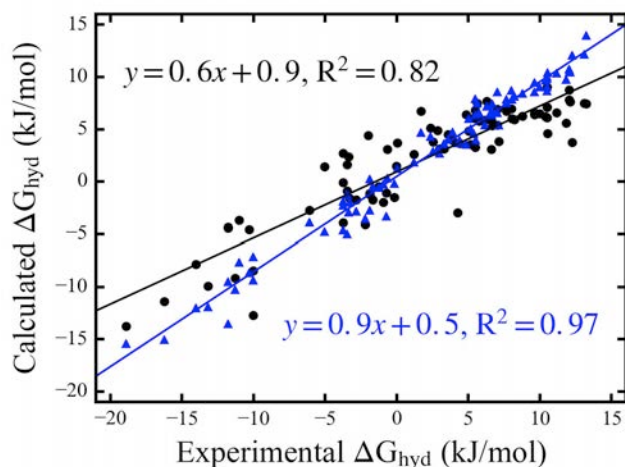
[1] Mitchell, M., et al, *Nat Struct Mol Biol.* **17**(4), 513-518 (2010).

## The Automated Topology Builder (ATB): A Big Data Approach to Empirical Force Field Parameterisation.

**Martin Stroet, Bertrand Caron, Thomas Lee, Katarzyna B. Koziara,  
Alpeshkumar K. Malde, Alan E. Mark**

*School of Chemistry and Molecular Biosciences, University of Queensland, St Lucia, QLD  
4072, Australia*

Computational drug design is critically dependent on whether empirical interaction potentials (force field) can accurately reproduce the structural and thermodynamic properties of protein:ligand complexes. While optimised force field parameters are readily available for common biomolecules such as proteins, nucleotides, lipids etc., this is not the case for ligand molecules such as co-factors, substrates and drugs. The Automated Topology Builder (ATB, [atb.uq.edu.au](http://atb.uq.edu.au)) provides empirical force field parameters and B3LYP optimised geometries for use in molecular simulations, computational drug design and x-ray refinement compatible with a range of packages including GROMOS, GROMACS, AMBER, LAMMPS, CNS and PHENIX [1]. The ATB database currently has optimised geometries, electrostatic potentials and Hessians for in excess of 130,000 compounds as well as over 2000 solvation free energy calculations in both polar and apolar solvents. This unique and rapidly expanding resource is being used to systematically refine



bonded and non-bonded parameters against a range of reference data including thermodynamic properties such as solvation free energy, Figure 1. We show how substructure matching using graph-theory methods combined with big data approaches provide a highly efficient means to develop consistent force field parameters for a diverse range of molecules.

**Figure 1.** Improvement of hydration free energy results after refinement of charge fitting and carbon 6-12 Lennard-Jones parameters for 81 hydrocarbons.

[1] A. K. Malde, L. Zuo, M. Breeze, M. Stroet, D. Poger, P. C. Nair, C. Oostenbrink, A. E. Mark, *J. Chem. Theory Comput.* **28**, 221 (2011).

## Mechanistic investigation of CO oxidation on a single gold atom deposited on MgO(001) surfaces

Kai Töpfer<sup>1</sup>, Jean Christophe Tremblay<sup>1</sup>

<sup>1</sup>*Institute for Chemistry and Biochemistry, Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany*

Understanding the observed catalytic oxidation of CO on Au<sub>n</sub> clusters deposited on defect-rich MgO(001) surfaces in mixed O<sub>2</sub>/CO atmospheres remains a subject of great actuality [1, 2]. A particularly puzzling aspect is that no catalytic activity is registered for the smallest clusters, Au<sub>1</sub> and Au<sub>2</sub>, presumably due to the absence of co-adsorbed states and to CO poisoning [2, 3]. To explain this peculiar behavior, we first investigate the catalytic reaction using cluster models and point charge embedding within a density functional theory framework. Our mechanistic investigations reveal that the smallest clusters are unable to protect the oxygen vacancy against reparation in an O<sub>2</sub>-rich atmosphere. After the formation of a first CO<sub>2</sub> molecule, the remaining O atom moves below the gold cluster into the vacancy, effectively ending the catalytic cycle. Further investigations on a clean MgO(001) surface uncover several co-adsorbed state of CO and O<sub>2</sub> molecules on a single gold atom. Even with an effectively weakened O<sub>2</sub> bond, the reaction barriers towards the CO<sub>2</sub> formation remains thermally unaccessible, explaining the observed absence of catalytic activity. The most stable co-adsorbed state hints at a reaction pathway which could become accessible by selective infrared excitation of a well isolated vibrational mode. We study by means of reduced dimension quantum dynamics possibilities for restoring the catalytic cycle using vibrational excitation by electromagnetic radiation.

- [1] N. Nikbin, N. Austin, D. G. Vlachos, M. Stamatakis, G. Mpourmpkis, *Catal. Sci. Technol.* **5**, 134-141 (2015).
- [2] M. Arenz, U. Landmann, U. Heiz, *ChemPhysChem* **7**, 1871-1879 (2006).
- [3] M. Amft, N. V. Skorodumova, *Phys. Rev. B* **81**, 195443 (2010).



## Hybrid Functionals Approach of the Structural, Electronic and Dynamical Properties of Semiconductors for Photovoltaic Applications.

**F. Lafond<sup>1, 2, 3</sup>, B. Civalieri<sup>4</sup>, Ph. Baranek<sup>1, 2, 3</sup>, A. Postnikov<sup>5</sup>**

<sup>1</sup>*EDF R&D, Department Economic and Technical Analysis of Energy Systems (EFESE), EDF Lab – Chatou, 6 quai Wattier, F-78400 Chatou Cedex, France*

<sup>2</sup>*Institut of Research and Development on Photovoltaic Energy (IRDEP), UMR 7174 CNRS/EDF R&D/Chimie ParisTech – PSL, 6 quai Wattier, F-78400 Chatou Cedex, France*

<sup>3</sup>*Institut Photovoltaïque d’Ile de France (IPVF), 8 rue de la Renaissance, F-92160 Antony, France*

<sup>4</sup>*Dipartimento di Chimica - Università’ di Torino, Via P. Giuria 7, I-10125 Torino, Italy*

<sup>5</sup>*University of Lorraine, Jean Bariol Institute, Laboratoire de Chimie et Physique – Approche Multi-échelle des Milieux Complexes (LCP-A2MC), 1 Bd Arago, F-57078 Metz, France*

The defects and dopants, either added intentionally or being technically unavoidable, in the semiconductors for photovoltaic applications, do strongly influence their performances. Their main impact concerns in particular the stability domains of different phases in their relation to the electrical properties of the materials. The first-principles many-body theory methods, such as GW, can give a clue and provide a quite accurate description, albeit a time consuming one, as for how does the crystal structure affect the electronic (optical) characteristics. An interesting alternative can be provided by so-called hybrid functionals in the Density Functional Theory, whereby the exchange operator includes a linear admixture from the exact Hartree-Fock one. In this work, the performance of different types of functionals, differing in the way and amount of the Hartree-Fock exchange incorporated in the exchange-correlation schemes (e.g. global and range-separated hybrids), is compared in what regards their ability to correctly describe electronic, structural and dynamical properties of IV(Si)-IV, III-V semiconductors and chalcopyrites CuAB<sub>2</sub> (with A = Ga, In and B = S, Se). For each compound, we determined the best combination of Hartree-Fock exchange with different LDA and GGA functionals in order to obtain a good description of their band structures. In that case, we systematically check whether other essential properties, such as the lattice parameters, phonon frequencies, dielectric and elastic constants, maintain a reasonable agreement with experimental data.

## Excited-State Dynamics of a Eumelanin Building Block: Photoprotection or Photodamage?

**Juan J. Nogueira, Moritz Heindl, and Leticia González**

*Institute of Theoretical Chemistry, Faculty of Chemistry, University of Vienna, Währinger  
Straße 17, 1090 Vienna, Austria*

Eumelanin is a polymer that presents a complex structure composed by the molecular units 5,6-dihydroxyindole (DHI) and 5,6-dihydroxyindole-2-carboxylic acid (DHICA) [1]. It is believed that eumelanin plays a crucial role in the protection of skin against the harmful effects of UV light by dissipation of the excitation energy [2]. Here, we present a theoretical investigation of the excited-state deactivation mechanism of DHI in aqueous solution and in methanol. Stationary electronically excited-state calculations shows that the earliest steps of the deactivation process are mediated by a sequential proton-coupled electron transfer mechanism [3], which involves the formation of a solvated electron and subsequent proton transfer from DHI to the solvent. Then, non-adiabatic surface-hopping molecular dynamics simulations predicts that several pathways are operative, including recombination of the transferred electron and proton with DHI, multiple proton transfers along solvent wires, and formation of hydrogen radical. The generation of very reactive species, i.e., solvated electrons and hydrogen radicals, opens a new scenario in the role of DHI and its possible participation in photodamage events.

- [1] M. d'Ischia, A. Napolitano, A. Pezzella, P. Meredith, T. Sarna, *Angew. Chem. Int. Ed.* **48**, 3914 (2009).
- [2] P. Meredith, T. Sarna, *Cell Res.* **19**, 572 (2006).
- [3] J. J. Nogueira, A. Corani, A. El Nahhas, A. Pezzella, M. d'Ischia, L. González, V. Sundström, *J. Phys. Chem. Lett.* **8**, 1004 (2017).

## Trends in the Au adsorption energy on oxide surfaces: A DFT study.

**Sergio Tosoni<sup>1</sup>, Gianfranco Pacchioni<sup>1</sup>**

*<sup>1</sup>Dipartimento di Scienza dei Materiali, Università di Milano Bicocca  
Via R. Cozzi 55, 20125 Milano (Italy)*

The deposition of dispersed gold nanoclusters on oxide surfaces is at the base of many applications in heterogeneous catalysis, from the CO oxidation to CO<sub>2</sub>, to the water-gas-shift reaction and many others. The interaction between metal particles and oxide surfaces determines the charge state and morphology of the supported nanoclusters, influencing thus also their catalytic activity. Moreover, the strength of the Au-oxide interaction is an important descriptor to predict the catalyst's stability at operating conditions: in general, if Au adheres strongly on an oxide surface, undesired ripening and particle coalescence processes, leading to the thermal deactivation of the catalyst, will be slower. For this reason, the trend in Au adhesion energy on oxide surfaces is a topic of paramount relevance in heterogeneous catalysis.

As recently pointed out by combining microcalorimetric and microscopy measurements, however, relatively unexpected trends arise when the adhesion energy of gold nanoparticles on several oxide surfaces is analyzed. In particular, it results that Au nanoparticles adhere on MgO and TiO<sub>2</sub> rutile with comparable strength, while the adhesion on ceria is much stronger.[1] We investigated on this trend by performing extensive DFT calculations on three model systems: i) adsorption of an isolated Au atom ii) adsorption of an Au<sub>20</sub> cluster and iii) an extended interface where a 5ML-thick periodic Au slab is in contact to the oxide surface. We considered three oxides, MgO, TiO<sub>2</sub> rutile and CeO<sub>2</sub>. When the isolated Au atom is placed in contact to surface oxygen atoms of MgO, titania, and ceria, similar adsorption energies are reported. For the Au<sub>20</sub> cluster, the adhesion on ceria (-4.52 eV) is stronger than on MgO (-3.51 eV), which in turns binds the cluster stronger than rutile TiO<sub>2</sub> (-2.82 eV). A similar trend is reported also for the extended interfaces. Interestingly, we were able to reconcile our data to the experimental trend only by taking into account the pronounced reducible character of titania and ceria with respect to a non-reducible oxide such as MgO. Indeed, when the Au<sub>20</sub> cluster is placed in contact to a surface oxygen vacancy, the experimental trend of adhesion energy (MgO  $\approx$  TiO<sub>2</sub> < CeO<sub>2</sub>) is correctly reproduced. We can thus conclude that the adhesion energy of gold on an oxide surface is determined by a non-banal interplay of several factors, such as the surface topology allowing (or not) for stabilizing Au-O interactions, but also the intrinsic tendency of an oxide to display defects such as oxygen vacancies.

[1] S. L. Hemmingson, C. T. Campbell, *ACS Nano* **11**, 1196 (2017).

## QM:QM Calculations on Molecular Crystals

**Oleksandr A. Loboda, Grygoriy A. Dolgonos, and A. Daniel Boese**

*Department of Chemistry, University of Graz, Heinrichstrasse 28 IV, 8010 Graz, Austria*

In recent years, advances in method developments have been leading to increasingly accurate calculations of structures of molecular crystals. This has been highlighted by the impressive results in the blind test prediction of crystal structures for organic molecules and, recently, also organic salts.[1] Much of this progress can be attributed to the increased application of density functional theory including dispersion corrections (DFT+D) using periodic boundary conditions. Along the lines of quantum mechanical methods embedded into other quantum mechanical methods,[2] we present an alternative to periodic DFT+D, in which a combination of BLYP or B3LYP embedded into density functional based tight binding (DFTB) is employed. For the X23 benchmark set of molecular crystals,[3] BLYP+D:DFTB+D yields essentially the same results as periodic BLYP+D, differing significantly from periodic DFTB+D calculations alone. As it is possible to achieve linear parallelization with this method up to the number of fragments computed, it can lead to a significant speedup in comparison to DFT+D.

[1] A. M. Reilly et al., *Acta Crystallographica B* **72**, 439 (2016).

[2] A. D. Boese and Joachim Sauer, *Cryst. Growth & Design* **17**, 1636 (2017).

[3] A. M. Reilly and A. Tkatchenko, *J. Chem. Phys.* **139**, 024705 (2013).

## **Raman technique and Density Functional Theory – the “R” & “D” in Research and Development of antibiotics**

**Ana-Maria-Raluca Gherman<sup>1,2</sup>, Nicoleta Elena Dina<sup>1</sup>, Ionuț Bogdan Cozar<sup>1</sup>, Vasile Chiș<sup>2</sup>**

*<sup>1</sup>Department of Molecular and Biomolecular Physics, National Institute of R&D of Isotopic and Molecular Technologies, 67-103 Donat, Cluj-Napoca 400293, Romania*

*<sup>2</sup>Faculty of Physics, Babeș-Bolyai University, 1 Kogălniceanu, Cluj-Napoca 400084, Romania*

Antibiotics are still a hot topic for research mainly because most of them tend to be bacterial resistant after a period of intensive use. As a result, the development of new and more effective antibiotics is requested increasingly more often. Understanding the geometrical and electronic structure of such molecules is a must when it comes to designing new drugs. These bring precious information for further investigations in different chemical reactions such as the bonding mechanism of an antibiotic to a specific component of bacterial cell-wall in order to have bactericidal effect.

Raman technique provides information related to electronic and geometric structure in the form of fingerprint-like spectra, unique for every molecule, what makes it suitable for detailed characterization of antibiotics from this point of view. This Raman study covers one assignee for each of the five classes of penicillins (in the order of the classes they belong to) – benzylpenicillin (BPN), oxacillin (OXN), ampicillin (APN), carbenicillin (CBN), and azlocillin (AZN). The similar features, due to the common component of their molecular structure – a penam core, represented by a 6-aminopenicillonic acid (6-APA), are explained. Also, fine-drawn features, on account of the differences in the molecular structures – various R side-chains attached to the sixth position of the penam core, are to be disentangled as well in order to unravel what has a say when it comes to the discrepancies regarding bactericidal activity.

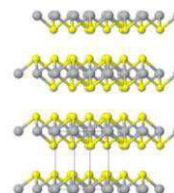
FT-Raman, Raman using different wavelengths of excitation sources both on solid phase and aqueous solution, and Surface Enhanced Raman spectra (SERS) are to be explained by quantum chemical frequency calculations on antibiotics' monomers by using Gaussian software package. For this, harmonic and anharmonic approximations were employed. Calculations were performed in gas phase and by using PCM solvation model with water as solvent.

## Thermal conductivity of group 4 layered transition metal disulfides: a first-principles study

Nina Glebko, Antti Karttunen

*Department of Chemistry and Materials Science, School of Chemical Engineering,  
Aalto University, Kemistintie 1, 02150 Espoo, Finland*

Transition metal disulfides such as  $\text{TiS}_2$ ,  $\text{ZrS}_2$ ,  $\text{HfS}_2$  are potential thermoelectric materials, in particular when intercalated with organic molecules to create hybrid inorganic-organic materials<sup>1</sup>. The phonon dispersion and lattice thermal conductivity of bulk group 4 transition metal disulfides ( $\text{TiS}_2$ ,  $\text{ZrS}_2$ ,  $\text{HfS}_2$ ) has been studied within Density Functional Theory approach using PBE0 hybrid functional. The phonon dispersion has been calculated numerically using finite displacement method combined with supercell approach, as implemented in the PHONOPY code package. In-plane and cross-plane lattice thermal conductivity, generally limited by Umklapp (phonon-phonon) scattering has been investigated by means of Boltzmann transport equation, as implemented in the PHONO3PY code. The use of the PBE0 hybrid functional in the lattice thermal conductivity calculations was enabled by the newly created interface to the CRYSTAL quantum chemistry package. Comparing the computational values with existing experimental data revealed them to be consistent.



[1] Chunlei Wan, Xiaokun Gu, Feng Dang, Tomohiro Itoh, Yifeng Wang, Hitoshi Sasaki, Mami Kondo, Kenji Koga, Kazuhisa Yabuki, G. Jeffrey Snyder, Ronggui Yang, Kunihiro Koumoto. *Nature Mater.* **14**, 622–627 (2015).

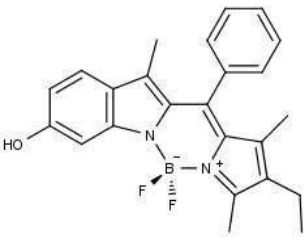

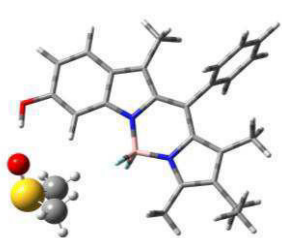
## Electronic excitations of 6-Hydroxyindole-based BODIPY fluorophore: polarization propagator approach and explicit solvation

A.D. Skitnevskaya<sup>1</sup>, A.B. Trofimov<sup>1,2</sup>

<sup>1</sup> *Laboratory of Quantum Chemistry, Irkutsk State University, 1 K. Marks St., 664003 Irkutsk, Russian Federation*

<sup>2</sup> *A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 1 Favorsky St., 664033 Irkutsk, Russian Federation*

BODIPYs bearing phenolic subunits such as 6-Hydroxyindole based borondipyrromethene (BODIPY-OH, see the structure below) are useful synthetic analogs of biological luminescent systems [1]. We have studied theoretically the vertical electronic excitations of BODIPY-OH in H<sub>2</sub>O and DMSO solutions treating explicitly the specific interactions. The BODIPY-OH·nH<sub>2</sub>O (n=1-3) and BODIPY-OH·DMSO complexes have been considered, where the initial orientations of molecules have been generated using the Coalescence Kick method [2]. The resulting structures have been filtered by stability at the semiempirical level of theory and further ranged using MP2/6-311++G\*\*/B3LYP/6-31+G\* approach. The solvent molecules preferably form a "bridge" between hydroxyl group and one of the fluorine atoms. The gap accommodates either one DMSO molecule or two H<sub>2</sub>O molecules. The energies of the vertical singlet electronic excitations,  $\Omega$ , have been calculated for the identified optimal structures and isolated BODIPY-OH molecule using the ADC(2) polarization propagator approach and the cc-pVDZ basis set.

			
	BODIPY-OH	BODIPY-OH·2H <sub>2</sub> O	BODIPY-OH·DMSO
$\Omega$ (eV)	2.34	2.19 (0.08)	2.17 (0.05)

The explicit treatment of the solvent molecules improves the agreement with experimental data [1] (the corresponding imparities are shown in the parentheses).

[1] C. Zhao, P. Feng, J. Cao, Y. Zhang, X. Wang, Y. Yang, Y. Zhang, J. Zhang, *Org. Biomol. Chem.* 10, 267 (2012).

[2] B. Averkiev, *All Graduate Theses and Dissertations*, paper 408 (2009).

This work has been supported by the Ministry of Education and Science of the RF, Grant № 4.1671.2017/4.6 and by Russian Foundation for Basic Research, Grant № 16-33-0098.

## Photoreactivity of Adenine and Cytosine with Water Molecules via Electron-Driven Proton-Transfer Processes

Xiuxiu Wu<sup>1</sup>, Tolga N. V. Karsili<sup>1</sup>, Andrzej L. Sobolewski<sup>2</sup> and Wolfgang Domcke<sup>1</sup>

<sup>1</sup> Department of Chemistry, Technical University of Munich, D-85747 Garching, Germany

<sup>2</sup> Institute of Physics, Polish Academy of Sciences, PL-02668 Warsaw, Poland

We investigated the mechanisms of excited-state deactivation in hydrogen-bonded adenine-water and cytosine-water complexes with *ab initio* wave-function-based electronic-structure calculations. Two excited-state decay mechanisms, which are specific for hydrogen-bonded clusters of DNA bases with water molecules, have been identified: electron/proton transfer from water to the photoexcited chromophore<sup>1</sup> as well as electron/proton transfer from the photoexcited chromophore to water.<sup>2</sup> In the former reaction, an electron from one of the p orbitals of a water molecule fills the  $\pi$ -hole existing in the  $\pi\pi^*$  excited state of adenine or cytosine. In the latter reaction, nonadiabatic coupling of the lowest  $\pi\pi^*$  excited state with the lowest  $^1\pi\sigma^*$  state of the DNA base provides the mechanism for photoejection of an electron and a proton into the aqueous environment. The energy profiles of the photoreactions have been computed as relaxed scans with the ADC(2) method. For all reaction channels, barrierless or nearly barrierless reaction paths towards low-lying  $S_1$ – $S_0$  conical intersections are found.<sup>1,2</sup> These reaction mechanisms, which are specific for adenine and cytosine in an aqueous environment and exist in addition to the well-established intramolecular excited-state decay mechanisms via ring-puckering conical intersections,<sup>3</sup> can explain the substantially shortened excited-state lifetimes of adenine and cytosine in water. Both photochemical reaction mechanisms illustrate the generic role of electron-driven proton-transfer processes in excited states of nucleobases in an aqueous environment and deserve further investigation by *ab initio* nonadiabatic nuclear-dynamics simulations.

### References

- [1] X. Wu, T. N. V. Karsili and W. Domcke, *ChemPhysChem* **17**, 1298 (2016).
- [2] X. Wu, T. N. V. Karsili, A. L. Sobolewski and W. Domcke, to be published.
- [3] R. Improta, F. Santoro and L. Blancafort, *Chem. Rev.* **116**, 3540 (2016).



## Low-lying Electronic Terms of Diatomic Molecules AB (A = Sc – Ni, B = Cu/Ag/Au)

**Davood Alizadeh Sanati, Dirk Andrae**

*Physikalische und Theoretische Chemie, Institut für Chemie und Biochemie  
Freie Universität Berlin, D-14195 Berlin, Germany*

Heteronuclear clusters formed by atoms of d-block elements are building blocks for catalytically and photochemically active systems, for nanostructured materials, and for electronic devices that receive considerable attention in both fundamental and applied research.[1]

We present a systematic study of the ground and low-lying excited electronic states of a total of 24 diatomic molecules AB (A = Sc – Ni, B = Cu/Ag/Au). In the  $\Lambda - S$  coupling scheme, the low-lying molecular states derive from the lowest-lying separated atom limit(s)  $A(3d^{m-2(1)}4s^{2(1)} : (2S+1)L) + B((k-1)d^{10}ks^1 : ^2S)$ , where the multiplicity  $2S + 1$  ranges from 1 to 7, L is either S, or P, or D, or F,  $m = 3(\text{Sc}) - 10(\text{Ni})$ , and  $k = 4(\text{Cu})$ ,  $5(\text{Ag})$ , or  $6(\text{Au})$ . Complete active space self-consistent field (CASSCF), followed by multi-reference configuration interaction (MRCI) was used to construct full potential energy curves for these electronic states. Relativistic effects were treated and probed in a two-step procedure. Scalar terms were considered using the spin-free Douglas-Kroll-Hess (DKH) Hamiltonian.[2] Spin-orbit coupling was subsequently calculated perturbatively *via* the spin-orbit terms of the Breit-Pauli Hamiltonian based on the CASSCF wavefunctions. Spectroscopic constants as well as dipole moments are also reported. Full spin-orbit coupled potential energy curves are constructed for the low-lying states of NiCu and NiAg. In addition, the exact 2-component (X2C) Hamiltonian along with the Kramers-restricted configuration interaction (KRCI) approach[3] was utilized for the atoms and for the copper-containing diatomics. The relativistic results were then compared with the scalar relativistic calculations plus perturbative treatment of spin-orbit coupling. In the case of CoCu, relativistic effects have been monitored through the variation of the fine structure constant ( $\alpha = 1/c$ ) at  $r = 2.30 \text{ \AA}$ , at  $r = 3.30 \text{ \AA}$ , and at  $r = 8.00 \text{ \AA}$ . Core correlation effects, spin-orbit coupling, and basis set incompleteness have been probed for some selected cases. For 23 out of the 24 diatomics considered in the present work, it is shown that there is a direct mapping from the ground states of the monocations  $A^+((2S+1)L_J)$  to the ground states of the diatomics  $AB(X^{(2S'+1)}\Lambda_\Omega^{max})$ :  $S = S'$ ,  $L \rightarrow \Lambda^{max}$ , and  $J = \Omega$ .

- [1] D. Sellmyer and R. Skomski, eds., *Advanced Magnetic Nanostructures*, Springer, New York, (2006).
- [2] G. Jansen and B. A. Hess, *Phys. Rev. A*, 39, 6016, (1989).
- [3] T. Fleig, J. Olsen, and L. Visscher, *J. Chem. Phys.*, 119, 2963, (2003).

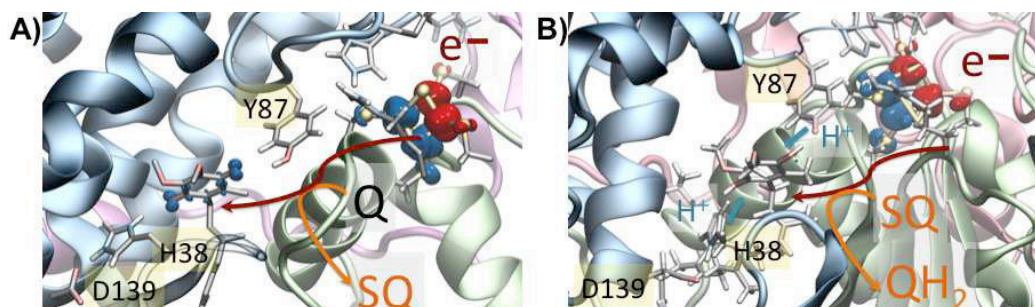
## Terminal Electron-Proton Transfer Dynamics coupled to Quinone reduction in Respiratory Complex I

Ana P. Gamiz-Hernandez<sup>1</sup>, Alexander Jussupow<sup>1</sup>, Mikael P. Johansson<sup>1,2</sup>,  
Ville R. I. Kaila<sup>1</sup>

<sup>1</sup>Department of Chemistry, Technical University of Munich, Lichtenbergstr. 4, D-85747, Garching, Germany

<sup>2</sup>Department of Chemistry, University of Helsinki, P. O. Box 55, FI-00014 Helsinki, Finland

Complex I (NADH:ubiquinone oxidoreductase) contains 8-9 iron sulfur clusters (ISC) in its hydrophilic domain responsible of transferring two electrons from NADH/FMN couple to the quinone binding site, thus initiating the signal that triggers proton pump across its membrane. Although the exact coupling for this long-range proton-electron transfer process remains unclear, emerging data indicates that the initial quinone (Q) reduction to quinol (QH<sub>2</sub>) process plays a central role in activating the proton pumping machinery. In order to probe the energetics, dynamics, and molecular mechanism for the proton-coupled electron transfer (PCET) process linked to Q reduction, we employ here multi-scale quantum and classical molecular simulations, to model the relevant electronic states from Q to QH<sub>2</sub> that may play a role in the activation of proton pump. We find that conformational changes in the hydrogen-bonded Q-binding modes regulate the rate of eT from the terminal N2 iron-sulfur center. Our combined data reveal how the dynamics of complex I-bound Q modulates the rate of terminal electron transfer, and how conserved residues in the Q-chamber contribute to the overall PCET process.



Sequence of eT and pT between N2 and Q based on our calculations. A) The first eT from N2 to Q forms anionic semiquinone (SQ). B) The second electron moves from N2 to the SQ, and couples with pT from H38 and Y87, leading to formation of QH<sub>2</sub>.

- [1] V. Sharma, G. Belevich, A. P. Gamiz-Hernandez, T. Rog, I. Vattulainen, M. L. Verkhovskaya, M. Wikström, G. Hummer, V. R. I. Kaila, *Proc. Natl. Acad. Sci. USA* **112**, 11571 (2015).
- [2] A. Di Luca, A. P. Gamiz-Hernandez, V. R. I. Kaila, *Proc. Natl. Acad. Sci. USA*, (in press), (2017).

## **Toward a W4-F12 approach: Can explicitly correlated and orbital-based ab initio CCSD(T) limits be reconciled?**

**Nitai Sylvetsky<sup>1</sup>, Kirk A. Peterson<sup>2</sup>, Amir Karton<sup>3</sup>, and Jan M. L. Martin<sup>1</sup>**

<sup>1</sup> *Department of Organic Chemistry, Weizmann Institute of Science, 76100 Rehovot, Israel*

<sup>2</sup> *Department of Chemistry, Washington State University, Pullman, Washington 99164-4630, USA*

<sup>3</sup> *School of Chemistry and Biochemistry, The University of Western Australia, Perth, WA 6009, Australia*

In the context of high-accuracy computational thermochemistry, the valence coupled cluster with all singles and doubles (CCSD) correlation component of molecular atomization energies presents the most severe basis set convergence problem, followed by the (T) component. In the present paper, we make a detailed comparison, for an expanded version of the W4-11 thermochemistry benchmark, between, on the one hand, orbital-based CCSD/AV{5,6}Z+d and CCSD/ACV{5,6}Z extrapolation, and on the other hand CCSD-F12b calculations with cc-pVQZ-F12 and cc-pV5Z-F12 basis sets. Apparent differences between orbital-based and CCSD-F12b basis set limits disappear if basis sets with additional radial flexibility, such as ACV{5,6}Z, are used for the orbital calculation. Counterpoise calculations reveal that, while total atomization energies with V5Z-F12 basis sets are nearly free of BSSE, orbital calculations have significant BSSE even with AV(6+d)Z basis sets, leading to non-negligible differences between raw and counterpoise-corrected extrapolated limits. Previous reports that all-electron approaches like HEAT (high-accuracy extrapolated ab-initio thermochemistry) lead to different CCSD(T) limits than “valence limit+CV correction” approaches like Feller-Peterson-Dixon and Weizmann-4 (W4) theory can be rationalized in terms of the greater radial flexibility of core-valence basis sets. For (T) corrections, conventional CCSD(T)/AV{Q,5}Z+d calculations are found to be superior to scaled or extrapolated CCSD(T)-F12b calculations of similar cost. For a W4-F12 protocol, we recommend obtaining the Hartree-Fock and valence CCSD components from CCSD-F12b/cc-pV{Q,5}Z-F12 calculations, but the (T) component from conventional CCSD(T)/aug'-cc-pV{Q,5}Z+d calculations using Schwenke's extrapolation; post-CCSD(T), core-valence, and relativistic corrections are to be obtained as in the original W4 theory. W4-F12 is found to agree slightly better than W4 with ATcT (active thermochemical tables) data, at a substantial saving in computation time and especially I/O overhead.

## Investigation of the Gas-Phase Hydrolysis of Organocuprates by Quantum Chemical and Master Equation Calculations

Thomas Auth<sup>1</sup>, Martin Diefenbach<sup>2</sup>, Aliaksei Putau<sup>1</sup>, Isabell Grübner<sup>2</sup>, Konrad Koszinowski<sup>1</sup>

<sup>1</sup>*Institut für Organische und Biomolekulare Chemie, Georg-August-Universität Göttingen, Tammannstraße 2, 37077 Göttingen, Germany*

<sup>2</sup>*Institut für Anorganische und Analytische Chemie, Johann Wolfgang Goethe-Universität Frankfurt, Max-von-Laue-Straße 7, 60438 Frankfurt am Main, Germany*

Electrospray ionization quadrupole ion-trap mass spectrometry (ESI-QIT-MS) has proven to be an appropriate tool for probing synthetically valuable organocuprate reagents and thus, to gain a better understanding of their reactivity.<sup>[1–3]</sup> Following this pioneering work, ESI-QIT-MS was applied to quantify the hydrolysis kinetics of various isolated organocuprates ( $[\text{Li}_{n-1}\text{Cu}_n\text{R}_{2n}]^-$ ,  $n = 1 - 3$ ,  $\text{R} = \text{Me, Bu, Ph}$ ) within the QIT ( $p(\text{H}_2\text{O}) \approx 10 \mu\text{bar}$ ) to unravel structure-reactivity relations (Figure 1).

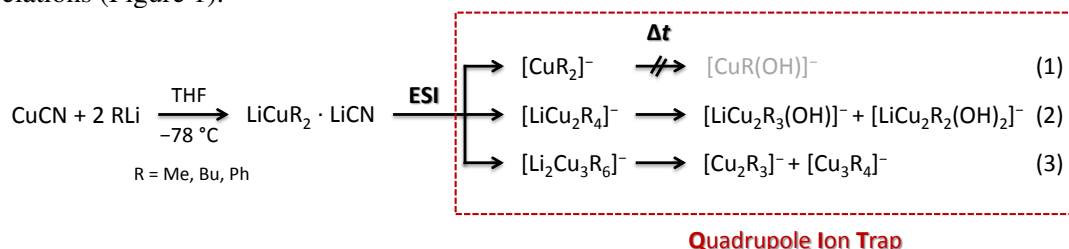


Figure 1: Observed gas-phase reactivity of organocuprates after isolation within a QIT. Organocuprates in the gas phase were obtained via ESI of solutions of cyanocuprates.

In order to understand the experimental results at a fundamental level, the PESs for the hydrolysis of the observed organocuprates were investigated. Taking into account crystal structures of organocuprates,<sup>[4]</sup> geometries were obtained by PBE0-D3BJ/6-31+G(d)/ECP10MWB calculations. Moreover, single point energies were calculated at the CCSD(T)-F12b/CBS(D,T)/ECP10MDF (for  $\text{R} = \text{Me}$ ) and DLPNO-CCSD(T)/CBS(T,Q)/ECP10MDF (for  $\text{R} = \text{Bu, Ph}$ ) level. To assess the quantum chemical results with respect to the experimental data, hydrolysis rate constants were determined by master equation calculations. These calculations involved the inverse Laplace transform method for barrierless association/dissociation steps and RRKM theory for unimolecular isomerizations along the reaction coordinate.

In conclusion, the detailed picture obtained from theory not only qualitatively, but also quantitatively predicts the observed reactivity for  $[\text{Li}_{n-1}\text{Cu}_n\text{R}_{2n}]^-$  ( $n = 1, 2$ ) and emphasizes the importance of the lithium counter-ion for the nucleophilic reactivity of organocuprates.

[1] A. Putau, K. Koszinowski, *Organometallics* **29**, 3593 (2010).

[2] A. Putau, K. Koszinowski, *Organometallics* **30**, 4771 (2011).

[3] A. Putau, M. Wilken, K. Koszinowski, *Chem. Eur. J.* **19**, 10992 (2013).

[4] R. P. Davies, *Coord. Chem. Rev.* **255**, 1226 (2011).

## Effect of dipole moment on formation of trap states in CdS nanocrystals

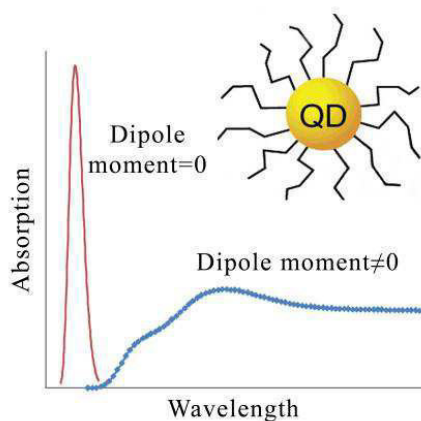
Anuar Aldongarov<sup>1</sup>, Irina Irgibaeva<sup>2,3</sup>, Aliya Assilbekova<sup>1</sup>

<sup>1</sup>*Department of Technical Physics, L.N. Gumilyov Eurasian National University, 2 Satpayev str., Astana, Kazakhstan*

<sup>2</sup>*Luminescent materials research center Ltd., 5/2 Abylay Khan av., Astana, Kazakhstan*

<sup>3</sup>*Laboratory of physical and quantum chemistry, L.N. Gumilyov Eurasian National University, 2 Satpayev str., Astana, Kazakhstan*

Passivation of quantum dots is a crucial condition determining their optical properties. Dangling bonds on the surface of nanocrystals are commonly considered as the main reason for trap states formation. Results obtained via density functional theory approximation indicate the importance of dipole moment value in formation of deep trap states. Correlation between dipole moment value and deepness of trap states location was demonstrated using Cd<sub>4</sub>S cluster as a model basis and different number of SH groups as passivating agents. Namely the high values of dipole moment provide higher number of trap states. Trap states density value was used for estimation of effect of dipole moment. Rearranging of the same number of SH groups also indicates dipole moment effect on electronic spectra. Application of electrostatic field oriented against dipole moment vector also confirms importance of dipole moment in formation of optical properties of nanocrystals. Therefore one may consider the passivation process as the way of decreasing of dipole moment of CdS nanocrystals.



**Spherical or Prismatic:  
A Computational Study of Metal-Doped Ten-Vertex Lead Clusters**

**Matei-Maria Uță<sup>1</sup>, Amr Ali Ahmed Ali Attia<sup>1</sup>, Robert Bruce King<sup>2</sup>**

<sup>1</sup>*Faculty of Chemistry and Chemical Engineering / Babeş-Bolyai University,  
11 Arany János str., RO-400028 Cluj-Napoca, Romania; e-mail: umatei@chem.ubbcluj.ro*

<sup>2</sup>*Department of Chemistry / University of Georgia  
Athens, Georgia, 30602, United States; e-mail: rbking@uga.edu*

Doped main group element clusters having ten vertices are known to exhibit various geometries. Among these, one of the most significant developments is the discovery of the clusters  $M@Ge_{10}^{3-}$  for  $M=Fe$ [1] and  $M=Co$ [2], in which the outer  $Ge_{10}$  polyhedron is a pentagonal prism with no triangular faces at all, rather than a deltahedral structure of the type predicted by the Wade-Mingos rules. Our DFT (Density Functional Theory) studies on these two clusters [3][4] were in accordance with the experimental results. It appeared this effect may be a consequence of the steric requirements of the interstitial metal atom since the reported  $Fe@Sn_{10}^{3-}$ [5] which consists of a larger  $Sn_{10}$  cage relative to a  $Ge_{10}$  cage, seems to exhibit a more spherical geometry. However, in a subsequent paper by the same group discussing the bonds in this type of clusters [6], the authors suggest that the occurrence of these unusual prismatic geometries is related to electronic effects.

In this work we have extended our computational studies to the ten-vertex lead clusters doped with iron and cobalt, in order to check the preferred geometries for these systems consisting of an even larger cage.

- [1] B. Zhou, M. S. Denning, D. L. Kays, J. M. Goicoechea, *J. Am. Chem. Soc.* **132**, 2802 (2009).
- [2] J. Q. Wang, S. Stegmaier, T. F. Fässler, *Angew. Chem. Int. Ed.* **48**, 1998 (2009).
- [3] M. M. Uță, D. Cioloboc, R. B. King, *J. Phys. Chem. A*, **116**, 9197 (2012).
- [4] M. M. Uță, D. Cioloboc, R. B. King, *Inorg. Chem.* **51**, 3498 (2012).
- [5] T. Krämer, J. C. A. Duckworth, M. D. Ingram, B. Zhou, J. E. McGrady, J. M. Goicoechea, *Dalton Trans.* **42**, 12120 (2013).
- [6] G. Espinoza-Quintero, J. C. A. Duckworth, W. K. Myers, J. E. McGrady, J. M. Goicoechea, *J. Am. Chem. Soc.* **136**, 1210 (2014).

## Revealing multi-centre bonding contributions from an electron density perspective using FALDI

**D. M. E. van Niekerk<sup>1</sup>, I. Cukrowski<sup>1</sup>, J. H. de Lange<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, Faculty of Natural and Agricultural Sciences, University of Pretoria, Lynnwood Road, Hatfield, Pretoria 0002, South Africa*

Fragment, Atomic, Localised, Delocalised and Interatomic (FALDI) electron density (ED) decomposition scheme [1] provides an exhaustive decomposition of the total ED at any coordinate  $\mathbf{r}$  in real-space into that which is localised to a specific atomic basin (*loc*-ED) and that which is delocalised between two atomic basins (*deloc*-ED). The total *deloc*-ED is further decomposed into contributions that concentrate (bonding), deplete (non-bonding) and remove (antibonding) ED, as coming from all atoms in a molecular system. In so doing, the multi-centre bonding character of an interaction can be determined by measuring these ED contributions at the quantum theory of atoms in molecules (QTAIM)-defined bond critical point (BCP).

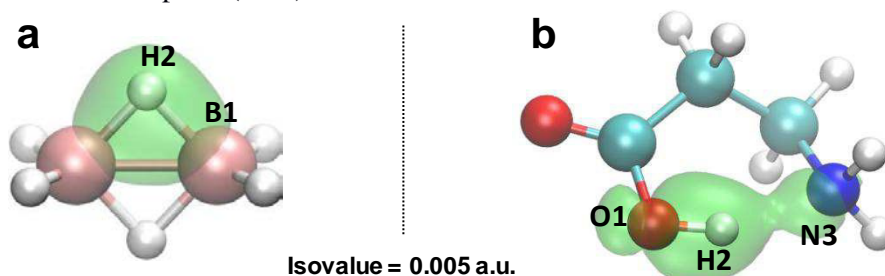


Fig. 1 FALDI-calculated isosurfaces of *deloc*-ED in 3D-space of atom pair B1–H2 of diborane (a) and atom pair O1–H2 plus atom pair H2–N3 of  $\beta$ -alanine (b).

We identified and quantified the specific bonding contributions from the *deloc*-ED distribution for three interactions that display varying degrees of multi-centre character: (i) covalent C–C bond of *n*-butane, predominantly bi-centric, (ii) B–H bond of diborane, large degree of multi-centre bonding character, Fig. 1a, and (iii) an intramolecular hydrogen bond of  $\beta$ -alanine, moderate degree of multi-centre bonding character, Fig. 1b. Our analyses so far show that all interactions (for molecules consisting of at least three atoms) have some degree of multi-centre bonding character. This novel methodology used to evaluate the nature of a chemical bond is consistent with contemporary interpretation – an interaction is not viewed as only a local event, but rather as a molecular-wide event [2].

- [1] J. H. de Lange, I. Cukrowski, *J. Comput. Chem.* **38**, 981 (2017).
- [2] I. Cukrowski, *Comput. Theor. Chem.* **1066**, 62 (2015).



## How to Quantify Charge Transfer Character of Excited States in Transition Metal Complexes

**Sebastian Mai<sup>1</sup>, Felix Plasser<sup>1</sup>, Hugo Gattuso<sup>2</sup>, María Fumanal<sup>3</sup>, Antonio Monari<sup>2</sup>, Chantal Daniel<sup>3</sup>, Leticia González<sup>1</sup>**

<sup>1</sup>*Institute of Theoretical Chemistry, Faculty of Chemistry, University of Vienna, Währinger Straße 17, 1090 Wien, Austria.*

<sup>2</sup>*Théorie-Modélisation-Simulation, CNRS/Université de Lorraine–Nancy, SRSMC Boulevard des Aiguillettes, Vandoeuvre-lès-Nancy, Nancy, France.*

<sup>3</sup>*Laboratoire de Chimie Quantique, Institut de Chimie Strasbourg, UMR-7177 CNRS/Université de Strasbourg, 1 Rue Blaise Pascal BP 296/R8, F-67008 Strasbourg, France.*

Analyzing and quantifying the excited-state wave function character of molecules with intricate electronic structure properties—like transition metal complexes—is a challenging task. An important aspect of this problem is the participation of charge transfer (CT), e.g., leading to states of metal-to-ligand or ligand-to-ligand CT character. Using analysis tools from the TheoDORÉ package [1] by one of us, here we investigate the excited states of such complexes. The analysis employs a fragment-based two-dimensional population analysis (see Figure 1) of transition density matrices obtained from time-dependent density functional theory calculations.

The exemplary system investigated is  $[\text{Re}(\text{ImH})(\text{CO})_3(\text{Phen})]^+$ , a transition metal complex which recently gained much interest as a chromophore in the study of long-range electron-transfer in proteins [2]. Besides this relevance,  $[\text{Re}(\text{ImH})(\text{CO})_3(\text{Phen})]^+$  possesses a complex electronic structure due to its different ligands and the strong interaction of the metal center and the carbonyls [3, 4]. Using our analysis method, we show quantitatively that the metal center and the carbonyl ligands are electronically tightly coupled and have to be considered as one electronic unit.

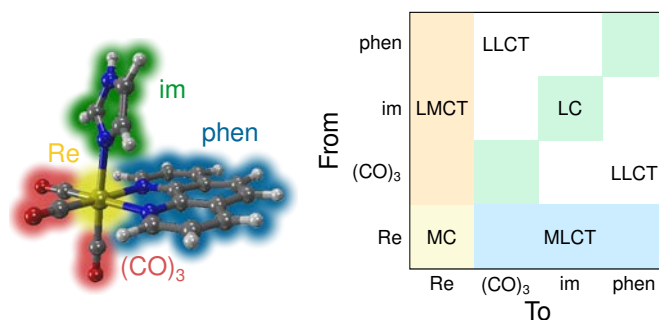


Figure 1: Possible fragmentation of  $[\text{Re}(\text{ImH})(\text{CO})_3(\text{Phen})]^+$  and charge transfer matrix.

[1] F. Plasser A. Dreuw, *J. Phys. Chem. A* **119**, 1023–1036 (2015).

[2] C. Shih et al., *Science* **320**, 1760–1762 (2008).

[3] R. Baková et al., *Coord. Chem. Rev.* **255**, 975 – 989 (2011).

[4] M. Fumanal C. Daniel, *J. Phys. Chem. A* **120**, 6934–6943 (2016).



## Performance of GGA and hybrid density functionals in calculation of lattice thermal conductivity of $\text{Cu}_2\text{O}$

J. Linnera<sup>1</sup>, A. J. Karttunen<sup>1</sup>

<sup>1</sup>*Department of Chemistry and Materials Science, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland*

One fundamental property of all materials is the conduction of heat energy. Depending on the application at hand, it is often necessary to either maximize it or bring it down as much as possible. Although the theory behind heat conductivity ( $\kappa$ ) is well established, accurate tailoring of  $\kappa$  is still a bit of a far reach. With modern computational capacity it is already feasible to calculate and predict *ab initio* the lattice thermal conductivity from simple Si and Ge to complex layered hybrid materials, which can guide materials design already in the early stages of research.

We present, to our knowledge, first lattice thermal conductivities calculated using hybrid density functional theory. We computed  $\kappa_l$  of  $\text{Cu}_2\text{O}$  with the GGA PBE and the hybrid functional PBE0 using CRYSTAL14 and Phono3py, and found striking differences in performance. Earlier calculations have shown that PBE can produce satisfactory results when compared to experiment, but in the case of  $\text{Cu}_2\text{O}$  it results in an error of more than -40 %. PBE0, on the other hand, has an error of only around 7 % in the relevant temperature range for applications ( $\geq 300$  K).

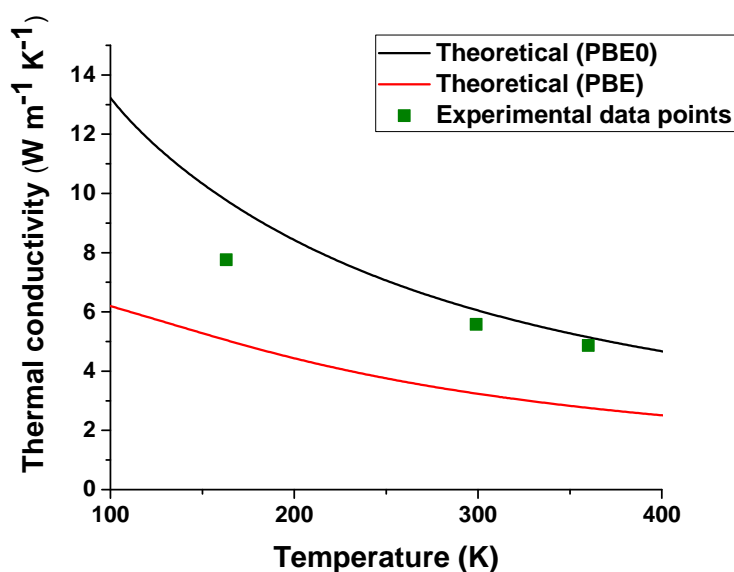


Figure 1: Calculated lattice thermal conductivity of  $\text{Cu}_2\text{O}$  between 100 and 400 K.

## Conformational scan across reaction path may give us fake transition states with low energy.

Andrus Metsala<sup>1</sup>, Sergei Žari<sup>1</sup>, Tõnis Kanger<sup>1</sup>

<sup>1</sup>Department of Chemistry and Biotechnology, Institute of Chemistry, Tallinn University of Technology

<sup>1</sup>Ehitajate tee 5, Tallinn, 19086, Estonia

In order to build a realistic reaction path sometimes conformational scan along reaction coordinate is performed. We clarify some problems which may arise when pursuing such a treatment. This is done with the help of molecular mechanical and ab initio methods on the example of Aza-Michael isatin imine reactions [1]. We use a method such as a conformer scan on the points of the reaction coordinate of approaching reagents. A close look is taken at the reaction coordinate development -- approaching fragments forming a covalent bond between fragments N and C atoms. The most probable reaction paths (Figure) and transition states are found. Some of the transition states are found to be nonreactive, although they are lower in energy than normal (reactive) states. The solvent effect is also taken into account. The main catalytic effect of the solvent seems to have been not simply lowering the activation barrier but rather opening totally new reaction paths.

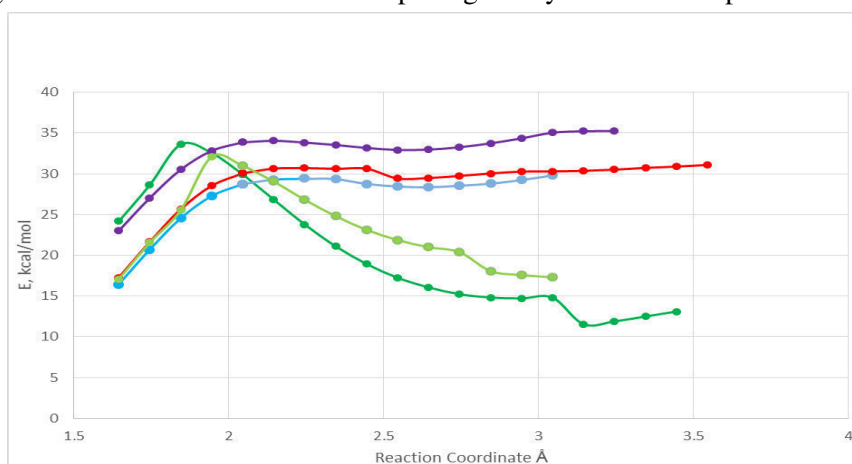


Figure. Reaction paths of the approaching reactants, forming a covalent bond (left) between fragments N and C atoms. Checking tentative transition states toward reagents (right) it appeared that some of them are not converging to the reactants (right, upper lines).

[1] A. Metsala, S. Žari, T. Kanger, *Chem.Cat.Chem.* **8**, 2961 (2016).

## Inevitability of *ab initio* calculations in determining large magnetic anisotropy

Arup Sarkar<sup>1</sup>, Gopalan Rajaraman<sup>2</sup>

<sup>1,2</sup>Department of Chemistry, IIT Bombay, Powai, Mumbai- 400076, India

The coordination complexes of transition metal systems exhibit various spectral and magnetic properties due to their diverse d-orbital electronic configurations. To deal with these types of systems one must consider also the effects of excited states along with the ground state. Fundamentally these excited state terms arise due to the electron-electron repulsion and ligand field effects. To account for these excited state properties theoretically, single determinant wave-function based theories are not useful to interpret the phenomena. In this regard, multi-determinant wave-function approach has been proven to be crucial in determine the microscopic properties of these systems in the recent years.

Though small but spin-orbit coupling (SOC) on these systems is an important perturbation after the ligand effects which induces zero-field splitting (ZFS) and molecular nanomagnet is among the several fields which is driven based on this parameter. The final spin-eigen states which determines the spin-reversal barrier for magnetization depends on the interplay between the spin free and spin-orbit states. For the first-row mono nuclear 3d-metal complexes, this ZFS values are generally not very large but still it can reach as high as  $\sim 200\text{--}400\text{ cm}^{-1}$ .<sup>1</sup> Quantification of such a huge magnetic anisotropy sometimes becomes very difficult from experimental point of view, because the energy gaps are beyond the spectroscopic limits. Advanced first principle methods such as CASSCF-NEVPT2 can compute this energy gap (or splitting) very precisely and also can elucidate the underlying theory behind this splitting.<sup>2</sup> Though full CI is not possible in these systems but a full CI within an active space of *n*-electrons in five d-orbitals is a reasonable technique to obtain reliable solution.

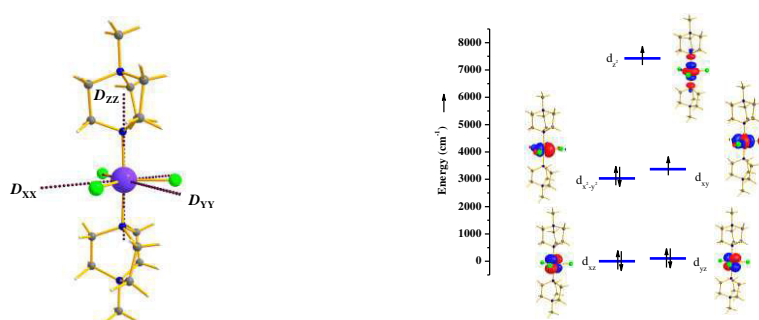


Figure: The *D*-tensor direction and the d-orbital splitting diagram of  $[\text{Ni}(\text{MeDABCO})_2\text{Cl}_3]^+$  complex.

- [1] K. E. R. Marriott, L. Bhaskaran, C. Wilson, M. Medarde, S. T. Ochsenbein, S. Hill and M. Murrie, *Chem. Sci.* **6**, 6823-6828 (2015).
- [2] M. Atanasov, D. Aravena, E. Suturina, E. Bill, D. Maganas and F. Neese, *Coord. Chem. rev.* **289-290**, 177-214 (2015).

## It's Getting Hot: Temperature-Dependent Wigner Sampling

**J. Patrick Zobel, Juan J. Nogueira, Leticia González**

*Institute of Theoretical Chemistry, University of Vienna, Währinger Straße 17, Vienna, Austria*

The photodynamics of molecular systems can be studied directly by simulating the excited-state processes with trajectory-ensemble-based methods such as surface hopping or multiple spawning. The fate of the ensemble relies on an accurate sampling of the initial conditions, i.e., initial coordinates and momenta. There are two approaches commonly used: “thermal sampling” (TS) where initial conditions are taken from snapshots of ground-state molecular dynamics trajectories, and “quantum sampling” (QS) where initial conditions are calculated from a (harmonic) Wigner distribution.[1] QS is typically performed at  $T = 0$  K and, thus, does not account for finite temperature effects, while in thermal sampling the zero-point vibrational energy (ZPE) is missing which accounts for the largest fraction of the total energy at moderate temperatures. This dilemma can elegantly be solved by making the Wigner distribution in the QS temperature-dependent[2], simply by allowing the population of excited vibrational states. Using a thermal Wigner sampling, one is able to use more realistic initial conditions in the excited-state simulations. By including the full energy of the system, i.e., the sum of ZPE and the thermal energy contribution, small energy barriers in the excited states can be overcome more easily thus increasing reaction rates. Additionally, due to the population of vibrationally excited states through finite temperature, an extended conformational space is sampled by moving away from the maximum probability of zero displacement in the vibrational ground state to larger displacements in excited vibrational states –which is especially important for low-frequency modes such as out-of-plane torsions of ring systems. As an example, we present our study on 2-nitronaphthalene, an organic compound exhibiting ultrafast intersystem crossing, and we show the effects that including temperature in the generation of the initial conditions has on its excited-state dynamics.[3]

[1] M. Barbatti and K. Sen, *Int. J. Quant. Chem.* **116**, 762 (2016)

[2] J. P. Zobel, J. J. Nogueira, and L. González, in preparation (2017)

[3] J. P. Zobel, J. J. Nogueira, and L. González, in preparation (2017)

## Conformational Dependence of Partial Charges Derived from Quantum-Mechanical Calculations

Jagna Witek<sup>1</sup>, Victor H. Rusu<sup>1</sup>, Charleen Don<sup>1</sup>, Sereina Riniker<sup>1</sup>

<sup>1</sup>*Department of Chemistry and Applied Biosciences/Laboratory of Physical Chemistry/Group for Computational Chemistry, ETH Zurich, Vladimir-Prelog-Weg 2, Zurich, Switzerland*

In molecular dynamics (MD) simulations, the accuracy of the underlying force field is crucial for the proper description of the properties of the simulated system, e.g. density, heat of vaporization, or free energy of solvation ( $\Delta G_{\text{solv}}$ ). While the amino-acid building blocks in protein force fields can be parametrized by fitting to experimental data, the current schemes to determine force-field parameters for small organic molecules require an individual parametrization for each molecule. The most popular approach to this aim is to inherit the parameters of the bonded and van der Waals interactions from a protein force field using a matching strategy, and to derive the partial charges from quantum-mechanical (QM) calculations.

A basic assumption of classical force fields is that the partial charges of the atoms are fixed, i.e. they do not vary as a function of the conformation or environment. The electron density in a QM calculation on the other hand does. The goal of this study is to quantify the impact that the conformation used in the QM calculation has on the resulting set of partial charges. To this end, a test set of 16 compounds with the ability to form an intramolecular hydrogen bond were selected from the FreeSolv database [1]. For each molecule, two conformations are used to derive partial charges, i.e. with and without the intramolecular hydrogen bond. To determine which of the two conformer-selection strategies is better suited, the solvation free energies in water are calculated with the different charge sets. Two different force fields are employed: (i) the GROMOS-compatible automatic topology builder (ATB) [2], and (ii) the general Amber force field (GAFF) [3]. The estimated solvation free energies are compared to the experimental values of  $\Delta G_{\text{solv}}$  reported in the FreeSolv database [1]. The results show that the differences in the charge sets due to the conformation used in the QM calculation can lead to substantial differences in the estimated  $\Delta G_{\text{solv}}$ .

[1] Mobley, D. L.; Guthrie, J. P.; *J. Comput. Aid. Mol. Des.*, **28**, 711–720 (2014).

[2] Koziara, K. B.; Stroet, M.; Malde, A. K.; Mark, A. E.; *J. Comput. Aid. Mol. Des.*, **28**, 221-233 (2014).

[3] Wang, J.; Wolf, R. M.; Caldwell, J. W.; Kollman, P. A.; Case, D. A.; *J. Comput. Chem.*, **25**, 1157-1174 (2004).

## **A general intermolecular force field based on tight-binding quantum chemical calculations (xTB-IFF)**

**Jana Pisarek, Christoph Bannwarth, Eike Caldeweyher, Andreas Hansen,  
Stefan Grimme**

*Mulliken Center for Theoretical Chemistry,  
Institut für Physikalische und Theoretische Chemie der Universität Bonn  
Berlingstr. 4, D-53115 Bonn, Germany*

A black-box type procedure is presented for the generation of a molecule-specific, intermolecular potential energy function [1]. The method uses quantum chemical (QC) information from our recently published extended tight-binding semi-empirical scheme (GFN-xTB) [2] and can treat non-covalently bound complexes and aggregates with almost arbitrary chemical structure. The necessary QC information consists of the equilibrium structure, Mulliken atomic charges, charge centers of localized molecular orbitals, and also of frontier orbitals and orbital energies. The molecular pair potential includes model density dependent Pauli repulsion, penetration, as well as point charge electrostatics, the newly developed D4 dispersion energy model [3], Drude oscillators for polarization, and a charge-transfer term. Only one element-specific and about 20 global empirical parameters are needed to cover systems with nuclear charges up to Radon ( $Z = 86$ ). The method is tested for standard small molecule interaction energy benchmark sets where it provides accurate intermolecular energies and equilibrium distances. Examples for structures with a few hundred atoms including charged systems demonstrate the versatility of the approach. The method is implemented in a stand-alone computer code which enables rigid-body, global minimum energy searches for molecular aggregation or alignment.

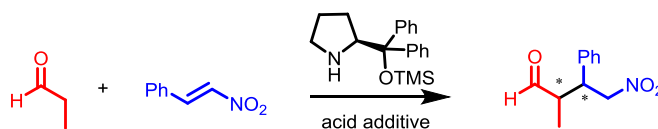
- [1] S. Grimme, C. Bannwarth, E. Caldeweyher, J. Pisarek, and A. Hansen, submitted: within the *J. Chem. Phys.* 'From Quantum Mechanics to Force Fields' special issue (2017).
- [2] S. Grimme, C. Bannwarth, and P. Shushkov, *J. Chem. Theory Comput.* (2017), **13**, 1989-2009.
- [3] E. Caldeweyher, C. Bannwarth, and S. Grimme, submitted: *J. Chem. Phys.* (2017).

## On the Controversial Stereoselectivity Models of Organocatalyzed Michael Additions of Aldehydes to Nitroalkenes

Tamás Földes, Ádám Madarász, Ágnes Révész, Zoltán Dobi, Szilárd Varga,  
Imre Pápai

*Institute of Organic Chemistry, Research Centre for Natural Sciences, Hungarian  
Academy of Sciences, H-1117 Budapest, Magyar tudósok körútja 2, Hungary*

Among the variety of organocatalytic transformations, enantioselective Michael additions between aldehydes and nitroalkenes catalyzed by diarylprolinol derivatives have been the subject of intensive mechanistic studies. Recent investigations have pointed to the importance of experimentally observed cyclic reaction intermediates [1-3], however, views on the specific role of these species in stereocontrol are still controversial. With the aim of gaining further mechanistic insight, we explored the reaction between propanal and nitrostyrene via DFT calculations and kinetic simulations (Figure).



In accordance with experiments, our computational results predict that the overall reaction rate is determined by the protonation of the cyclic intermediates that occurs subsequently to the C-C bond formation [4]. However, the obtained free energy profile suggests that the experimentally observed enantioselectivity cannot be interpreted in the terms of the recently proposed Curtin-Hammett scenario that associates the rate and the stereoselectivity with the protonation step, but a more complex multistep model is applicable. Our suggested model not only resolves the reported controversies regarding the the interpretaion of the stereoselectivity, but it is also consistent with the results of mass spectrometric back reaction screening experiments we carried out.

- [1] D. Seebach, X. Sun, M. Ebert, W. B. Schweizer, N. Purkayastha, A. K. Beck, J. Duschmalé, H. Wennemers, *Helv. Chim. Acta*, **96**, 799-852 (2013)
- [2] J. Burés, A. Armstrong, D. G. Blackmond, *J. Am. Chem. Soc.*, **134**, 6741-6750 (2012)
- [3] G. Sahoo, H. Rahaman, Á. Madarász, I. Pápai, M. Melarto, A. Valkonen, P. M. Pihko, *Angew. Chem. Int. Ed.*, **51**, 13144-13148, (2012)
- [4] T. Földes, Á. Madarász, Á. Révész, Z. Dobi, Sz. Varga, A. Hamza, P. R. Nagy, P. M. Pihko, I. Pápai in preparation.

### A three-state model for the Photo-Fries rearrangement

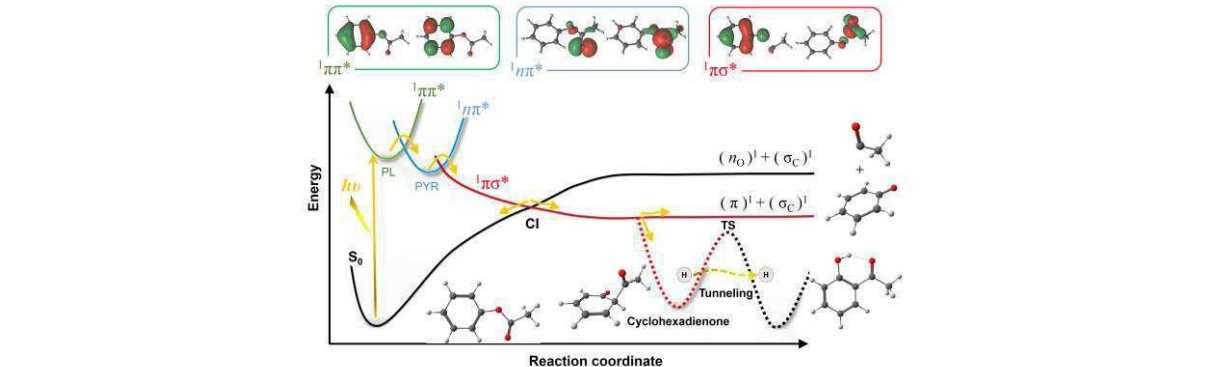
**Josene M. Toldo<sup>1,2</sup>, Mario Barbatti<sup>2</sup>, Paulo F. B. Gonçalves<sup>1</sup>**

*<sup>1</sup>Department of Physical Chemistry/ Institute of Chemistry/ Federal University of Rio Grande do Sul, Av. Bento Gonçalves-9500, Porto Alegre-RS, Brazil*

<sup>2</sup>*Aix Marseille Univ, CNRS, ICR, Marseille, France*

Photo-Fries rearrangement (PFR) is a photochemical conversion of aryl esters to *ortho*- and *para*-hydroxyphenones. This reaction is a key step in the synthesis of a large number of compounds and plays an important role in the design of functional polymers and in the photodegradation of drugs and agrochemicals, being a greener synthetic route, since it can be achieved under milder conditions. Although there are a large number of experimental studies about the mechanism of PFR, the last theoretical work is from 1992 and some points of PFR reaction are still under debate. Given the knowledge gap between theory and the most recent experimental works, our aim has been to provide a comprehensive picture of PFR, based on high-level multiconfigurational theoretical methods.

In this work, we present a three-state model for the Photo-Fries rearrangement (PFR) based on CASSCF(14,12)/CASPT2(14,12) calculations (Figure 1). It provides a comprehensive mechanistic picture of all steps of the reaction, from the photoabsorption to the final tautomerization. The three states participating in the PFR are an aromatic  $^1\pi\pi^*$ , which absorbs the radiation; a pre-dissociative  $^1n\pi^*$ , which transfers the energy to the dissociative region; and a  $^1\pi\sigma^*$ , along which dissociation occurs. The transfer from  $^1\pi\pi^*$  to  $^1n\pi^*$  involves pyramidalization of the carbonyl carbon, while transfer from  $^1n\pi^*$  to  $^1\pi\sigma^*$  takes place through CO stretching. Different products are available after a conical intersection with the ground state. Among them, a recombined radical intermediate, which can yield *ortho*-PFR products after an intramolecular 1,3-H tunneling. The three-state model is developed for phenyl acetate, the basic prototype for PFR, and it reconciles theory with a series of observations from time-resolved spectroscopy. It also delivers a rational way to optimize PFR yields since diverse substituents can change the energetic order of the  $^1\pi\pi^*$  and  $^1n\pi^*$  states, preventing or enhancing PFR.



**Figure 1.** Schematic overview of the three-state model for PFR applied to phenyl acetate.



## Investigation of Perfluorinated Compound-Binding to Human Hepatocyte Nuclear Factor (HNF4 $\alpha$ )

Boz, Esra<sup>1,2</sup> and Stein, Matthias<sup>1</sup>

<sup>1</sup>*Max Planck Institute for Dynamics of Complex Technical Systems, Molecular Simulations and Design Group, Magdeburg, Germany*

<sup>2</sup>*Istanbul Technical University, Department of Chemistry, Istanbul, Turkey*

Hepatocyte nuclear factor 4 $\alpha$  (HNF4 $\alpha$ ) is a member of the nuclear receptor family of ligand-dependent transcription factors but displays properties distinct from other members of this superfamily. It is the most abundant DNA-binding protein in the liver and especially involved in the hepatic glucose and lipid metabolism. It works as a homodimer, which has conserved DNA-binding (DBD) and ligand binding domains (LBD). HNF4 $\alpha$  plays a central regulating role in the control of gene expression in the liver and a large number of critical metabolic pathways are under regulation by this receptor. Inhibition of HNF4 $\alpha$  leads to an increase of hepatic tumors. It is reported that the transactivity of HNF4 $\alpha$  is regulated by several kinds of fatty acids. Also, the crystal structure of human HNF4 $\alpha$  (PDB ID: 4IQR) is found as a complex with a myristic acid (MYR) ligand.

In this study, we investigate the possible competitive binding of several fluorinated long chain organic acid analogues to HNF4 $\alpha$  which have a similar structure to MYR and are known to be potentially toxic for humans. The physiological and industrial compounds are similar in chain length but differ in terms of charge distribution from the physiological ligand due to the highly electronegative fluorine atoms. In order to have a reliable charge distribution model, the charges on the ligand atoms were derived from quantum chemical calculations and incorporated into a force field. Then, several 70ns of MD simulations were carried for a number of receptor-ligand systems.

First, the stability of perfluorooctanoic acid (PFOA) in the receptor was tested by analysing the dynamics of PFOA and comparing them with MYR. The critical interactions of the carboxylic acid group with Ser181, Gly237 and Arg226 residues were observed in a similar fashion for both ligands. They also showed similar hydrophobic interactions with several residues and stabilized in the binding pocket. These results show that PFOA is a possible competitor to MYR binding. Then, docking studies of several fluorinated compounds were performed into the binding cavity of the receptor. Extra precision (XP) scores were obtained for eight perfluorinated compounds ranging from -8.39 to -5.38. The top docking poses of the first four high ranked compounds were submitted to further MD simulations.

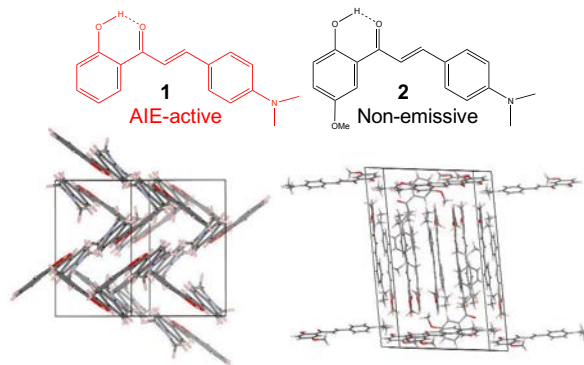
## The role of conical intersections in aggregation induced emission

**Michael Dommett, Miguel Rivera, Rachel Crespo-Otero<sup>1</sup>**

<sup>1</sup>*School of Biological and Chemical Sciences, Materials Research Institute,  
Queen Mary University of London, Mile End Road, London, E1 4NS*

Aggregation induced emission (AIE) occurs when non-emissive chromophores in dilute solution become luminescent upon aggregation. AIE offers a route the manufacture of optoelectronic devices, where highly efficient and tunable luminescence in the solid state is required for optimum performance.<sup>1</sup> A promising class of AIE-active compounds are those exhibiting excited state intramolecular proton transfer (ESIPT). 2'-hydroxychalcones are such species, and have been used as molecular probes in enzyme detection, fingerprint analysis, and as organic lasers.<sup>2</sup> Pertinently, the identity of substituents on the 2'-hydroxychalcone skeleton determines the crystalline structure and the quantum yield of fluorescence. Compound **1** exhibits AIE, whilst compound **2** is dark in both solution and the solid state.<sup>3,4</sup>

To understand the AIE mechanism of **1** and its absence in **2**, we use a hierarchy of models to decouple the influence of i) the electrostatic potential from the crystal ii) exciton coupling and charge transfer iii) electron donating substituents. In particular, we examine how each influence the energy of the nearest conical intersections of the potential energy surfaces, a crucial factor in the competition between radiative and non-radiative relaxation. This systematic approach enables a full evaluation of the mechanism of AIE and extends our understanding to complex chromophores with multiple decay channels.



[1] J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam and B. Z., Tang, *Chem. Rev.*, **115**, 11718–11940 (2015).

[2] V. S. Padalkar and S. Seki, *Chem. Soc. Rev.*, **45**, 169–202 (2015).

[3] X. Cheng, K. Wang, S. Huang, H. Zhang, H. Zhang and Y. Wang, *Angew. Chem., Int. Ed.*, **54**, 8369–8373 (2015).

[4] M. Dommett and R. Crespo-Otero, *Phys. Chem. Chem. Phys.*, **19**, 2409–2416 (2017).

## Carbocatalysis: a computational insight into the metal-free oxidation of ethylbenzene by carbonnanotubes

Tainah Dorina Marforio<sup>1</sup>,

Matteo Calvaresi<sup>1</sup>, Andrea Bottoni<sup>1</sup>

<sup>1</sup>Dipartimento di Chimica "Giacomo Ciamician", UNIBO, Via F. Selmi 2, Bologna, Italy

During the last two decades it has been demonstrated that nanostructured carbon materials (*i.e.* graphene sheets, carbon nanotubes and fullerenes) can play an active role as catalysts in heterogeneous catalysis.<sup>1</sup>

Experiments on oxidized carbonnanotubes (o-CNTs) have shown that ketonic carbonyl groups on the o-CNT surface are responsible for the oxidative dehydrogenation of ethylbenzene (ODE) to styrene with the loss of a water molecule.<sup>2</sup>

Up to date, the ODE reaction mechanism is still unclear. A very general hypothesis suggests a mechanism that proceeds through a first hydrogen radical abstraction. Our purpose was to investigate, at a quantum-mechanical level (DFT), the potential energy surface of the reaction and elucidate the mechanism in detail.

For the sake of simplicity, we studied a (6,6) armchair CNT (12 Å long) and we considered two adjacent oxidized sp<sup>2</sup> carbons (carbonyl groups) on the rim of the tube. Once we proved that the adsorption of ethylbenzene over the o-CNT (see Figure 1) was a favorable process, we calculated the reaction path. We found that the reaction proceeds through a two-step mechanism, with the formation of a stable radical intermediate.

Also, we investigated the possibility that the reaction occurs on the outer surface of the tube. To this purpose we considered two epoxydic groups on the external wall. We found that the reaction proceeds through a first hydrogen abstraction (radical process) followed by the abstraction of a proton and the formation of styrene, water and a defect on the tube surface.

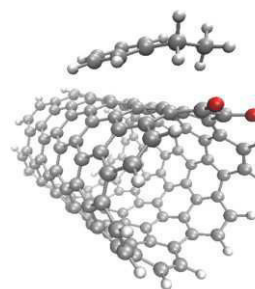


Figure 1

[1] C. K. Chua et al., *Chem. Eur. J.* **21**, 12550 (2015).

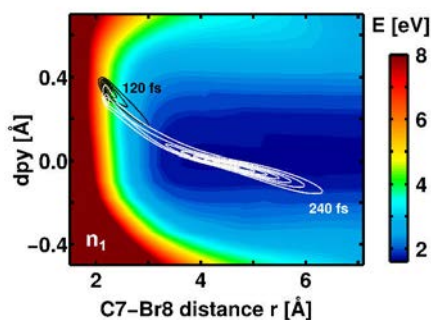
[2] W. Qi et al., *Angew. Chem. Int. Ed.* **54**, 13682 (2015).

## Dynamical studies on the photodissociation of diphenylmethyl bromide

Franziska Schüppel, Matthias K. Roos, Regina de Vivie-Riedle

Department of Chemistry, Ludwig-Maximilians-Universität, Butenandtstr. 5-13,  
Munich, Germany

Carboradicals and -cations are key intermediates for many chemical reactions. They may be generated by UV-laser excitation of carbohalide compounds such as diphenylmethyl bromide. Here, a local  $\pi\pi^*$  excitation occurs, followed by the C-Br bond cleavage leading to radical or ion pairs within a femtosecond timescale. We use both, quantum dynamical and semiclassical on-the-fly dynamical methods to simulate the reaction. In both approaches we employ an ONIOM two-layer method with CASSCF as high level method. In the quantum dynamics we take the solvent environment into account using the Dynamic Continuum ansatz [1] developed in our group. We verify for both simulations the decisive role of two consecutive conical intersections for the product splitting, like we recently showed [2] for chlorine as leaving group. Nonetheless, we report remarkable differences compared to the chlorine case and we especially discuss the role of the pyramidalization of the central carbon atom clearly visible in the wave packet dynamics. We evaluate product ratio and delay times for both approaches and compare them with experimental results. Furthermore we calculate time-resolved spectra using the velocity autocorrelation function obtained by the on-the-fly dynamics. Here we see the importance of different normal modes for both reaction channels. To compare our results with experimentally measured transient absorption spectra we evaluate the quantum dynamics simulation by calculation of the product signal as we recently did with chlorine [3].

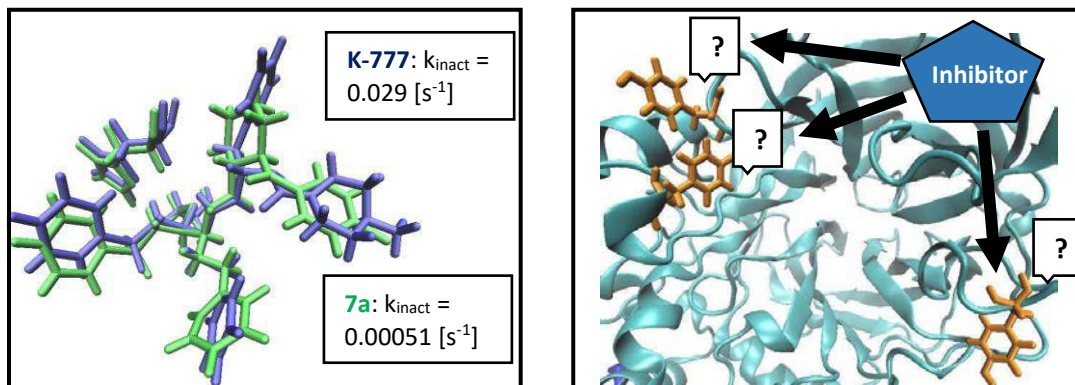


- [1] S. Thallmair, M. Kowalewski, J. P. P. Zauleck, M. K. Roos, R. de Vivie-Riedle, *J. Phys. Chem. Lett.* **5** 3480-3485 (2014).
- [2] S. Thallmair, M. K. Roos, R. de Vivie-Riedle, *Struct. Dyn.* **3** 043205 (2016).
- [3] E. Riedle, M. K. Roos, S. Thallmair, C. F. Sailer, N. Krebs, B. P. Fingerhut, R. de Vivie-Riedle, *Chem. Phys. Lett.* (2017).

## Predicting selectivity for covalent inhibitors from QM/MM, Docking and MD – What is possible?

Thien Anh Le<sup>1</sup>, Bernd Engels<sup>1</sup>

<sup>1</sup>*Institute of physical and theoretical chemistry, University Würzburg, Emil-Fischer-Str.  
42, Würzburg, Germany*



One part of this work concentrates on the investigation of the **accuracy** of MM and QM/MM methods in respect to the selectivity of different vinylsulfones in cysteine proteases of the papain superfamily and have been compared to experimental values obtained by Kerr et al. [1] Therefore, Docking, MD and QM/MM studies have been performed.

Another aspect of interest was the **determination** of the binding site of a covalent inhibitor of *B. megaterium* levansucrase. [2] By performing MD simulations of the covalent protein-inhibitor complex it was possible to investigate the occupation of the active site.

### Why are covalent inhibitors of interest?

Most drugs consist of ligands which interact with their target non-covalently. They have the advantage that they are so unreactive that unintended reactions with DNA or proteins do not take place. However, they have the drawback that generally their free energy of binding does not exceed 15 kcal/mol. Higher binding affinities can only be achieved with ligands which form a covalent bond with their target. Despite famous examples as Penicillin or Aspirin in the past the industry hesitated to develop new covalent drugs because they fear unintended side reactions resulting from the reactivity of ligands. [3] Since about 2005 covalent ligands undergo an intensive renaissance in academia and industry, because various very selective drugs were detected in the last few years. [4][5]

- [1] I. D. Kerr et al., *JBC* **284**, 25697-25703 (2009).
- [2] C. P. Strube et al, *JBC* **286**, 17593-17600 (2011).
- [3] J. Singh et al., *Nat. Reviews*, **10**, 307-317 (2011).
- [4] V. Hirsch, *BioDrugs*, **29**, 167-183 (2015).
- [5] T. Schirmeister et al, *JACS*, **138**, 8332-8335 (2016).

## Systematic calibration of a transferable polarizable force field parameter set

**Koen M. Visscher<sup>1</sup>, William C. Swope<sup>2</sup>, Daan P. Geerke<sup>1</sup>**

<sup>1</sup>*AIMMS Division of Molecular and Computational Toxicology, Faculty of Sciences, Vrije Universiteit Amsterdam, the Netherlands, and* <sup>2</sup>*IBM Almaden Research Center, IBM Research, San Jose, CA 95120*

A systematic approach is followed to develop a polarizable biomolecular force field. Starting from a well-calibrated nonpolarizable force field, condensed-phase interaction parameters can be calibrated using a QM/MM approach for fitting of electrostatic parameters [1], for which we propose a generalization here. We show that transferability of force field parameters can be further improved by a systematic (analytical) approach to the calibration effort [2]. Application of our approaches is demonstrated in the calibration of force field parameter sets for small organic molecules, optimized to reproduce relevant properties of model systems.

- [1] C. R. Vosmeer, A. S. Rustenburg, J. E. Rice, H. W. Horn, W. C. Swope, D. P. Geerke, *J. Chem. Theory Comput.* **8**, 3839 (2012).
- [2] K. M. Visscher, C. R. Vosmeer, R. A. Luirink, D. P. Geerke, *J. Comput. Chem.* **38**, 508 (2017).

## Excited states of molecular aggregates predicted by a model Hamiltonian tuned toward high-level quantum-chemical calculations

Sofia Canola<sup>1</sup>, Nicola Ciarlariello<sup>1</sup>, Yasi Dai<sup>1</sup>, Gaetano Ricci<sup>1</sup>, Wenlan Liu<sup>2</sup>, Reinhold F. Fink<sup>3</sup> and Fabrizia Negri<sup>1</sup>

<sup>1</sup> *Dipartimento di Chimica "G. Ciamician", University of Bologna, via F. Selmi 2, Bologna, Italy.*

<sup>2</sup> *Institut für Theoretische Chemie, University of Stuttgart, Pfaffenwaldring 55, Stuttgart, Germany and InnovationLab GmbH, Speyerer St. 4, Heidelberg, Germany*

<sup>3</sup> *Institut für Physikalische und Theoretische Chemie, University of Tübingen, Auf der Morgenstelle 1, Tübingen, Germany.*

The analysis of the excited states of a molecular aggregate is of great importance in order to provide a theoretical modeling of its opto-electronic and energy transfer properties. As an aggregate model, a molecular dimer is usually taken into account. It has been widely proven that a comprehensive theoretical description of its electronic properties requires the inclusion of charge transfer excitations (CT) along with excitations localized on single molecular units (LE) [1,2]. Perylene-bisimide (PBI) is a well known dye employed in organic opto-electronic, due to its favorable optical and charge transport properties. The electronic properties of PBI dimers have been extensively studied with different methods and in particular by means of a simple 4×4 model Hamiltonian, which accounts for the interactions between localized excitations and charge transfer configurations, and whose matrix elements have been parametrized at different levels of theory [1,3]. However, the study of the excited states of larger aggregates is desirable, since opto-electronic processes occur in the condensed phase [2]. In the present study larger molecular aggregates of PBIs have been considered: the model Hamiltonian employed for the dimer has been extended and its elements have been parametrized at the TD-DFT level of theory. In order to validate the approach, a general procedure to transform the excited states of larger aggregates from delocalized to localized excitations, employing a unitary transformation, has been set up. Interestingly, it has been demonstrated that the matrix elements of the dimer model Hamiltonian suffice to describe larger aggregates. The results of the investigation confirm the high degree of mixing of CT and LE configurations in the description of low lying excited states.

[1] W. Liu, B. Lukenheimer, V. Settels, B. Engels, R. F. Fink, A. Köhn *J. Chem. Phys.* **143**, 084106 (2015).

[2] C. Walter, V. Krämer, B. Engels *Int. J. Quantum Chem.* **117**, e55337 (2017).

[3] W. Liu, S. Canola, A. Köhn, B. Engels, F. Negri, R. F. Fink, *in preparation*.



## The Effect of a Mobile Solvent Environment on Quantum Control of Chemical Reactions

Daniel Keefer, Regina de Vivie-Riedle

*Department of Chemistry, Ludwig-Maximilians-Universität,  
Butenandtstr. 5-13, Munich, Germany*

In quantum control, shaped laser pulses are used to steer molecular motion. With a view to applying this principle to synthetic chemistry, solvent effects have to be included in a proper theoretical description. Going beyond commonly used continuum or bath approaches, we recently introduced a combined quantum/molecular dynamics method which explicitly includes solvent molecules in quantum control optimizations [1, 2]. The explicit environment was identified to drastically influence the relevant molecular properties for successful control. However, the reaction was regarded to take place in frozen solvent cages so far and movement of solvent molecules was not accounted for.

With our present study we overcome this approximation and extend our approach toward a fluctuating environment. Besides introducing the methodological procedure on a synthetically relevant example, we mainly ask and answer the question of controllability: What is the timescale at which the environmental influence shifts from one extreme case to another, and is a controlling laser pulse able to dynamically adapt to not only highly inhomogeneous but also constantly fluctuating properties? Overcoming these difficulties is essential for a successful application of the principles of quantum control to the regime of chemical synthesis.

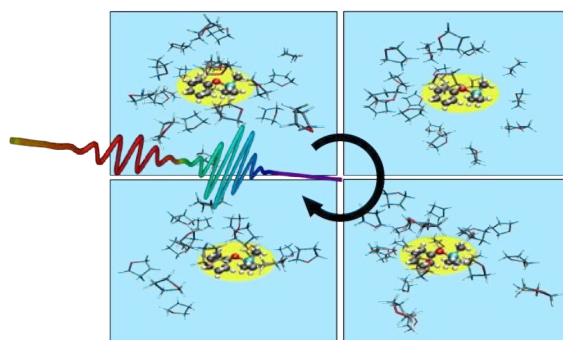


Figure 1: Optimized light fields are required to control the chemical reaction in a fluctuating solvent environment

[1] D. Keefer et al. *J. Phys. B* **48**, 234003 (2015).

[2] S. Thallmair et al. *J. Chem. Theory Comput.* **11**, 1987 (2015).



## **Influence of Neighboring Nucleobases on the Photostability of Uracil: Quantum Dynamics in Explicit Biological Environments**

**Sebastian Reiter, Daniel Keefer, Regina de Vivie-Riedle**

*Department of Chemistry, Ludwig-Maximilians-Universität,  
Butenandtstr. 5-13, Munich, Germany*

Exposure to ultraviolet radiation can induce significant photochemical damage in nucleic acids, thereby weakening the integrity of the genetic code. To largely prevent this from happening, the five canonical nucleobases exhibit ultrafast, non-radiative relaxation pathways. This process is extensively investigated both theoretically and experimentally, mostly on isolated nucleobases. For the example of uracil, recent studies elucidate the relaxation process after optical excitation with femtosecond laser pulses. [1, 2]

In our present theoretical work, we take the next step and consider uracil in its native RNA environment, where the sugar phosphate backbone and neighboring nucleobases as well as solvent molecules might influence the ultrafast population decay and thereby photostability. For this purpose, we employ an approach that combines molecular dynamics (MD) with quantum dynamics and has recently been developed in our group. [3] In particular, we run MD simulations for several different RNA fragments solvated in water and extract snapshots at random geometries. Using a hybrid QM/MM technique, we are able to model the effects of the explicitly included environment in different snapshots. The thus obtained environment potential energy surfaces (PESs) are subsequently combined with a high level (MRCI(12,9)/cc-pVDZ) gas phase PES [2] of the  $S_2$ -state of uracil, spanning the coordinate space between Franck-Condon point,  $S_2$ -minimum and a conical intersection to  $S_1$ . To simulate the relaxation mechanism through the conical intersection, we perform wave packet dynamics on the resulting PESs.

We discuss the influence of the biological environment on the path of the wave packet after photoexcitation. A key focus of this study is to explore whether certain neighboring nucleobases have different effects on the photostability of uracil.

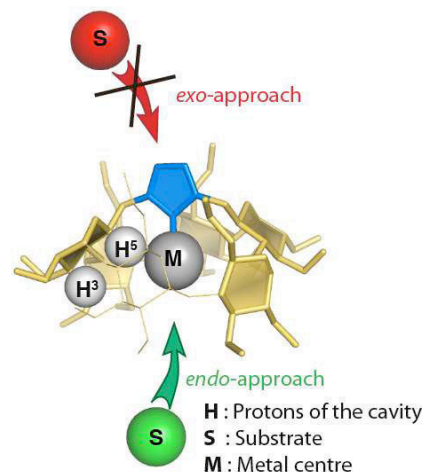
- [1] S. Matsika, M. Spanner, M. Kotur, T. C. Weinacht, *J. Phys. Chem. A* **117**, 12796 (2013).
- [2] D. Keefer, S. Thallmair, S. Matsika, R. de Vivie-Riedle, *J. Am. Chem. Soc.* **139**, 5061 (2017).
- [3] S. Thallmair, J. P. P. Zauleck, R. de Vivie-Riedle, *J. Chem. Theory Comput.* **11**, 1987 (2015).

## Mimicking metalloenzymes with cyclodextrins: what can we learn from modeling?

Etienne Derat<sup>1</sup>, Thomas Driant<sup>1</sup>, Louis Fensterbank<sup>1</sup>, Matthieu Sollogoub<sup>1</sup>

<sup>1</sup>*Institut Parisien de Chimie Moléculaire, Université Pierre et Marie Curie – Paris 6, Sorbonne Universités, 4 place Jussieu, Paris, France*

Encapsulating a metallic center in a cavity with a defined and specific shape is an efficient way to promote selectivity in catalytic processes. This is the strategy that nature uses in metalloenzymes, and it has naturally become a source of inspiration to chemists. Mimicking metalloenzymes active site by using a cyclodextrin cavity is one of the many options. Our lab recently synthesized in a selective manner and for the first time various cyclodextrins capped with N-heterocyclic carbene (CD-NHC, see figure below).



When the CD-NHC is capped with a metal (Cu, Au, Ag), various catalytic activities were investigated experimentally. Since unusual reactivities were observed in some cases, modeling with various theoretical methods of the catalytic events was undertaken. First, we will show how understanding the network of weak interactions inside the cavity allows us to interpret NMR correlation data. Second, a mechanistic switch exerted by the cyclodextrin when compared to bulk solvent reactivity will be presented. Third, we will demonstrate how the cavity size ( $\alpha$ -cyclodextrin vs.  $\beta$ -cyclodextrin) can also influence the mechanism.

[1] M. Ménand, S. A. de Beaumais, L.-M. Chamoreau, E. Derat, S. Blanchard, Y. Zhang, L. Bouteiller, M. Sollogoub, *Angew. Chem. Int. Ed.* **53**, 7238 (2014).

[2] P. Zhang, C. Tugny, J. Meijide Suárez, M. Guitet, E. Derat, N. Vanthuyne, Y. Zhang, O. Bistri, V. Mouriès-Mansuy, M. Ménand, S. Roland, L. Fensterbank, M. Sollogoub, *Chem* (2017), *in press* DOI: 10.1016/j.chempr.2017.05.009

[3] P. Zhang, J. Meijide Suárez, T. Driant, E. Derat, Y. Zhang, M. Ménand, S. Roland, M. Sollogoub, submitted to *Angew. Chem. Int. Ed.*

## **Förster resonance energy transfer in a novel light-harvesting polymer investigated state-of-the-art multiconfigurational methods and TDDFT**

**Michael Siegmann<sup>1</sup>, Stephan Kupfer<sup>1</sup>, Stefanie Gräfe<sup>1</sup>**

*<sup>1</sup>Institute of Physical Chemistry, Friedrich-Schiller-University, Helmholtzweg 4, Jena, Germany*

Thiazol-based dyes, which are structurally closely related to luciferin, the chromophore of fireflies, were found to be excellent light harvesting units, e.g. in the scope of dye-sensitized solar cells and photo catalysis. Substituted by different electron-pushing and withdrawing groups, a set of three thiazoles is able to harvest sunlight's entire visible range. Incorporated in a polymer backbone, such a set of dyes is able to collect photons of different energy and to transfer this energy via Förster resonance energy transfer (FRET) to a photo catalysator [1]. This way the efficiency of photovoltaic and photo catalytic processes can be improved significantly.

For a better understanding of the underlying photophysical principles the dyes were investigated by means of density functional theory using different hybrid as well as range separated functionals and benchmarked against state-of-art multiconfigurational methods (MS-CASPT2/CASSCF) [2,3]. A matter of particular interest was the description of the ground state equilibrium structure by means of different functionals, the charge-transfer character of excited states and the influence of London-dispersion for the  $\pi$ -stacking between the dyes. Absorption and fluorescence-wavelengths were calculated to estimate the FRET efficiency. Additionally, potential energy surfaces for dye dimer structures were obtained, while distinct structural configurations correlated to FRET were investigated by means of CASSCF.

- [1] A. M. Breul, I. R. de Moraes, R. Menzel, M. Pfeffer, A. Winter, M. D. Hager, S. Rau, B. Dietzek, R. Beckert, U. S. Schubert, *Poly. Chem.* **5**, 2715 (2014).
- [2] P. A. Malmqvist, A. Rendell, B. O. Roos, *J. Phys. Chem.* **94**, 5477 (1990).
- [3] V. Sauri, L. Serrano-Andres, A. R. M. Shahi, L. Gagliardi, S. Vancoillie, K. Pierloot, *J. Chem. Theo. Comput.* **7**, 153 (2011).

## Canonical formats in chemical kinetics and Slow Manifold approximation

Alessandro Ceccato<sup>1</sup>, Paolo Nicolini<sup>2</sup>, Diego Frezzato<sup>1</sup>

<sup>1</sup>*Department of Chemical Sciences, University of Padova, Via Marzolo 1, Padova, Italy*

<sup>2</sup>*Department of Control Engineering–K335, Faculty of Electrical Engineering, Czech Technical University in Prague, Karlovo náměstí 13, 121 35 Prague 2, Czech Republic*

Mass-action law is the paradigm for the description of chemical kinetics in macroscopic, well-stirred and isothermal systems. Recently [1–3] we proved that, given a suitable transformation which recasts the original ordinary differential equations into a special extended format devoid of any system-dependent parameter (termed by us “canonical format”), it is possible to characterize general features in the space of the new dynamical variables which mirror specific properties in the original space. We focused in particular upon the Slow Manifold (SM) feature. The SM is the hyper-surface in the concentration space toward which the trajectories bundle in the slow part of the evolution. Its localization is potentially relevant in the field of dimensional reduction strategies. Exploiting concepts developed in our previous works [2, 3] we devised and tested on benchmark cases (namely, two different models of hydrogen combustion) a low-computational-cost C++ code aimed at producing points in the concentration space lying close to the SM for a given kinetic mechanism [4]. The software, called DRIMAK (Dimensional Reduction of Isothermal Mass-Action Kinetics), is freely available online.

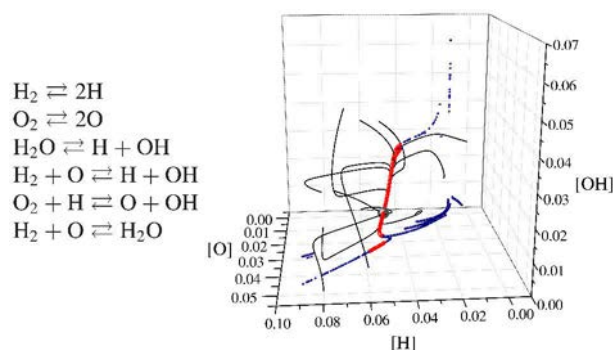


Figure 1: Rough output (in blue) and “filtered” results (in red) produced by the software for the sketched model scheme (radical subspace). See ref. [4] for parameters and details.

[1] P. Nicolini, D. Frezzato, *J. Chem. Phys.*, **138**, 234101 (2013).

[2] P. Nicolini, D. Frezzato, *J. Chem. Phys.*, **138**, 234102 (2013).

[3] A. Ceccato, P. Nicolini, D. Frezzato, *J. Chem. Phys.*, **143**, 224109 (2015).

[4] A. Ceccato, P. Nicolini, D. Frezzato, *Int. J. Chem. Kinet.*, **49**, 477-493 (2017).

## Catalytic Mechanism and Molecular Engineering of Quinolone Biosynthesis in Dioxygenase AsqJ

**Sophie L. Mader<sup>1</sup>, Alois Bräuer<sup>1</sup>, Michael Groll<sup>1</sup>, Ville R. I. Kaila<sup>1</sup>**

<sup>1</sup>*Department Chemistry, Technical University Munich, Lichtenbergstrasse 4, 85747 Garching, Germany*

The recently discovered dioxygenase AsqJ from *Aspergillus nidulans* stereoselectively catalyzes the one-pot multistep synthesis of quinolone alkaloids, natural products with important biomedical applications [1]. AsqJ catalyzes a stepwise desaturation and epoxidation of the quinolone by proton-coupled electron transfer (PCET) reactions. In order to probe the mechanistic principles of this catalytic process, we integrate multi-scale quantum and classical molecular simulations with X-ray crystallography and *in vitro* biochemical activity studies. We find that methylation of the substrate is central for the catalytic activity of AsqJ, introducing molecular strain that fine-tunes dispersive interactions within the active site. In order to rationally engineer AsqJ for non-methylated substrates, we strengthen the dispersive interactions within the active site by mutating one residue in the surroundings, and show that the engineered enzyme has an improved catalytic activity for non-methylated substrates [2]. Our combined results provide important mechanistic insight into the function of AsqJ and showcase how integration of computational and experimental data allows to rationally engineer this enzyme.

[1] A. Bräuer, P. Beck, L. Hintermann, M. Groll, *Angew. Chem. Int. Ed.* **55**, 3517 (2016).

[2] S. L. Mader, A. Bräuer, M. Groll, V. R. I. Kaila, *in preparation*.

## The Polarizable Density Embedding Coupled Cluster Method

Dalibor Hršak<sup>1</sup>, Jógvan Magnus Haugaard Olsen<sup>1</sup>, Jacob Kongsted<sup>1</sup>

<sup>1</sup>*Department of Physics, Chemistry and Pharmacy, University of Southern Denmark,  
Campusvej 55, Odense M, Denmark*

In this work we present the theory and implementation of the polarizable density embedding (PDE) model [1] in combination with coupled cluster (CC) theory, denoted PDE-CC. This model has been implemented in the Dalton package by adapting the CC code to the Polarizable Embedding library (*PElib*). In this new PDE-CC model, the small, chemically important core region is described with a high-level CC method. The environment is separated into two levels of description: the inner and the outer region. The inner region is described with an embedding potential consisting of a set of frozen densities calculated on isolated fragments with a QM method such as HF or DFT and with a set of atom-centered dipole-dipole anisotropic polarizabilities. The outer region is described with distributed atom-centered multipoles and polarizabilities, in other words in the same way as in the previous polarizable embedding (PE) model [2].

The PDE-CC model contains operators that account for the electrostatic and polarization interactions between the core region and the environment, as well as for the non-electrostatic (*i.e.* exchange / Pauli) repulsion. The latter operator plays a key role in an accurate description of short-range interactions in cases with an overlap between the orbitals of the core and the inner region. In PDE-CC such complicated manybody phenomena are described in a convenient form through one-electron operators, thus being able to efficiently account for the response of the environment due to the change in the electron density of the core region. This allows accurate calculations of response properties (*e.g.* electronic excitations) of molecules immersed into environments such as solvents.

- [1] J. M. H. Olsen, C. Steinman, K. Ruud, J. Kongsted, *J. Phys. Chem. A* **119**, 5344–5355, (2015)
- [2] J. M. H. Olsen, J. Kongsted, *Adv. Quant. Chem.* **61**, 107–143, (2011)
- [3] K. Sneskov, T. Schwabe, J. Kongsted, O. Christiansen, *J. Chem. Phys.* **134**, 104108, (2011)

## Hydrodesulfurization mechanisms of dibenzothiophene molecules catalyzed by CoMoS catalysts: a DFT study

A.S. Dumon<sup>1</sup>, P. Raybaud<sup>1</sup>

<sup>1</sup>IFP Energies nouvelles - Rond-point de l'échangeur de Solaize -  
BP 3,69360 Solaize - France

Within the context of strong environmental regulations, hydrodesulfurization (HDS) reactions become ever more crucial to produce cleaner fuels from petroleum resources.[1] Even if the cobalt promoted MoS<sub>2</sub> phase (CoMoS) is highly active for HDS, polyaromatic molecules such as dibenzothiophenes (Figure 1) are known to remain difficult to desulfurize. It is thus challenging for theoretical approaches to elucidate the HDS mechanism of these molecules impacting numerous experimental works.[2, 3]

Using periodic density functional theory with PBE-dDsC functional and a systematic search of transition states, we investigate the main HDS pathways of DBT on relevant active sites of CoMoS models [4], and identify their rate limiting steps.

We simulate the most relevant and experimentally invoked mechanisms leading to the C-S bond cleavage: 1/ the direct hydrogenolysis of the C-S bond [3], 2/ the selective dihydrogenation in  $\alpha$  and  $\beta$  followed by  $\beta$  elimination with simultaneous C-S bond cleavage (E2 type mechanism) [2], 3/ the full pre-

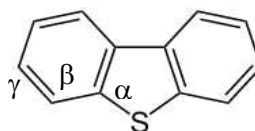


Fig. 1 : Dibenzothiophene

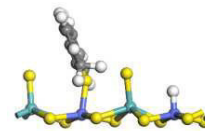


Fig. 2 :  $\beta$  hydrogenation

hydrogenation of one aromatic cycle followed by the C-S cleavage [2].

We notably found that the hydrogenolysis mechanism exhibits a kinetically costly  $\alpha$  hydrogenation step (1.40 eV for activation energy,  $E_a$ ), followed by an easy C-S breaking ( $E_a=0.10$  eV). By contrast, the  $\beta$  hydrogenation (Figure 2) is much easier as a first step ( $E_a=0.85$  eV), and is followed either by a fast  $\alpha$  hydrogenation ( $E_a=0.20$  eV) or by a moderate  $\gamma$  hydrogenation ( $E_a=0.60$  eV). Considering also the subsequent steps leading to the C-S bond cleavage, we will discuss the selectivity towards the three different pathways and the role of the catalytic hydrogenating sites involved: Mo-SH vs. Co-H groups. A comparison with available experimental data will be finally discussed.

[1] S. Humbert, G. Izzet, P. Raybaud, *J. Catal.* **33**, 76 (2016)

[2] F. Bataille et al. *J. Catal.* **191**, 409 (2000)

[3] M. Egorova and R. Prins, *J. Catal.* **225**, 417 (2004)

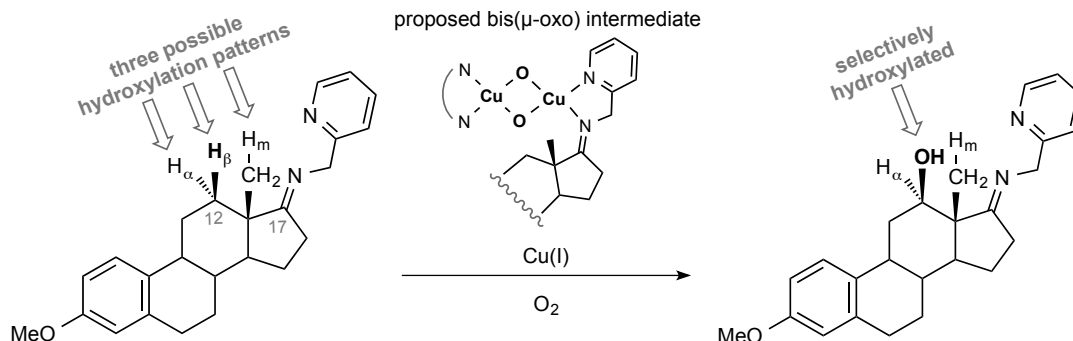
[4] E. Krebs, B. Silvi, P. Raybaud, *Catal. Today*. **130**, 160 (2008)

## Computational Bioinorganic Chemistry of $[\text{Cu}_2\text{O}_2]^{2+}$ Complexes: Selective Hydroxylation of Aliphatic C–H Bonds

Moritz Förster and Max Holthausen

*Institut für Anorganische und Analytische Chemie, Goethe-Universität, Max-von-Laue-  
Straße 7, Frankfurt am Main, Germany*

The regio- and stereoselective copper-mediated hydroxylation of a non-activated aliphatic C–H bond in a steroid, reported by Schönecker, has evolved into an useful synthetic tool.[1] We benchmarked the applied BLYP-D3/def2-TZVP(SDD) level of DFT by comparison to experimental reference data, followed by a mechanistic study to address the origins for the observed selectivity.[2] The computational results are in agreement with the experimental findings of a selective  $\beta$ -hydroxylation at the C12 position. NBO analyses revealed that a substantial pre-activation of the C–H $_{\beta}$  bond by the bis( $\mu$ -oxo)-dicopper core favors the  $\beta$ -hydroxylation pathway over competing reaction channels. Both the treatment of  $[\text{Cu}_2\text{O}_2]^{2+}$  complexes with the BLYP functional and the mechanistic concept (stereochemical arrangement of the ligand determining the hydroxylation selectivity) can be transferred to related systems.[3]



**Figure:** Regio- and stereoselective C12 hydroxylation of a non-activated C–H bond.

[1] B. Schönecker, T. Zheldakova, Y. Liu, M. Kötteritzsch, W. Günther, H. Görls, *Angew. Chem. Int. Ed.* **42**, 3240 (2003).

[2] P. Gupta, M. Diefenbach, M. C. Holthausen, M. Förster, *Chem. Eur. J.* **23**, 1427 (2017).

[3] Cooperation with S. Schindler, P. R. Schreiner and A. Fokin, *manuscript in preparation*.

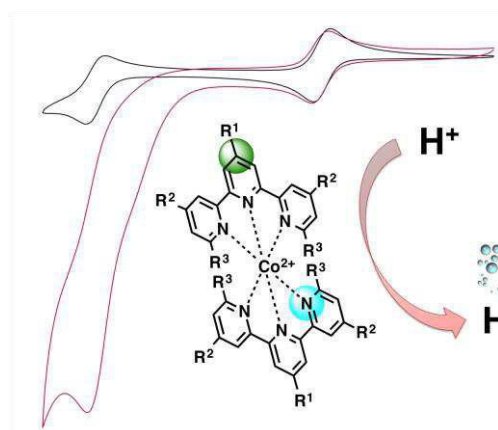


## Hydrogen Evolution Mechanisms of Bis-Terpyridyl Cobalt Catalysts: A Ligand-Based vs. A Metal-Based Pathway

**Tanya K. Todorova, Safwan Aroua, Victor Mougel, Marc Fontecave**

*Laboratoire de Chimie des Processus Biologiques, Collège de France  
11 Place Marcelin Berthelot, 75321 Paris, France*

The design of molecular catalysts for the hydrogen evolution reaction (HER) is an attractive strategy for the conversion of solar energy to chemical fuels. Experimentally, several classes of bis-terpyridyl-based cobalt complexes have been observed to catalyze the electrochemical reduction of protons to hydrogen [1,2]. Mechanistic studies of the HER typically invoke the formation of reactive cobalt hydride species. Herein, DFT computations (M06-L with SMD continuum solvation) were employed to investigate the complete catalytic cycle of these complexes based on the free energies of reaction and activation, as well as reduction potentials for all catalytically relevant elementary steps [2]. For the first time, a ligand-based pathway has been proposed, which occurs at the central pyridyl ring and leaves the cobalt coordination sphere unchanged. Alternatively, depending on the acid strength, as well as the nature and basicity of the ligands, the classical metal-based pathway can be invoked. Interestingly, the calculations reveal that the cobalt hydride intermediate is formed through initial protonation of the distal pyridyl nitrogen that acts as a proton relay.



- [1] S. Aroua, T. K. Todorova, P. Hommes, L.-M. Chamoreau, H.-U. Reissig, V. Mougel, M. Fontecave, *Inorg. Chem.* **56**, 5930 (2017).  
[2] S. Aroua, T. K. Todorova, V. Mougel, P. Hommes, H.-U. Reissig, M. Fontecave, *ChemCatChem* (DOI: 10.1002/cctc.201700428R1).

## Bringing order to unordered compounds: The Phase System Li-Ag-Ge

Jasmin V. Dums<sup>1</sup>, David Fischermeier<sup>1</sup>, Antti J. Karttunen<sup>2</sup>, Thomas F. Fässler<sup>1</sup>

<sup>1</sup>*Department of Chemistry, TU Munich, Lichtenbergstraße 4, 85747 Garching, Germany*

<sup>2</sup>*Department of Chemistry and Materials Science, Aalto University, Finland*

Salts containing lithium and silver ions show rather high ion conduction among solid ionic conductors. It has been shown that the substitution of Ag<sup>+</sup> by Li<sup>+</sup> in silver argyrodites leads to a new innovative family, which shows fast lithium ion conduction.<sup>[1]</sup> In contrast, lithium silicides and germanides which we studied recently,<sup>[2]</sup> represent good (active) anode materials with a much high capacity in comparison to carbon. In addition we have also investigated the lithium mobility in charged anodes such as lithium-rich silicides.<sup>[3]</sup>

In this context we were interested in the properties of silver in contrast to lithium in intermetallic compounds and investigated the Li-Ag-Ge phase diagram.<sup>[4]</sup> Various new ternary compounds such as Li<sub>2</sub>AgGe, Li<sub>2.53</sub>AgGe<sub>2</sub> and Li<sub>2</sub>Ag<sub>1-x</sub>Ge<sub>1+x</sub> were discovered and Ag interestingly – as a general rule - substitutes Ge atoms rather than Li atoms.

All compounds show a basic structural unit, in which Ag and Ge form a wurtzite-type network, hosting lithium atoms in its cavities or channels, thus the structures can be compared and traced back to the cubic NaTl structure type. Depending on the ratio of Ag and Ge the compounds form different superstructures ending up with unit cells longer than 40 Å.

Quantum chemical calculations at the DFT-HSE06/TZVP level of theory were performed using CRYSTAL14 code to get a better insight in the electronic structure of the ternary phases, and to better understand why specific ordering occurs and why super structures are formed. The various supercells were traced back according to the Bärnighausen family tree formalism and are compared to each other.<sup>[5]</sup> The calculations reveal that there exist preferred super structures for the Ag:Ge ratio 1:1 and 0.8:1.2 and pseudo bandgaps above the Fermi level hint for the possibility of substitution with more electron rich elements.

[1] H.-J. Deiseroth, S.-T. Tong, H. Eckert, J. Vannahme, C. Reiner, T. Zaiß, M. Schlosser, *Angew. Chem. Int. Ed.* **47**, 755-758 (2008).

[2] M. Zeilinger, I. Kurylyshyn, U. Häussermann, T. F. Fässler, *Chem. Mater.* **25**, 4623-4632 (2013). M. Zeilinger, D. Benson, U. Häussermann, T. F. Fässler, *Chem. Mater.* **25**, 1960-1967 (2013).

[3] V. Baran, L. van Wüllen, T. F. Fässler *Chem. Eur. J.* **22** 6598–6609 (2016).

[4] A. Henze, V. Hlukhyi, T. F. Fässler, *Inorg. Chem* **54**, 1152-1158 (2015).

[5] H. Bärnighausen, *Commun. Math. Chem.* **9**, 139 (1980).

## An accurate *ab-initio* parametrization of density functional dispersion coerrrection (DFT-D4) for the 86 elements H-Rn.

Eike Caldeweyher, Christoph Bannwarth, Stefan Grimme

Mulliken Center for Theoretical Chemistry,  
Institut für Physikalische und Theoretische Chemie der Universität Bonn  
Berlingstr. 4, D-53115 Bonn, Germany

The method of using a dispersion correction as an add-on to standard Kohn-Sham density functional theory (DFT-D) has been further refined regarding higher accuracy, broader range of applicability, and less limitations. As in D3 atom-pairwise specific dispersion coefficients and cutoff radii are derived from first principles[1]. System (geometry) dependent information is used by employing the concept of fractional coordination numbers (*CNs*). *CNs* are used to interpolate between reference polarizabilities at imaginary frequencies of atoms in different chemical environments. In DFT-D4, additionally the electronic structure (charge) is included by employing a partial charge dependent scaling function to match cationic and anionic environments. These atomic polarizabilities are then scaled with respect to their self-consistently derived Mulliken charges[2]. A recently developed semi-empirical quantum mechanical tight binding (TB) scheme, termed GFN-xTB[3], with a (partially) polarized minimal basis set is used to obtain Mulliken charges. TB partial charges were shown to agree rather well with DFT Hirshfeld charges[4]. All good properties of DFT-D3 are preserved within the new scheme while the accuracy of molecular  $C_6$  dispersion coefficients is substantially improved (MAD(D3)=4.7%; MAD(D4)=2.9% for small to medium-sized molecules,  $H_2$  to  $C_8H_{18}$ ). Furthermore, electronically more demanding cases, i.e., cation- $\pi$  interactions, which are described badly by D3, could be described rather well by D4. Overall, the method only requires adjustment of two damping parameters for each density functional, is asymptotically exact, and easily allows the computation of atomic forces. As a by-product of the D4 procedure, accurate charge-dependent atomic static polarizabilities are obtained, which may have an application in classical force-fields (see for example Ref.[5]).

- [1] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, *J. Chem. Phys.* **132**, 2010, 154104.
- [2] E. Caldeweyher, C. Bannwarth, and S. Grimme, submitted to *J. Chem. Phys.*, 2017.
- [3] S. Grimme, C. Bannwarth, and P. Shushkov, *J. Chem. Theory Comput.* **13**, 2017, 1989.
- [4] S. Grimme and C. Bannwarth, *J. Chem. Phys.* **145**, 2016, 054103.
- [5] S. Grimme, C. Bannwarth, E. Caldeweyher, J. Pisarek, and A. Hansen, submitted to the *J. Chem. Phys.* special issue 'From Quantum Mechanics to Force Fields', 2017.

## GW based Methods in Quantum Chemistry

Christof Holzer<sup>1</sup>, Willem Klopper<sup>1</sup>

<sup>1</sup>*Institut für Physikalische Chemie, Karlsruher Institut für Technologie, Fritz-Haber-Weg 2, Karlsruhe, Germany*

The GW ansatz is a promising method for applications in molecular quantum chemistry. Starting from DFT or Hartree-Fock references the central object, the Green's function, is evaluated and used to significantly improve upon various molecular properties. The simplest GW method is  $G_0W_0$  with screening from the random-phase-approximation, i.e. non-interacting electron-hole pairs (RPA). This yields an improved set of quasi-particle (QP) energies (resembling IPs) from the starting orbital energies.[1] These QP energies can then be used as starting point for several further calculations, e.g. solving the Bethe-Salpeter equation to obtain optical excitation spectra, circular dichroism or interaction energies of van der Waals bound systems.[2] The main drawback of  $G_0W_0$  is its dependency on the DFT/HF starting point. Therefore one may aim at a self-consistent solution of the QP equations (QP-scGW) as proposed by Faleev et al. which has previously been implemented into TURBOMOLE.[3, 4] Although working,  $G_0W_0$  as well as QP-scGW could only treat small molecules due to their steep  $N^6$  scaling behaviour in previous implementations, even within the resolution-of-identity (RI) approximation.

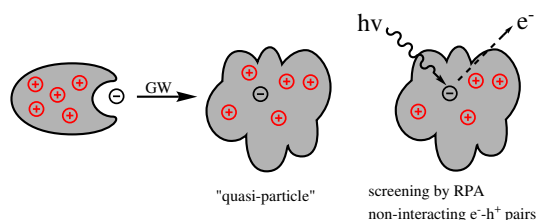


Figure 1: Schematic representation of a quasi-particle state obtained by GW

We now present an improved methodology implemented in TURBOMOLE for  $G_0W_0$  and QP-scGW that can treat molecules with significant size ( $>100$  atoms) using large basis sets. The updated algorithm is able to take full advantage of point group symmetry, and makes optimal use of the RI approximation. Within this implementation the lossless treatment of systems with over 700 electrons and 4000 basis functions could be demonstrated.

- [1] M.J. van Setten, F. Weigend, F. Evers, *J. Chem. Theory Comput.* **9**, 1 (2012)
- [2] C. Holzer, W. Klopper, *to be published* (2017)
- [3] M. van Schilfgaarde, T. Kotani, S. Faleev, *Phys. Rev. Lett.* **96**, 22 (2006)
- [4] F. Kaplan, M.E. Harding, C. Seiler, F. Weigend, F. Evers, M.J. van Setten, *J. Chem. Theory Comput.* **12**, 6 (2016)

## Density functional studies of tetrapyrroles on Ag(111)

Jan-Niclas Luy<sup>1</sup>, J. Michael Gottfried<sup>1</sup>, Ralf Tonner<sup>1</sup>

<sup>1</sup>*Fachbereich Chemie and Material Sciences Center, Philipps-Universität Marburg,  
Hans-Meerwein-Straße 4, 35032 Marburg, Germany*

Coordination of a metal atom by a tetrapyrrole changes its electronic structure and reactivity. This is leveraged in a wide variety of applications ranging from gas transport [1] over energy conversion [2] to catalysis [3]. These molecular systems have also sparked the interest of researchers in the field of surface science. [4] Here, tetrapyrroles were initially proposed as scaffolds for reactive metal ions to facilitate the growth of 2D-lattices. [5] However, it was shown that some tetrapyrroles are non-innocent ligands. [6] We propose that this non-innocence offers the possibility of fine-tuning properties by changing chemical functionalization. We use periodic density functional theory to determine the adsorption behavior of complexes and free-base ligands on transition metal surfaces such as Ag(111). The electronic structure and selectivity of different adsorption sites is analyzed while generating theoretical spectroscopic data. Furthermore, kinetic and thermodynamic values such as adsorption energy are investigated. Follow-up reactions that occur on the surface are modeled *in silico* to compare to and predict experimental results.

- [1] J. Clayden, N. Greeves, S. Warren and P. Wothers, *Organic Chemistry*, Oxford University Press, 1406 (2001).
- [2] E. Schunck, L. Marchlewski, *Liebigs Ann.*, **290**, 306 (1896).
- [3] R. Bernhardt, *J. Biotechnol.*, **124**, 128 (2006).
- [4] J.M. Gottfried, *Surf. Sci. Rep.*, **70**, 259 (2015).
- [5] W. Hieringer, K. Flechtner, A. Kretschmann, K. Seufert, W. Auwärter, J.V. Barth, A. Görling, H.-P. Steinrück, J.M. Gottfried, *J. Am. Chem. Soc.*, **133**, 6206 (2011).
- [6] B.O. Roos, V. Veryazov, J. Conradie, P.R. Taylor, A. Ghosh, *J. Phys. Chem. B*, **112**, 14099 (2008).

We thank the Deutsche Forschungsgemeinschaft (SFB 1083) for support.

## Detailed Quantitative and Visual Analysis Methods for Electronic Excitation Processes

Felix Plasser<sup>1</sup>, Stefanie A. Mewes<sup>2</sup>, Sebastian Mai<sup>1</sup>, Juan J. Nogueira<sup>1</sup>, Andreas Dreuw<sup>2</sup>, Leticia González<sup>1</sup>

<sup>1</sup>*Institute for Theoretical Chemistry, Faculty of Chemistry, University of Vienna, Austria*

<sup>2</sup>*Interdisciplinary Center for Scientific Computing, Heidelberg University, Germany*

Owing to a tremendous effort in method development and to the availability of supercomputers it is possible nowadays to perform highly accurate simulations of complex excited state phenomena even in large systems. However, the wavefunctions produced in these computations are difficult to interpret if many interacting configurations and orbitals are involved. Even more, for large systems excitonic effects come into play, which are difficult to comprehend in a standard molecular orbital picture. Therefore, new analysis methods are direly needed to get full insight into the computations performed.

This contribution will provide an overview over our recently developed wavefunction analysis framework [1, 2, 3], which provides detailed visual and quantitative analysis tools for excited state computations. The power of these methods will be illustrated in three examples. First, a recent study on the absorbing states in single-stranded DNA will be presented [4]. In this case a rigorous and automated quantitative analysis is particularly beneficial when combined with structural sampling in this flexible multichromophoric system. Second, it will be discussed how the same analysis strategy can be extended to the case of transition metal complexes [5] and recent results on a Rhenium complex will be presented. Finally, the emergence of excitonic effects will be discussed in the case of conjugated polymers [6]. It will be shown that the exciton size in these systems scales uniformly with the system size and is independent of the molecular details. The description of these excitonic effects within time-dependent density functional theory will be discussed.

[1] F. Plasser, H. Lischka, *J. Chem. Theory Comput.* **8**, 2777 (2012).

[2] S. A. Bäppler, F. Plasser, M. Wormit, A. Dreuw, *Phys. Rev. A* **90**, 052521 (2014).

[3] F. Plasser, L. González, *J. Chem. Phys.* **145**, 021103 (2016).

[4] J. J. Nogueira, F. Plasser, L. González, *Chem. Sci.* **in revision**.

[5] F. Plasser, A. Dreuw, *J. Phys. Chem. A*, **119**, 1023 (2015).

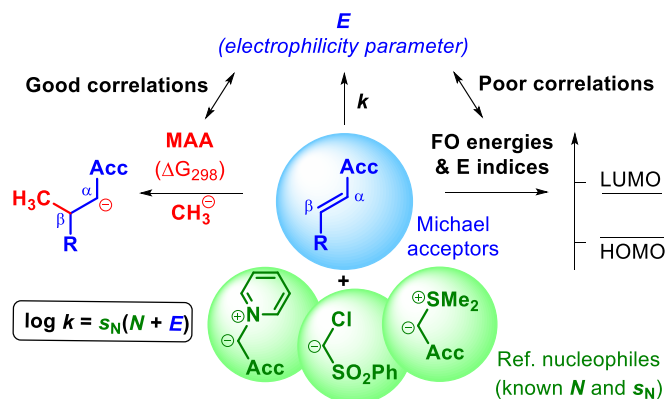
[6] S. A. Mewes, F. Plasser, A. Dreuw, *J. Phys. Chem. Lett.* **8**, 1205 (2017).

## Quantification and Theoretical Analysis of the Electrophilicities of Michael Acceptors

Dominik S. Allgäuer<sup>1</sup>, Harish Jangra<sup>1</sup>, Haruyasu Asahara<sup>1</sup>, Zhen Li<sup>1</sup>, Quan Chen<sup>1</sup>, Hendrik Zipse<sup>1</sup>, Armin R. Ofial<sup>1</sup>, and Herbert Mayr<sup>1</sup>

<sup>1</sup>Department of Chemistry, Ludwig-Maximilians-Universität München, Butenandtstr. 5-13, D-81377 München, Germany

To quantify the electrophilic reactivities of common Michael acceptors (MAcs), we measured the kinetics of the reactions of mono-acceptor-substituted ethylenes and styrenes with pyridinium ylides<sup>1a</sup>, a sulfonium ylide<sup>1b</sup>, and a sulfonyl substituted chloromethyl anion<sup>1c</sup>. From the second-order rate constants  $k$  determined in this work and the previously published  $N$  and  $s_N$  parameters of the nucleophiles<sup>1</sup> we have calculated [by using  $\log k = s_N(E + N)^2$ ] the electrophilicity parameters  $E$  of the MAcs. DFT calculations were performed to elucidate the origin of the electrophilic reactivities. The  $E$  correlate poorly with frontier orbital (FO) energies or with global and local electrophilicity indices ( $\omega$  &  $\omega_\beta$ ). Moreover, our study highlights the inherent discrepancy in these indices. Good correlations were found between  $E$  and their calculated methyl anion affinities (MAAs), particularly when solvation by DMSO was taken into account. Because of the large structural variety of MAcs considered, which cover a reactivity range of 17 orders of magnitude, we consider the calculation of MAA to be the method of choice for a rapid estimate of electrophilic reactivities.



[1] (a) D. S. Allgäuer, P. Mayer, H. Mayr, *J. Am. Chem. Soc.* **135**, 15216 (2013). (b) R. Appel, N. Hartmann, H. Mayr, *J. Am. Chem. Soc.* **132**, 17894 (2010). (c) Z. Li, Q. Chen, P. Mayer, H. Mayr, *J. Org. Chem.* **82**, 2011 (2017).

[2] (a) H. Mayr, M. Patz, *Angew. Chem. Int. Ed.* **33**, 938 (1994). (b) H. Mayr, T. Bug, M. F. Gotta, N. Hering, B. Irrgang, B. Janker, B. Kempf, R. Loos, A. R. Ofial, G. Remennikov, *J. Am. Chem. Soc.* **123**, 9500 (2001). (c) H. Mayr, S. Lakhdar, B. Maji, A. R. Ofial, *Beilstein J. Org. Chem.* **8**, 1458 (2012).

## Quantum Molecular Trajectory: the Road to Quantum Description of Molecular Motions

Francesco Avanzini<sup>1</sup>, Giorgio J. Moro<sup>1</sup>

<sup>1</sup>*Department of Chemical Sciences, University of Padua, Via Marzolo 1, Padua, Italy*

Despite the quantum nature of molecules, Classical Mechanics is usually employed to characterize molecular motions that play a fundamental role in a wide range of phenomena, e.g., conformational changes and reaction paths [1, 2]. Indeed, the identification of the specific spatial position of the nuclei of the atoms is essential in order to recognize the instantaneous molecular geometry and its time evolution, whereas conventional Quantum Mechanics supplies only probabilistic predictions. On the other hand, one would like to use a Quantum Molecular Trajectory that establishes the instantaneous nuclear positions guaranteeing, at the same time, the validity of the Quantum Mechanics predictions unlike the classical trajectory. We argue that such a Quantum Molecular Trajectory corresponds to a single Bohm trajectory for a given initial condition [3]. The Bohm theory [4] is a formulation of Quantum Mechanics where the state of a quantum system is characterized according to both the wave function and an ensemble of all the possible configurations. In this framework, each configuration evolves drawing a continuous trajectory, the so called Bohm trajectory, leading to an ensemble of evolving trajectories. We prove that if one assumes that a single Bohm trajectory describes the molecular geometry and the molecular motions, then all the quantum predictions emerge in terms of statistical properties of the trajectory. From a theoretical point of view, the undeniable advantage of this approach is that of dealing with a full quantum methodology without any reference to Classical Mechanics. However, from a computational point of view, computing the Bohm trajectory is extremely demanding and it can be done only for system composed of few degrees of freedom. Therefore, we derive also stochastic equations for the dynamics of relevant degrees of freedom, through projection operator technique [5]. The resulting Fokker-Planck equation is of Smoluchowski type leading to the characterization of molecular motions in terms of diffusive processes. In this way the self consistent representation of the molecular motions according to the Quantum Molecular Trajectory is combined with the low computational cost of solving stochastic equations.

- [1] E. Titov, et al., *J. Phys. Chem. Lett.* **7**, 3591 (2016).
- [2] U. Raucci, et al., *J. Phys. Chem. B* **119**, 2650 (2015).
- [3] F. Avanzini, B. Fresch, G. J. Moro, *Found. Phys.* **46**, 575 (2016).
- [4] D. Bohm, *Phys. Rev.* **85**, 180 (1952).
- [5] R. Zwanzig, *J. Chem. Phys.* **33**, 1338 (1960).



## Ab Initio Prediction of Co-adsorption of Gases by GCMC Simulations on a Lattice of Sites

Arpan Kundu<sup>1</sup>, Kaido Sillar<sup>1,2</sup>, Joachim Sauer<sup>1</sup>

<sup>1</sup>*Humboldt Universität zu Berlin, Unter den Linden 6, 10099 Berlin, Germany.*

<sup>2</sup>*University of Tartu, Ravila 14a, 50411, Tartu, Estonia*

The metal-organic frameworks (MOF) are a new class of porous materials that has high potential for carbon capture and storage (CCS). CPO-27-Mg (Mg-MOF-74) is one such MOF that has under-coordinated  $\text{Mg}^{2+}$  sites where  $\text{CO}_2$  gas molecules can bind selectively at low partial pressure (below 1 bar). Prerequisite to a rational design of improved material with optimized separation conditions is the reliable prediction of co-adsorption equilibria. Generic force fields, which have often been employed in classical Grand Canonical Monte Carlo (GCMC) simulations to forecast co-adsorption of gas mixtures, are found to be inadequate in describing the molecule-surface interactions in MOFs with open metal sites. Although the tedious ab initio parametrization of force fields improve the description, these standard GCMC simulations still neglect the zero point vibrations (ZPV) and framework relaxation (FR) effects on adsorption.

We developed an alternative GCMC simulation methodology [1], which utilizes Gibbs free energies of adsorption of individual sites and the lateral (adsorbate–adsorbate) interaction energies obtained from ab initio calculations, which define the Hamiltonian of the coarse-grained lattice-gas description of the adsorbent surface. The former includes the ZPV and FR effects whereas the latter can be treated exactly in the proposed scheme, which avoids cumbersome fitting of the force field parameters. Possibility of applying very accurate quantum chemical methods for lateral interactions or Gibbs free energies of the individual sites makes it a powerful tool for benchmarking standard GCMC simulations.

Hybrid MP2:(PBE+D2)+ $\Delta$ CCSD(T) scheme, which were shown to produce accurate Gibbs free energies (within 1 kJ/mol) [2-4], are used for each individual sites, whereas CCSD(T) lateral interaction energies are employed in this work. Together, they yield pure gas isotherms that are in close agreement with experiment. Our simulations reveal the importance of lateral interactions on co-adsorption of gas mixtures that are relevant to CCS.

### References

- [1] A. Kundu, K. Sillar, J. Sauer, *J. Phys. Chem. Lett.* **8**, 2713 (2017).
- [2] A. Kundu, G. Piccini, K. Sillar, J. Sauer, *J. Am. Chem. Soc.* **138**, 14047 (2016).
- [3] K. Sillar, A. Kundu, J. Sauer, *J. Phys. Chem. C* DOI: 10.1021/acs.jpcc.7b02806 (2017).
- [4] K. Sillar, J. Sauer, *J. Am. Chem. Soc.* **134**, 18354 (2012).

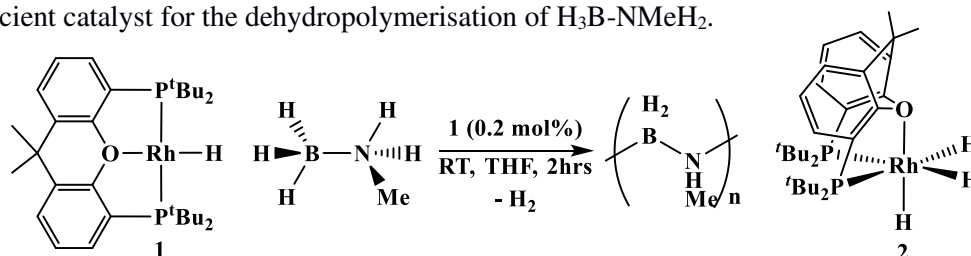
# DFT Investigations into the Dehydropolymerisation of Amine-Boranes using $[(tBuXantphos)Rh(H)]$

**Nicholas A. Beattie<sup>1</sup>, Annie L. Colebatch<sup>2</sup>, Stuart A. Macgregor<sup>1</sup>, Andrew S. Weller<sup>2</sup>**

<sup>1</sup>*Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS*

<sup>2</sup>*Department of Chemistry, University of Oxford, Mansfield Road, Oxford, OX1 3TA*

Polyamino-boranes are made through the dehydropolymerisation of amine-boranes and have uses as high-performance ceramics, piezoelectric materials and precursors to white graphene.[1,2] Experimentally, we have shown  $[(\kappa^3-P,O,P-tBuXantphos)Rh(H)]$ , **1**, to be an efficient catalyst for the dehydropolymerisation of  $H_3B-NMeH_2$ .



We use DFT calculations to characterize the mechanism of the dehydrocoupling of  $H_3B-NMeH_2$  with **1**. The results allow us to propose four possible pathways with very similar activation barriers ( $\pm 2$  kcal mol<sup>-1</sup>). All pathways involve concerted B-H and N-H activation steps to form free  $H_2B=NMeH$  and proceed through *fac*- $[(\kappa^3-P,O,P-tBuXantphos)Rh(H)_3]$ , **2**. Intermediates *fac*- $[(\kappa^2-P,P-tBuXantphos)Rh(H)_3(H_3B-NMeH_2)]$ , **3**, and *fac*- $[(\kappa^2-P,P-tBuXantphos)Rh(H)_3(H_2)]$ , **4**, are also thought to be important in catalysis. Furthermore, this system has proved to be a challenge in terms of producing realistic barriers for a reaction proceeding efficiently at room temperature as well as the identity of the resting state during catalysis. Experimentally this is observed to be complex **1** but computationally isomers of intermediate **2** are found to be competitive. A range of functionals were assessed for their ability to capture both these aspects.

[1] E. M. Leitao, T. Jurca, I. Manners, *Nat. Chem.*, **2013**, 5, 817

[2] H. C. Johnson, E. M. Leitao, G. R. Whittell, I. Manners, G. C. Lloyd-Jones, A. S. Weller, *J. Am. Chem. Soc.*, **2014**, 136, 9078

## Conformational analyses of bis(L-asparaginato)copper(II) in the gas phase and in aqueous solution

Marijana Marković<sup>1,2</sup>, Michael Ramek<sup>2</sup>, Iliana Mutapčić<sup>2</sup>, Jasmina Sabolović<sup>1</sup>

<sup>1</sup>*Institute for Medical Research and Occupational Health, Ksaverska cesta 2,  
P. O. Box 291, HR-10001 Zagreb, Croatia,*

<sup>2</sup>*Institute of Physical and Theoretical Chemistry, Graz University of Technology, (NAWI  
Graz), Stremayrgasse 9, A-8010 Graz, Austria*

We performed conformational analyses of bis(L-asparaginato)copper(II) [Cu(L-Asn)<sub>2</sub>] in the gas phase and in implicit simulated aqueous medium by using the density functional theory (DFT) method and the unrestricted B3LYP functional. One L-asparagine can bind to copper(II) via four donor atoms: amino nitrogen (N<sub>am</sub>), carboxylato oxygen (O), the amide (–CONH<sub>2</sub>) group nitrogen and oxygen. By bidentate chelation of the donor atoms in an equatorial plane, a combination of ten coordination modes can be obtained in both, *cis* and *trans* configurations.

The *trans*-Cu(L-Asn)<sub>2</sub> conformers are generally energetically more stable than the *cis*-conformers in both environments. Among the most stable gas phase and aqueous conformers, strong intra- and inter-residual hydrogen bonds between the amide group atoms and the O and/or N<sub>am</sub> atoms (Figure 1) are formed. In this presentation we discuss how intra- and inter-residual intramolecular interactions as well as stereochemical effects influence the relative stability of the title complex conformers.

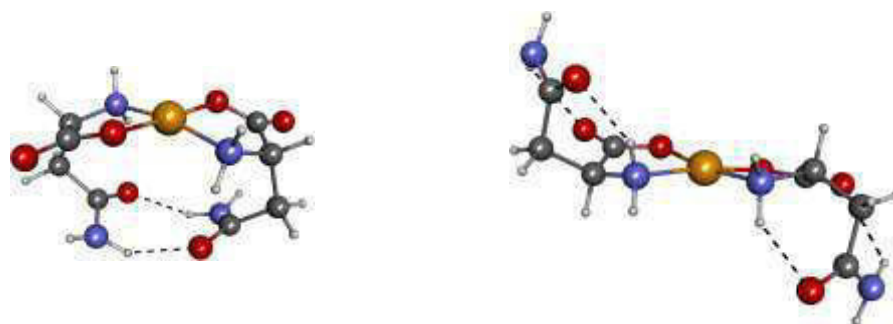


Figure 1. The most stable DFT/B3LYP optimized geometries of Cu(L-Asn)<sub>2</sub> in *trans* and *cis* configuration in the gas phase. The hydrogen bonds are indicated as black dashed lines.

Funding: This work has been funded by the Croatian Science Foundation (Project Grant IP-2014-09-3500).

## Electron-driven solvent effects alter photochemistry of 2-thiocytosine.

Mikołaj Janicki<sup>1,3</sup>, Rafał Szabla<sup>2</sup>, Robert W. Góra<sup>1</sup>

<sup>1</sup>Department of Physical and Quantum Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370, Wrocław, Poland

<sup>2</sup>Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland

<sup>3</sup>E-mail: mjj.janicki@gmail.com

Recently, there has been a growing interest in thiobases which are analogs of the canonical nucleic acid bases in which one of the oxygen atoms is replaced by sulphur. The most attractive feature of these species is their potential applicability in photochemotherapy. Therefore, understanding of photochemical properties of thiobases, which might be related with desired anticancer activity, is of utmost importance. Thiocytosine is one of thiobases which shows anti-tumor [1] and antibacterial activity [2]. Transient absorption (TA) spectroscopy and theoretical studies indicate that photoexcitation of 2-thiocytosine in the gas phase might lead to efficient population of the triplet manifold by very fast intersystem crossing (ISC) [3]. However, there is a growing amount of evidences that in solution water molecules interacting with a chromophore may substantially alter its photochemistry, and actively participate in formation of new photorelaxation channels, which are not accessible in the gas phase [4, 5].

In this contribution we shall elucidate photodeactivation mechanisms in the microhydrated 2-thiocytosine, based on the results of state-of-the-art ab initio calculations. Our results indicate a particular importance of direct interactions between sulphur and water molecules in excited states (Fig. 1), which enable new deactivation channels. The latter may be directly related to the biological activity of 2-thiocytosine.

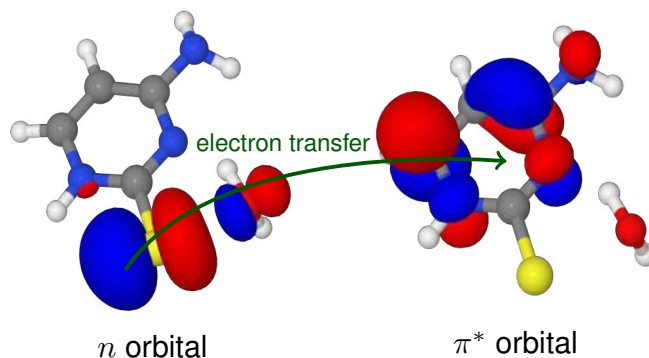


Figure 1: Water-to-chromophore electron transfer in the  $T_1$   $n\pi^*$  state of microhydrated 2-thiocytosine

- [1] C. Vetter, et al., *Inorg. Chim. Acta.* **362**(1), 189 (2009).
- [2] M. F. Fillat, et al., *Eur. J. Inorg. Chem.* **2011**(9), 1487 (2011).
- [3] S. Mai, et al., *Nat. Commun.* **7**, 13077 (2016).
- [4] Szabla, et al., *Faraday Discuss* **195**, 237 (2016).
- [5] Barbatti M., et al., *J. Am. Chem. Soc.* **136**(50), 10246 (2014).

## **A down-folded effective Hamiltonian combining many-body perturbation theory with configuration interaction**

**Marc Dvorak<sup>1</sup>, Patrick Rinke<sup>1</sup>**

<sup>1</sup>*Aalto University, Centre of Excellence in Computational Nanoscience (COMP),  
P.O. Box 11100, FI-00076 AALTO, Finland*

We are developing a new method to predict optical excitations and ionization energies in correlated molecules. Our down-folding approach relies on a partitioning of the Hilbert space into an active space and a bath [1]. Correlation in the bath is treated with many-body perturbation theory (MBPT), while correlation in the active space is treated with configuration interaction. The novelty of our method is the coupling between the spaces. The coupling is through the exact many-body Hamiltonian and the Green's function from the bath space. Because the hybridization between spaces is with the exact Hamiltonian, the accuracy of our approach is limited only by the basis size in the active space and the accuracy of the bath Green's function. Calculation of the bath Green's function can follow any of the already developed routes in MBPT. We use the standard  $GW$ +Bethe-Salpeter Equation (BSE) framework, subject to a modified polarizability to avoid double-counting correlation from the active space. Our method is therefore systematically improvable, without empirical parameters, and well-suited to multi-reference systems or double excitations. We present preliminary results for  $N_2$ , benzene, and tetrazine molecules, which show an improvement over the conventional  $GW$ +BSE approach for optical excitation energies. Our computed molecular dissociation curves also show good agreement with full configuration interaction results.

- [1] V. A. Dzuba, V. V. Flambaum, and M. G. Kozlov, *Phys. Rev A* **54**, 3948 (1996).

## Bonding situation in $C_2E_2$ ( $E = N, P, As, Sb, Bi$ ) ligand stabilized complexes

Diego M. Andrada and Gernot Frenking

*Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße, 35032 Marburg, Germany.*

The chemistry of low-valent main group 13-15 compounds has done a remarkable progress in the last decade.[1] The  $\sigma$ -donor ligands (L) such as phosphines  $PR_3$ , *N*-heterocyclic carbene (NHC) and cyclic (alkyl) (amino) carbenes (cAAC) turned out to be the key for broadening the scope in this area. Arguably, the synthesis of the disilicon molecule  $Si_2L_2$  and carbondicarbene  $CL_2$  are the major discoveries.[2,3] Since then, monoatomic  $EL_2$ , diatomic  $E_2L_2$  ( $E = B, N, P, As, Si, Ge, Sn$ ) and cyclic triatomic  $E_3L_3$  ( $E = B, Si$ ) species have been reported. In this context, theoretical studies played a crucial role through reinterpretation of the bonding situation and with predicting possible new compounds.[1] Recently, we have found that  $\sigma$ -donor ligands are capable to stabilize cyclic  $C_2P_2$  core molecule via donor-acceptor interactions.[4,5] Computational calculations has suggested a weak covalent transannular  $P\cdots P$  interaction. Interestingly,  $C_2P_2$  can adopt both cyclic and acyclic trans-bent structure depending on the nature of the ligand (Figure 1). Inspired by those finding, in this work we present a detailed theoretical study on the electronic structure of the complete series of group 15  $(C_2E_2)L_2$  ( $E = N, P, As, Sb, Bi$  and  $L = NHC$  and cAAC). In order to gain further insight into origins of the different scaffolds, we have performed a detailed bonding analysis in the light of Energy Decomposition Analysis (EDA).

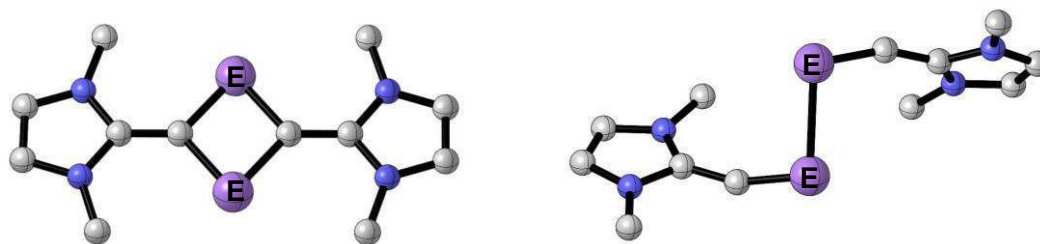


Figure 1. Different molecular structures of  $(C_2E_2)NHC_2$  ( $E = N, P, As, Sb, Bi$ ) compounds. Hydrogen atoms were omitted for clarity.

[1] G. Frenking, M. Hermann, D. M. Andrada, N. Holzmann *Chem. Soc. Rev.* 45, 1129 (2016).

[2] Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. V. R. Schleyer, G. H. Robinson *Science* **321**, 1069 (2008).

[3] C. A. Dyker, V. Lavallo, B. Donnadieu, G. Bertrand *Angew. Chem, Int. Ed.*, 47, 3206 (2008).

[4] Z. Li, X. Chen, D. M. Andrada, G. Frenking, Z. Benkö, Y. Li, J. R. Harmer, C.-Y. Su, H. Grützmacher *Angew. Chem., Int. Ed.* **56**, 5744 (2017).

[5] R. Ghadwal, D. Rottschaefer, B. Neumann, H.-G. Stammler, *Chem. Eur. J.* DOI: 10.1002/chem.201702433.

## **Aggregation of MB in water and water/urea mixtures: the role of solute polarization.**

**Cleiton Maciel<sup>1,2</sup> and Maurício Domingues Coutinho-Neto<sup>2</sup>**

<sup>1</sup>*Instituto Federal de São Paulo, Rua Primeiro de Maio, 500, CEP 08571-050, Itaquaquecetuba, Brazil.*

<sup>2</sup>*Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Avenida dos Estados, 5001, CEP 09210-580, Santo André, Brazil.*

Methylene Blue (MB) is a phenothiazine compound used in several important applications, especially in photodynamic therapy (PDT). In PDT, cell damage and death is triggered by reactive oxygen species (ROS) such as singlet oxygen formed from the interaction between light sensitive chemical compounds and light with a specific wavelength. Aggregation of Phenothiazines and other photosensitizers in solution, leads to a significant loss of photochemical efficiency and consequent reduction of therapy efficacy.

In this work, we investigate the driving force behind Methylene Blue (MB) aggregation in water and in a water/urea 2M mixture by using a combination of Density Functional Theory (DFT) and Molecular Dynamics (MD) methods. An iterative procedure for obtaining a converged average solute-solvent potential was used to investigate the role of solute induction and polarization by the solvent.

Molecular dynamics simulations were performed for monomers and dimers MB in order to study the aggregation in a molecular point of view. To achieve this goal, cubic cells were modeled with 4000 SPC water molecules in a NPT ensemble using GROMOS 53a6 force field. Micro-heterogeneous solutions were modeling by adding urea molecules to the aqueous solutions in a 2M concentration. Running-lengths of 20 ns were adopted to extract thermodynamic properties from each calculation. Solvation free energies were computed by using Thermodynamic Integration (TI) technique. All the molecular dynamics simulations were performed using GROMACS 4.5 package.

A self consistent protocol was employed to compute a converged average solute-solvent potential and to obtain the polarized charge distribution of MB in solution. The solute-solvent interaction potential was described by a simple point charge representation of the solvent. The final induced dipole of MB in water and in a 2M water/urea mixture show a circa 80% increase in value when compared to gas phase calculations. Surprisingly, the pure water and 2M water/urea mixture produce virtually identical results for the final dipole and charge distributions. The most notorious effect of the solvent induced polarization, besides the dipole increase, was the localization of a negative charge on the ring N atom, resulting in stronger hydrogen bonds with solvent molecules. All the DFT calculations were done using the Orca 3.03 code. The functional B3LYP and def2-PVTZ basis set were used throughout.

The authors acknowledge FAPESP, CAPES and UFABC for financial support.

**Keywords:** Methylene Blue, Molecular Dynamics, Density Functional Theory, Polarization, Aggregation.



## Multi-Level QM:QM Adsorption Studies within MonaLisa Program.

Maristella Alessio<sup>1</sup> and Joachim Sauer<sup>1</sup>

<sup>1</sup>*Institut für Chemie, Humboldt-Universität zu Berlin, Unter den Linden 6, 10999 Berlin, Germany*

MonaLisa program [1] enables to design a large variety of multi-level potential energy surfaces (PES). A key feature is the implementation of the mechanical embedding scheme for hybrid QM:QM methods. We rely on the latter to determine accurate electronic energies and to predict equilibrium structures of periodic systems with hundreds of atoms in the unit cell. Our hybrid QM:QM method combines high-level MP2 on cluster models with low-level DFT+D on periodic models. The hybrid MP2:DFT+D PESs are counterpoise corrected (CPC) for the basis set superposition error (BSSE) and extrapolated to the complete basis set (CBS) limit. A posteriori, CCSD(T) coupled-cluster correlation effects are estimated as CCSD(T)-MP2 energy differences. The applicability of such hybrid MP2/CPC-CBS:DFT+D+ $\Delta$ CCSD(T) methods has been recently confirmed for selected catalytic reaction steps, *i.e.* adsorption processes of small alkanes in H-Chabazite zeolite [2] and methylation reactions of small alkenes in H-ZSM-5 zeolite [3]. In the present work we focus on two further adsorption studies: (i) methane and ethane on the MgO(001) surface (low and monolayer coverage) and (ii) methanol and ethanol over the acidic catalytic site of the H-ZSM-5 zeolite. We show how the hybrid MP2/CPC-CBS:DFT+D+ $\Delta$ CCSD(T) approach is a fundamental computational step to obtain accurate electronic energies and to reproduce the experimental references within the limits of chemical accuracy ( $\pm 1$  kcal/mol  $\approx \pm 4$  kJ/mol). With the obtained electronic adsorption energies and minima we enlarge the set of benchmarking ab initio results available for extended periodic systems.

- [1] F. Bischoff, M. Alessio, M. John, M. Rybicki and J. Sauer, *Multi-Level Energy Landscapes: The MonaLisa Program*, available from: <https://www.chemie.hu-berlin.de/de/forschung/quantenchemie/monalisa/>, Humboldt-University: Berlin, (2017).
- [2] G. Piccini, M. Alessio, J. Sauer, Y. Liu, R. Kolvenbach, A. Jentys and J. A. Lercher, *J. Phys. Chem. C* **119**, 6128 (2015).
- [3] G. Piccini, M. Alessio and J. Sauer, *Angew. Chem.* **128**, 5321 (2016).



## Excited State Hydroxide Ion Transfer in Aqueous Media: Ab-Initio MD Simulation of a Bifunctional Chromophore

Felix Hoffmann<sup>1</sup>, Daniel Sebastiani<sup>1</sup>

<sup>1</sup>*Institut für Chemie, Martin-Luther-Universität Halle-Wittenberg, Von-Danckelmann-Platz 4, 06120 Halle (Saale), Germany*

Photoacids and -bases undergo drastic  $pK_a$  changes upon electronic excitation and are therefore able to initiate proton or hydroxide ion transport in water.

This way, they enable the study of kinetics, elementary steps and co-solvent effects of solvent ion transfer in bulk solutions. [1, 2] Moreover, well-defined hydrogen bonded solvent bridges can be investigated via bifunctional chromophores that carry photo-acidic and -basic functionalities at specific molecular sites; [3] the example of 7-hydroxyquinoline (7HQ) is shown in Figure 1. Similarly to ion channels in biological systems, these configurations facilitate ultrafast charge transport through a hydrogen bonded network, because their life-times lie significantly beyond hydrogen bond reorientation times in the bulk.

In our current study, we report results on the excited state solvent ion transport in methanol-water mixtures triggered by 7HQ. By means of *ab-initio* simulations in the ground and first excited state, employing TD-DFT, we investigated the initial steps of the reaction and its dependency on the microscopic solvent composition. Our main findings are that the reaction takes place via the formation of hydroxide and methanolate ions that are transferred in a Grotthus-like mechanism as opposed to the more commonly discussed hydronium ion transport. Microscopically, the transfer is largely limited by the reorientation time of methanol. This illustrates the importance of considering non-aqueous components for the understanding of charge transport in crowded biochemical systems such as protein channels.

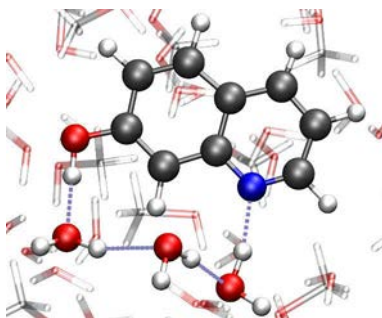


Figure 1: MD snapshot of 7HQ in 7:3 water-methanol solution. A hydrogen bonded solvent bridge is indicated by dashed lines.

- [1] G. Bekçioğlu, F. Hoffmann, D. Sebastiani, *J. Phys. Chem. A* **119**, (2015) 9244.
- [2] F. Hoffmann, M. Ekimova, G. Bekçioğlu-Neff, E. Nibbering, D. Sebastiani, *J. Phys. Chem. A* **120**, (2016) 9378.
- [3] G. Bekçioğlu, C. Allolio, D. Sebastiani, *J. Phys. Chem. B* **119**, (2015) 4053.

## Computational study of DNAzyme 9DB1: prediction of the pre-catalytical conformation and the reaction mechanism.

**Juan Aranda<sup>1</sup>, Hansel Gómez<sup>1</sup> and Modesto Orozco<sup>1</sup>**

*Institute for Research in Biomedicine (IRB Barcelona), The Barcelona Institute of Science and Technology, Baldori Reixac 10-12, 08028 Barcelona, Spain*

Although the catalytic power of RNA (ribozymes) has been broadly studied over the past 20 years, less is known about the possible catalytic features of DNA. In the past years DNA acting as a catalyst (DNAzymes) has emerged as a blooming field. DNA as a catalyst was first developed as a therapeutically tool to silence genes through the cleavage of mRNA targets. These DNAzymes that cleave RNA are the most studied ones till the date, although catalysis for other reactions has been also developed. Different ligation reactions of RNA and DNA, oxidative DNA cleavage or excision of nucleobases, DNA phosphodiester hydrolysis, RNA hydrolysis, kinase activity through 5'-phosphorylation and adenylation has been achieved with newly synthesized DNAzymes.<sup>[1]</sup>

It has not been till recently that the first structure of a DNAzyme was resolved.<sup>[2]</sup> This structure sheds light into the pseudoknot type folding of the 44-nucleotide DNA strand in complex with the already ligated 15-nucleotide RNA strand. The 9DB1 DNAzyme characterized by A. Ponce-Salvatierra catalyzes the ligation reaction of two RNA strands by forming the phosphodiester bond between the 3'OH atom of one strand and the 5'P atom belonging to a GTP bound RNA strand in the presence of Mg<sup>2+</sup> or Mn<sup>2+</sup> cations. However the structure of the 9DB1 was crystalized in its post-catalytical state, making it difficult to establish which is the Michaelis Complex that undergoes catalysis, the correct positioning of the reactants and the reason for the transition state stabilization. Moreover, the role of metal ions necessary for catalysis could not be understood as no ions were found near the linkage site.

In order to unravel the mechanistic features of the 9DB1 ligating DNAzyme we have performed extensive calculations into the system. We have performed classical molecular dynamics (MD) simulations to simulate the post-catalytical state and to construct the pre-catalytical active state. With the use of Molecular Interaction Potential (CMIP) calculations and classical MD simulations we were able to obtain a catalytically competent structure that was confirmed with extensive QM/MM and QM/MM-MD calculations. Calculations were also performed to confirm and identify the preferred binding site of the metal ions by CMIP calculations. We have also made use of the hybrid quantum-mechanics molecular-mechanics (QM/MM) methodology to perform MD simulations to unravel the most preferred mechanism in terms of free energy at a high QM DFT level. These mechanistic insights could be used to enhance the catalytic power as well as the efficiency and clarify the role of ions in catalysis.

[1] S. K. Silverman, *Angew. Chemie - Int. Ed.* **49**, 7180 (2010).

[2] A. Ponce-Salvatierra, K. Wawrzyniak-Turek, U. Steuerwald, C. Höbartner, V. Pena, *Nature* **529**, 231 (2016).

## Random Phase Approximation for Periodic Systems Employing Direct Coulomb Lattice Summation

Martin M. J. Grundei<sup>1</sup>, Asbjörn M. Burow<sup>1</sup>

<sup>1</sup>*Department of Chemistry, LMU Munich, Butenandtstr. 7, 81377 Munich, Germany*

For practical calculations of complex chemical systems, the correlation energy must be approximated with simple computational schemes, e.g., MP2 or DFT based approaches. However, the first approach fails for transition metal complexes while the second fails for weakly bound subsystems. In contrast, the *Random Phase Approximation* (RPA) provides a good compromise between accuracy and efficiency.[1, 2] RPA is parameter-free, non-perturbative and takes dispersion interactions into account. This has led to renewed interest in RPA and the development of low scaling approaches.[3, 4] Though RPA is on the fourth rung of Jacob's ladder of DFT, RPA is often applied as a post-DFT method.

Our RI-RPA scheme uses resolution of the identity based on *Gaussian type functions* (GTF) for periodic systems.[5] This makes modeling of 1D and 2D periodic systems explicit and efficient. The generalized RI-RPA expression includes *k-point sampling* and recovers a previously derived RI-RPA equation for molecules.[6] Molecular correlation energies are shown for the A24 test set; periodic correlation energies and timings are assessed by a methane test system. Periodic RPA binding energies for naphthalene and benzene 1D chains are compared to molecular oligomers.

- [1] H. Eshuis, J. E. Bates, F. Furche, *Theor. Chem. Acc.* **131**, 1084 (2012).
- [2] X. Ren, P. Rinke, M. Scheffler, *Phys. Rev. B* **80**, 045402 (2009).
- [3] J. Wilhelm, P. Seewald, M. Del Ben, J. Hutter, *J. Chem. Theor. Comput.* **12**, 5851 (2016).
- [4] H. F. Schurkus, C. Ochsenfeld, *J. Chem Phys.* **144**, 031101 (2016).
- [5] M. M. J. Grundei, A. B. Burow, *J. Chem. Theor. Comput.* **13**, 1159 (2017).
- [6] H. Eshuis, J. Yarkony, F. Furche, *J. Chem. Phys.* **132**, 234114 (2010).

## Investigation of electron transfer rates in a Ru-Pd molecular photocatalyst

M. Staniszevska<sup>1</sup>, S. Kupfer<sup>2</sup>, D. Kinzel<sup>3</sup>, J. Guthmuller<sup>1</sup>

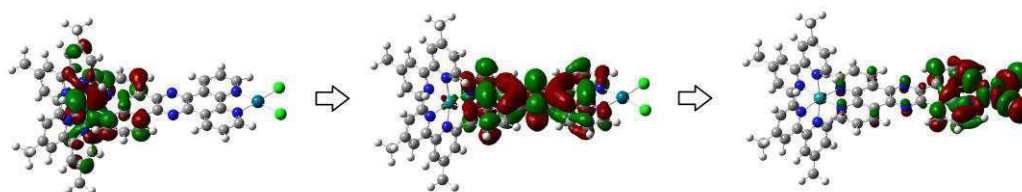
<sup>1</sup>*Faculty of Applied Physics and Mathematics, Gdańsk University of Technology,  
Narutowicza 11/12, 80-233, Gdańsk, Poland*

<sup>2</sup>*Institute for Physical Chemistry, Friedrich-Schiller University Jena, Helmholtzweg 4,  
07743, Jena, Germany*

<sup>3</sup>*Leibniz Institute of Photonic Technology Jena, Albert-Einstein-Straße 9,  
07745 Jena, Germany*

The design of molecular photocatalysts, storing solar energy in molecular hydrogen, is of tremendous importance for the development of new and clean energy sources. Such systems are usually composed of a sensitizer, of a bridge and of a catalytic center. A detailed understanding of the electron transfer mechanisms, occurring after the initial photoexcitation, is required to optimize the efficiency of hydrogen production.

In this contribution, the triplet excited states playing a role in the electron transfer processes of a Ru-Pd photocatalyst [1,2] are investigated by DFT/TDDFT calculations (Figure 1). The energy, geometry and potential energy surfaces of the triplet states are computed to identify the most favorable reaction paths. Then, the electron transfer rates are determined by Marcus theory and compared to time-resolved experimental data [3].



**Figure 1:** Example of orbitals involved in the electron transfers. The left arrow describes the initial photoexcitation to a MLCT state. The right arrow represents the subsequent electron transfer from the bridge to the catalytic center.

### Acknowledgments

The authors are grateful to the Narodowe Centrum Nauki (Project No. 2014/14/M/ST4/00083) for financial support. The calculations have been performed at the Universitätsrechenzentrum of the Friedrich-Schiller University of Jena and at the Wrocław Center for Networking and Supercomputing (grant no. 384).

### References

- [1] S. Rau et al., *Angew. Chem. Int. Ed.* **45**, 6215 (2006).
- [2] M. Wächter et al., *Chem. Eur. J.* **21**, 7668 (2015).
- [3] S. Tschierlei et al., *Chem. Eur. J.* **15**, 7678 (2009).

## Computational study of halloysite as a tubular nanocarrier to control drug release

**Ana Borrego-Sánchez<sup>1,2</sup>, Esperanza Carazo<sup>2</sup>, Carola Aguzzi<sup>2</sup>, César Viseras<sup>1,2</sup>, C. Ignacio Sainz-Díaz<sup>1</sup>**

<sup>1</sup>*Instituto Andaluz de Ciencias de la Tierra, CSIC-University of Granada, Av. de las Palmeras 4 18100, Armilla, Granada*

<sup>2</sup>*Department of Pharmacy and Pharmaceutical Technology, University of Granada, Campus de Cartuja s/n 18071, Granada*

Clay minerals are biocompatible and low cost materials which are abundant in nature. They have high adsorption, cation exchange capacity and swelling properties [1]. Their characteristics are directly related to their colloidal size and crystalline structure. In particular, halloysite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ ) is a multilayer nanotubular material resulting from the wrapping of 1:1 layers of kaolinite with 500-1000 nm in length and 15-100 nm in inner diameter. Halloysite nanotubes are common excipients in pharmaceutical products and can modify drug bioavailability. They can retain organic molecules and, after administration, release the retained bioactive compounds under controlled conditions.

The aim of this work was to perform a computational study of the interaction between drugs and halloysite nanotubes, as a first stage in the development of modified drug delivery systems. Different solid models were generated from the atomic coordinates of a slice of a halloysite nanotube [2], applying periodic boundary conditions to create a periodical crystal structure (Figure 1). The optimization of this nanotube and the adsorption of drugs on the internal surface of halloysite were performed with quantum mechanical calculations by using Density Functional Theory (DFT) with CASTEP code.

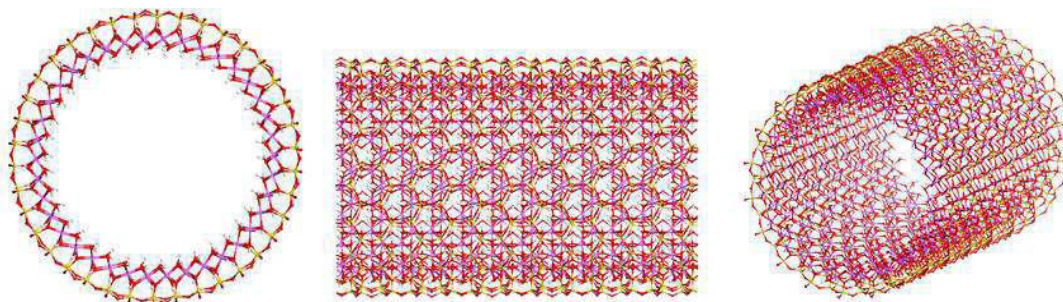


Figure 1. Structure of the halloysite nanotube optimized with CASTEP.

[1] C. Viseras, P. Cerezo, R. Sánchez, I. Salcedo, C. Aguzzi, *Appl. Clay Sci.* **48**, 291 (2010).

[2] L. Guimarães, A.N. Enyashin, G. Seifert, H.A. Duarte, *J. Phys. Chem. C* **114**, 11358 (2010).

## Frozen virtual natural orbitals for coupled cluster properties

Ashutosh Kumar<sup>1</sup>, T. Daniel Crawford<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Virginia Tech, Blacksburg, Virginia, USA*

Frozen virtual natural orbitals (FVNO) approach[1, 2], a very useful reduced scaling technique for calculating ground state correlation energies, has been extended to calculate higher order properties at CCSD and EOM-CCSD level of theory. Compared to the correlation energies, properties like polarizabilities and optical rotation were found to be much more sensitive to the truncation of virtual space in the natural orbital basis, with the errors increasing linearly with respect to the number of frozen virtual natural orbitals[3]. The performance of the FVNO approach for such properties, can be improved by employing a correction using relatively less accurate methods like CC2. However, these corrections based strategies soon become computationally prohibitive for larger systems. Finally, a new strategy called FVNO++ was devised, where diffuse orbitals (up to a given cutoff of diffusivity) are retained in the correlated calculations, followed by the usual truncation of the remaining virtual space based on occupation number cutoffs. The FVNO++ method produces very small errors compared to the regular FVNO approach and thus is more suitable for property calculations. Quite surprisingly, the canonical scheme, where truncation is based on orbital energies, produced relatively lower errors for most of the properties due to inherent cancellation of errors and a new criterion was devised to help find the size of the optimal domain for truncation of virtual molecular orbitals in the canonical basis. Interestingly, the observations noted above are reversed in the case of finite difference calculations of static properties, illustrating the significance of orbital relaxation which is absent in the coupled cluster based linear response theories.

- [1] P. O. Löwdin, *Phys. Rev.* **97**, 1474 (1955).
- [2] T. L. Barr, E. R. Davidson, *Phys. Rev. A* **1**, 644 (1970).
- [3] A. Kumar, T. D. Crawford, *J. Phys. Chem. A* **121**(3), 708 (2017).

## Quantum chemical studies of a hemithioindigo-based photodriven molecular motor

Florian Rott<sup>1</sup>, Sven Oesterling<sup>1</sup>, Ludwig Huber<sup>1</sup>, Roland Wilcken<sup>2</sup>, Henry Dube<sup>1</sup>, Eberhard Riedle<sup>2</sup>, Regina de Vivie-Riedle<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Ludwig-Maximilians-Universität, Butenandtstr. 5-13, Munich, Germany*

<sup>2</sup>*Lehrstuhl für Biomolekulare Optik, Ludwig-Maximilians-Universität, Oettingenstr. 67, Munich, Germany*

In recent years photodriven molecular motors received increasing interest due to their ability to convert light energy into directional motion. Dube *et al.* [1] synthesised a hemithioindigo-based photodriven molecular motor. This motor performs a full rotation after excitation with visible light, showing > 95% unidirectionality at a very fast rate of 1 KHz at 20°C.

The full rotation is believed to be a four step process consisting of two light induced and two thermal steps. However, the underlying mechanism of the rotation is not completely understood. To elucidate the reaction path we performed excited state quantum chemical calculations at the CASSCF level of theory. We present several possible pathways for the light-induced steps that compare to the femtosecond pump-probe experiments performed in the Riedle group.

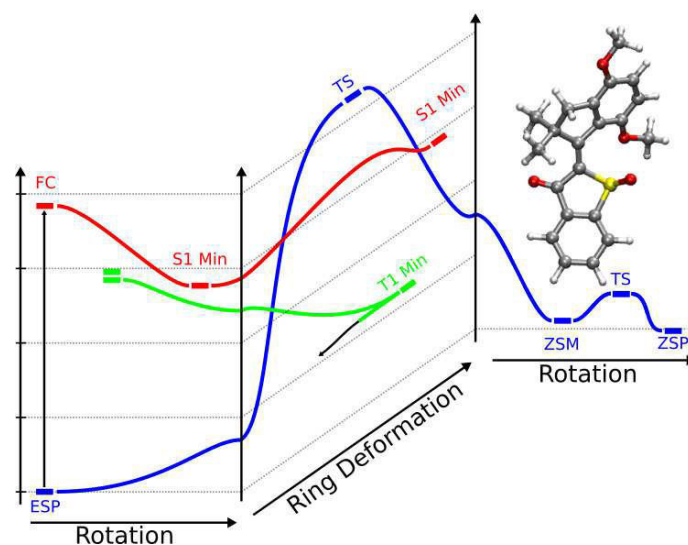


Figure 1: Possible pathways for one of the light-induced steps.

- [1] M. Guentner, M. Schildhauer, S. Thumser, P. Mayer, D. Stephenson, P. J. Mayer, H. Dube, *Nat. Commun.* **6**, 8406 (2015).



## Electronic excited states of organic molecules adsorbed on Cu(100).

**Fernando Aguilar-Galindo<sup>1</sup>, Sergio Díaz-Tendero<sup>1,2,3</sup>, Andrei Borisov<sup>4</sup>**

<sup>1</sup>*Departamento de Química, Universidad Autónoma de Madrid, Madrid E-28049, Spain*

<sup>2</sup>*Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, Spain*

<sup>3</sup>*Institute for Advanced Research in Chemical Sciences (IAdChem), Universidad Autónoma de Madrid, Spain*

<sup>4</sup>*Institut des Sciences Moléculaires d'Orsay (ISMO), CNRS-Université Paris Sud, France*

Adsorption of organic molecules on metal surfaces is a process of high interest due to the large number of applications in which it is involved: heterogeneous catalysis, hybrid materials, photovoltaic devices, optoelectronic devices... The electronic excited states of the adsorbed molecules play an important role in some of these examples. For example, to turn the solar radiation into electric energy, an electron is promoted to a higher empty level, where it can move to the active part of the system.

In this communication we present a theoretical study of some molecules, as carbon monoxide, acrylonitrile or acrolein, adsorbed on Cu(100). In particular, we focus on the changes in the properties of the electronic excited states upon adsorption.

To this, we have used the Wave Packet Propagation (WPP) method [1]. In addition to the energy position in the spectrum and the wavefunctions, it allows to obtain the lifetimes of the states. It is a very important quantity that, in the case of molecule-surface systems, is strongly affected by the coupling of the molecular electronic structure with the surface levels.

The geometry of the adsorbed molecules and the potential used for the WPP is obtained with Density Functional Theory (DFT). Since the physisorption is mainly governed by weak interactions (van der Waals forces), we have used the OPTPBE [2] functional, which includes explicitly these effects.

[1] E. V. Chulkov et al, *Chem. Rev. (Washington D.C.)*. **106**, 4160 (2006).

[2] M. Dion et al, *Phys. Rev. Lett.* **92**, 246401 (2004).



## Homogeneous Volcano Plots: In Search of New Metal-Pincer Complexes for the Hydrogenation of Carbon Dioxide

**Boodsarin Sawatlon, Matthew D. Wodrich and Clémence Corminboeuf**

*Laboratory for Computational Molecular Design (LCMD),  
Institute of Chemical Sciences and Engineering (ISIC), École Polytechnique Fédérale de Lausanne  
(EPFL), CH-1015 Lausanne, Switzerland*

Volcano plots, commonly employed tools for identifying potential catalysts in heterogeneous and electrochemical applications,[1] were previously demonstrated to be both applicable and beneficial for the study of homogeneous systems.[2] The thermodynamic and kinetic profiles of perspective catalysts can be predicted by computing a simple descriptor variable (the magnitude of catalyst/ substrate binding interaction) which relates to the relative energies of all catalytic cycle intermediates and transition states through linear free energy scaling relationships. Thus, knowing the value of this descriptor gives a complete energetic picture of the catalytic cycle for any potential species. This concept was shown to be quite successful for studying C-C cross coupling and hydroformylation reactions where the findings closely aligned with known experimental results. Given increasing atmospheric CO<sub>2</sub> concentrations, the hydrogenation of carbon dioxide to formic acid/formate is intriguing from the perspective of recycling waste into useful chemicals. However, existing catalysts facilitating this process require high pressure and generally have low efficiency. With the ability of volcano plots to predict new catalytic species; we explored the hydrogenation of carbon dioxide to formate using metal-pincer catalysts based on the mechanism proposed by Yang, [3]. The position of the highly efficient Ir(H)<sub>3</sub>PNP catalyst (PNP = 2,6-bis(di-isopropylphosphinomethyl) pyridine) on the volcano plot matches its known experimental traits, however other experimentally uncharacterized catalysts are predicted to have equal or greater activity.

[1] J. K. Nørskov, T. Bligaard, J. Rossmeisl and C. H. Christensen, *Nat. Chem.* **1**, 37-46 (2009).

[2] (a) M. Busch, M. D. Wodrich and C. Corminboeuf, *Chem. Sci.* **6**, 6754-6761 (2015). (b) M. D. Wodrich, M. Busch and C. Corminboeuf, *Chem. Sci.* **7**, 5723-5735 (2016).

[3] X. Yang, *ACS Catal.* **1**, 849-854 (2011).

## Keto-enol tautomerization on the bioluminescence emitter in fireflies

**Romain Berraud-Pache<sup>1</sup>, Isabelle Navizet<sup>1</sup>**

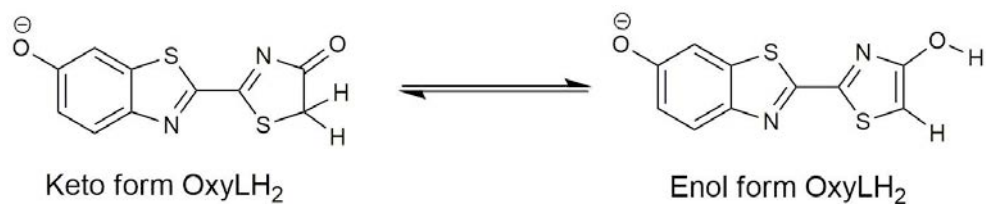
<sup>1</sup>*Laboratoire Modélisation et Simulation Multi-Echelle, Université Paris-Est Marne-la-Vallée, MSME UMR 8208 CNRS, 5 Bd Descartes 77454 Marne-la-Vallée Cedex 2, France*

The bioluminescence process corresponds to the emission of visible light through a chemical reaction in living things. Those species can be found all around the globe from mushrooms and worms on land to jellyfish in the ocean.

In fireflies, this process involves two molecules, a protein called luciferase and a substrate called luciferin. During the bioluminescent mechanism, the luciferin reacts to give an emitter, named oxyluciferin or OxyLH<sub>2</sub> that emits in the yellow-green area of the visible spectra. However researchers are still arguing on one question: What is the chemical form of the emitter of the bioluminescence?

Indeed, two different tautomers are nowadays in competition, the phenolate-keto form and the phenolate-enol form[1]. It has been admitted from previous calculations[2] that the resulting tautomer from the bioluminescence reaction is the phenolate-keto. But is it still possible to observe a keto-enol tautomerization in protein?

To decipher this behaviour, QM/MM calculations (Quantum Mechanics/Molecular Mechanics) will be carried out in order to estimate the energetic barrier between the phenolate-keto form and the phenolate-enol form inside the protein. The study has to be done at the ground state but also at the 1<sup>st</sup> singlet excited state to fully understand the mechanism of isomerization.



[1] S-F. Chen, Y.-J. Liu, I. Navizet, N. Ferré, W.-H. Fang and R. Lindh, *Journal of Chemical Theory and Computation*, **7**, 798 (2011).

[2] I. Navizet, Y.-J. Liu, N. Ferré, D. Roca-Sanjuán and R. Lindh, *ChemPhysChem*, **12**, 3064, (2011).

## Modelling Environmental Effects for Excitations in Molecular Crystals

**Miguel Rivera, Michael Dommett, Rachel Crespo-Otero<sup>1</sup>**

*School of Biological and Chemical Sciences, Materials Research Institute, Queen Mary  
University of London, Mile End Road, London, UK, E14NS*

<sup>1</sup>*r.crespo-otero@qmul.ac.uk*

The photochemistry of molecular crystals has recently attracted attention due to their technological applications in crystal lasing, solar cells, OLEDs and field effect transistors. In order to accurately model the phenomena central to these systems, excited state calculations need to be carried out. However this becomes prohibitively expensive when in a periodic environment and there remains a lack of methodology when it comes to modelling excitations in molecular crystals.

To address this issue, existing hybrid methods are being built upon. In this protocol, periodic DFT calculations are combined with refined population analysis methods to provide a background charge distribution for single molecule TDDFT calculations embedded in clusters of molecules treated at ground state Hartree-Fock level. The resulting long range Coulomb potential combined with a fully quantum short range interaction favours photochemical mechanisms present only in the condensed phase. This method benefits from only treating one molecule at a high level of theory while describing the electrostatic influence coming from different cell geometries on the molecule. It supports geometry optimisation as well as Minimal Energy Conical Intersection (MECI) search.

Calculations are carried out on several photoactive molecular crystals in order to assess the influence of a crystalline environment on their fluorescence and their conical intersection energies. This poster describes the theory and protocol behind the calculations and the results, comparing them to experimental studies. The limitations of the protocol are discussed and possible improvements are suggested, as well as candidate systems for future development.

## Algebraic-Diagrammatic Construction with Coupled-Cluster Amplitudes: Improved Static Dipole Polarizabilities

Manuel Hodecker<sup>1</sup>, Dirk R. Rehn<sup>2</sup>, Andreas Dreuw<sup>1</sup>

<sup>1</sup>*Interdisciplinary Center for Scientific Computing, Universität Heidelberg, Im Neuenheimer  
Feld 205, 69120 Heidelberg, Germany*

<sup>2</sup>*KTH Royal Institute of Technology, Stockholms Universitet, Roslagstullsbacken 15, 11421  
Stockholm, Sweden*

A new modification of the algebraic-diagrammatic construction scheme for the polarization propagator (ADC) called CCD-ADC(2) is presented, inspired by similar work on the related SOPPA method [1, 2]. In order to remedy the sometimes weak Møller–Plesset (MP) ground-state description in ADC, the MP correlation coefficients were replaced by coupled cluster doubles (CCD)  $T_2$  amplitudes for the calculation of vertical excitation energies and transition moments via the second-order ADC scheme. Furthermore, coupled-cluster amplitudes have been used in the newly implemented ADC scheme for the complex polarization propagator for the calculation of static polarizabilities [3]. Here, either both first-order MP doubles and second-order MP singles coefficients were replaced by the corresponding CCSD  $T_2$  and  $T_1$  amplitudes or only the former by the corresponding CCD  $T_2$  amplitudes, and they were replaced either everywhere or only in the vectors of modified transition moments, but not in the ADC secular matrix.

The static dipole polarizabilities of several atomic and molecular systems were calculated and compared to FCI results or to experiment. Minor improvements could be obtained for small systems like HF or H<sub>2</sub>O. It is shown that the influence of the amplitudes is more distinct in the vectors of modified transition moments than in the secular matrix, and that CCD amplitudes seem to be better for ADC(2) than CCSD ones. However, the differences are in general rather small. For the aromatic system benzene, which had proven to be a problematic case for standard ADC approaches [3], a clear improvement can be observed. Hence, more aromatic systems like pyridine or naphthalene shall be investigated in the future, provided that experimental data are available to confirm the general applicability of the novel approach.

[1] J. Geertsen, J. Oddershede, *J. Chem. Phys.* **85**, 2112 (1986).

[2] S. P. A. Sauer, *J. Phys. B: At. Mol. Opt. Phys.* **30**, 3773 (1997).

[3] T. Franson, D. R. Rehn, A. Dreuw, P. Norman, *J. Chem. Phys.* **146**, 094301 (2017).

## MODELING THE MODULATION OF EMISSION BEHAVIOR IN E/Z ISOMERS OF DIPHENYLDIPYRROETHENE

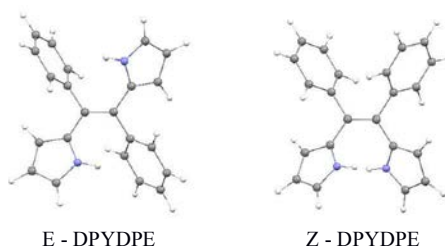
**Laura Le Bras<sup>1</sup>, Carlo Adamo<sup>1,2</sup>, Aurélie Perrier<sup>1,3</sup>**

<sup>1</sup> *Chimie ParisTech, PSL Research University, CNRS, Institut de Recherche de Chimie Paris (IRCP), F-75005 Paris, France.*

<sup>2</sup> *Institut Universitaire de France, 103 Boulevard Saint Michel, F-75005 Paris, France.*

<sup>3</sup> *Université Paris Diderot, Sorbonne Paris Cité, 5 rue Thomas Mann, F-75205 Paris Cedex 13, France.*

Phenomena that induce change in the expression of emission properties of organic chromophores is of major interest nowadays with potential applications in optoelectronic devices such as fluorescent sensors in cell imaging [1]. Those phenomena are known as Aggregation Caused Quenching (ACQ) and Aggregation Induced Emission (AIE) or Crystallization Induced Emission (CIE). Depending on whether ACQ or AIE (CIE) is considered, properties in a given phase (dilute or concentrated solution, solid films, ...) will be radically different, resulting in a quenching or enhancement of the emission behavior for the molecule. Here we attempt to describe and rationalize, thanks to theoretical tools, the different behavior of isomer E and Z of DPYDPE [2] in terms of emission properties in three different phases, namely the solution, crystal and aggregate. Both isomers will be studied with the help of (TD-)DFT in solution (PCM model), crystalline phase (QM/QM') and in aggregated phase (Molecular Dynamics combined with QM/QM'). To get a deeper comprehension of the AIE and CIE effects, Huang Rhys [3] (HR) factors and reorganization energies (that strongly influence the non-radiative decay rate) were calculated to explain the emission behavior of an isomer in the three different phases but also the observed difference between isomers E and Z.



[1] (a) B. Wang, X. Wang, W. Wang, F. Liu, *J. Phys. Chem. C* **120**, 21850 (2016). (b) G. Sun, Y. Zhao, W.-Z. Liang, *J. Chem. Theory Comput.* **11**, 2257 (2015).

[2] K. Garg, E. Ganapathi, P. Rajakannu, M. Ravikanth, *Phys. Chem. Chem. Phys.* **17**, 19465 (2015).

[3] Y.-C. Duan, Y. Wu, J.-L. Jin, D.-M. Gu, Y. Geng, M. Zhang, Z.-M. Su, *Chem. Phys. Chem.* **18**, 755 (2017).

## Watson-Crick $\leftrightarrow$ Hoogsteen transitions in duplex DNA: a systematic MD study.

Hansel Gómez<sup>1</sup>, Leonardo Darré<sup>1</sup>, Pablo D. Dans<sup>1</sup>, Federica Battistini<sup>1-2</sup>,  
Modesto Orozco<sup>1-2</sup>

<sup>1</sup>*Institute for Research in Biomedicine (IRB) Barcelona, the Barcelona Institute of Science and Technology, Baldiri Reixac 10-12, 08028, Barcelona, Spain.*

<sup>2</sup>*Joint BSC-CRG-IRB Research Program in Computational Biology, Barcelona, Spain.*

<sup>3</sup>*Department of Biochemistry and Molecular Biology, University of Barcelona, 08028 Barcelona, Spain.*

Hoogsteen (HG) base pairing is an alternative to the common Watson-Crick (WC) interaction between nucleotides in DNA. The formation of a HG from a WC base pair takes place by a 180° rotation of the purine about its glycosidic bond (*anti* to a *syn* transition), generating a different structural and chemical environment. It has been typically assumed that deviations of WC base-pairing are driven by DNA damage, or interactions between DNA and proteins or small ligands. However, recent NMR and computational studies indicate that WC-HG structures might be in equilibrium even in naked B-DNA duplexes, and that HG is actually an accessible alternative to WC base-pairing [1-2].

In the present study, the WC $\leftrightarrow$ HG transition free energy landscape was obtained from all-atom molecular dynamics (MD) simulations, using a state-of-art force field (ParmBSC1 [3]) for DNA. Eight different DNA sequences were considered; both in solution and in the context of a nucleosome core particle which, to our knowledge, is the first systematic study focused on WC $\leftrightarrow$ HG transitions. Sequence and environment impact on the energy landscape were explained in terms of changes in the pattern of hydrogen bond and stacking interactions. Although the obtained results suggest that the WC-HG equilibrium is influenced by factors like the electrostatic environment or the DNA topology, similar transition paths involving only minor (if any) flip-out movements of the target adenine were obtained. This result reinforces the idea that HG base-pairs are found even in normal conditions, thus expanding the structural complexity of DNA.

[1] E. N. Nikolova, E. Kim, A. A. Wise, P. J. O'Brien, I. Andricioaei, H. M. Al-Hashimi, *Nature* **470**, 498 (2011).

[2] C. Yang, E. Kim, Y. Pak, *Nucleic Acids Res.* **43**, 7769 (2015).

[3] I. Ivani, et al., *Nat. Methods* **13**, 55 (2016).

## Testing the effectiveness of the isoelectronic substitution principle through the transformation of aromatic osmathiophene derivates.

Alejandro Vásquez-Espinal,<sup>1</sup> Jordi Poater,<sup>2,3</sup> Miquel Solà,<sup>4</sup> William Tiznado<sup>5</sup>  
and Rafael Islas\*<sup>5</sup>

<sup>1</sup>*Doctorado en Fisicoquímica Molecular, Facultad de Ciencias Exactas, Universidad Andrés Bello, Av. República 275, Santiago, Chile*

<sup>2</sup>*Departament de Química Inorgànica i Orgànica & Institut de Química Teòrica i Computacional (IQTCUB), Universidad de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Catalonia, Spain*

<sup>3</sup>*ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Spain*

<sup>4</sup>*Institut de Química Computacional i Catàlisi (IQCC) and Departament de Química, Universitat de Girona, Campus Montilivi s/n, 17003 Girona, Catalonia, Spain*

<sup>5</sup>*Departamento de Ciencias Químicas, Facultad de Ciencias Exactas, Universidad Andrés Bello, Av. República 275, Santiago, Chile*

In this research the effectiveness of the isoelectronic substitution (IS) principle [1] is evaluated in a series of complexes with the general formula  $\text{OsCl}_2(\text{SX}_3\text{H}_3)(\text{PH}_3)_2$ , where  $\text{X}_3$  represents the moieties CCC, CCB, CCN, CBN, CNB or NCB, formed by substitution of the carbon atoms in CCC by either the isoelectronic  $\text{B}^-$  or  $\text{N}^+$  separately, or by both. The  $\text{SX}_3\text{H}_3$  moiety forms, together with Os, an aromatic five-membered ring (5-MR) called osmathiophene. The preservation of stability and aromaticity in the resulting systems is used to indicate the effectiveness of the IS principle. The aromaticity of the proposed molecules is analyzed according to the magnetic (induced magnetic field,  $\mathbf{B}^{\text{ind}}$ ) [2] and electronic (through the multicenter index (MCI)) criteria. [3] In addition a chemical bonding analysis on selected species is performed by the adaptive natural density partitioning (AdNDP) method. [4]

[1] P. P. Power, A. Moezzi, D. C. Pestana, M. A. Petrie, S. C. Shoner and K. M. Waggoner, *Pure Appl. Chem.* **63**, 859 (1991).

[2] R. Islas, T. Heine and G. Merino, *Acc. Chem. Res.* **45**, 215 (2012).

[3] P. Bultinck, R. Ponec and S. Van Damme, *J. Phys. Org. Chem.* **18**, 706 (2005).

[4] D. Y. Zubarev and A. I. Boldyrev, *Phys. Chem. Chem. Phys.* **10**, 5207 (2008).

## **Modulation of energetic landscape under different electron conducting regimes in bacterial nanowires.**

**Alexandre Barrozo, Mohamed Y. El-Naggar, Anna I. Krylov**

*Department of Chemistry, University of Southern California, Los Angeles 90089, USA*

*Shewanella oneidensis* MR-1 can stretch out its outer membrane and periplasm, creating nanowires to scavenge for electron acceptors to perform extracellular electron transport[1]. The components responsible for the transport across the lipid bilayer are decaheme membrane protein complexes, which uses multiple heme-c cofactors for the electron transfer. However, the arrangement of these cofactor makes the electron transport nontrivial[2], and despite numerous experimental and theoretical studies on the mechanisms of electron transfer[3, 4, 5], important issues remain to be addressed. We studied the energetic landscape in two components of the membrane protein complex responsible for binding electron acceptors, MtrC and its homologue MtrF. We assessed different electron transfer scenarios, where electron and hole hopping cases are taken into account, and compared with experimental results to rule in which oxidation state these proteins are most likely to be found. Our results suggest that different mechanisms should be studied, as the energetic landscape can be strongly affected in systems with multiple redox centers.

- [1] S. Pirbadian et al, *Proc. Natl. Acad. Sci. USA* **111**, 12883-12888 (2014).
- [2] T. A. Clarke et al, *Proc. Natl. Acad. Sci. USA* **108**, 9384-9389 (2011).
- [3] H. S. Byun et al, *ChemElectroChem* **1**, 1932-1939 (2014)
- [4] M. Breuer, K. M. Rosso and J. Blumberger, *Proc. Natl. Acad. Sci. USA* **111**, 611-616 (2014).
- [5] H. C. Watanabe, Y. Yamashita and H. Ishikita, *Proc. Natl. Acad. Sci. USA* **114**, 2916-2921 (2017).



## On the Mechanism of Frustrated Lewis Pair Catalysed Hydrogenation of Carbonyl Compounds

Shubhajit Das<sup>1</sup>, Swapan K Pati<sup>2</sup>

<sup>1</sup>New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, India

<sup>2</sup>Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, India

We have explored the reaction mechanism of the metal-free B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalysed hydrogenation of carbonyl compounds to the corresponding secondary alcohols by density functional theory calculations. Possible reaction routes have been investigated in detail and the results provide solid support for the mechanism proposed on the basis of experimental observations. The critical role of the ethereal solvent, as an active participant in the hydrogenation process, is highlighted with the ether–borane frustrated Lewis pair shown to be involved in the heterolytic activation of H<sub>2</sub>. The feasibility of an alternative direct hydrogenation route featuring carbonyl–borane-mediated H<sub>2</sub> cleavage has also been examined. We have also investigated the moisture sensitivity of the catalyst and possible decomposition routes. We found that the catalyst shows appreciable water-tolerance and that even in the presence of moisture the hydrogenation proceeds through the same mechanism as that followed under anhydrous conditions.

[1] T. Mahdi, D. W. Stephan, *J. Am. Chem. Soc.* **136**, 15809 (2014).

[2] D. J. Scott, M. J. Fuchter, A. E. Ashley *J. Am. Chem. Soc.* **136**, 15813 (2014).

[3] D. J. Scott, T. R. Simmons, E. J. Lawrence, G. G. Wildgoose, M.J. Fuchter, A.E. Ashley *ACS Catal.* **5**, 5540 (2015).

[4] S. Das, S. K. Pati *Chem-Euro. J.* **23**, 1078 (2017).

## Simulation of Structure and Electronic Spectra of 1,3,4-Oxadiazole Chromophores

Juozas Sulskus<sup>1</sup>, Ignas Gaiziunas<sup>1</sup>, Vidmantas Gulbinas<sup>2</sup>

<sup>1</sup>*Department of Theoretical Physics, Vilnius University, Sauletekio 9, Vilnius, Lithuania*

<sup>2</sup>*Department of Molecular Compound Physics, Center for Physical Sciences and Technology, Sauletekio 3, Vilnius, Lithuania*

In experimental measurements of chloroform solution and thin films of PPI dendrimers and PEI polymers with incorporated oxadiazole moieties it was found that there is a shift of fluorescence spectra peak in thin films [1]. Absorption spectra in solution ( $\text{CHCl}_3$ ) have maximum at about 300-320 nm and fluorescence spectra – at about 370-390 nm. A fluorescence spectra in film have maximum at about 390-450 nm. It was also experimentally found that additional fluorescence peak appears at far wavelength at about 550 nm of the spectra in thin film of PEI polymer with incorporated oxadiazole moieties [2].

The objective of this work is to explain the experimental absorption and fluorescence spectra of dendrimers and polymers with incorporated 1,3,4-oxadiazole moieties using DFT and TDDFT methods of quantum chemistry.

1,3,4-oxadiazole monomers, dimers and bigger aggregates were used for modelling spectra of PPI dendrimers and PEI polymers in solutions and in vacuum. It was found that a peaks of absorption and fluorescence spectra of chloroform solutions of PPI dendrimers and PEI polymers may be quite accurate described by monomer excitations mainly. Changes of geometry of oxadiazole monomer during relaxation in first excited state and possible dimers and bigger aggregates structures of chromophores in the ground and excited electronic states were determined. It was found that the fluorescence peak at 550 nm can't be explained by TDDFT calculations of excited states. This peak is attributed to fluorescence of bigger aggregates and exciton theory level should be used for its description.

[1] S. Hernández-Ainsa, J. Barberá, M. Marcos, J. L. Serrano, *Macromolecules* **45**, 1006, (2012).

[2] V. Gulbinas, (Center for Physical Sciences and Technology, Vilnius), *private commun.*

## A direct spin-orbit CAS-CI program designed for molecule magnets

Tilmann Bodenstein<sup>1</sup>, Andreas Heimermann<sup>2</sup>,

Christoph van Wüllen<sup>2</sup>, Karin Fink<sup>3</sup>

<sup>1</sup>*Department of Chemistry, Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark*

<sup>2</sup>*Fachbereich Chemie, Theoretische Chemie, Technische Universität Kaiserslautern, Erwin-Schrödinger-Straße 52, 67633 Kaiserslautern, Germany*

<sup>3</sup>*Institut für Nanotechnologie, Karlsruher Institut für Technologie (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

A complete active space configuration interaction (CAS-CI) program has been developed. The new program is designed for a routine treatment of magnetic properties of exchange coupled systems, like polynuclear transition metal or lanthanoid complexes.

Usually, spin-orbit effects are considered in a two-step procedure after the CAS-CI by means of quasi-degenerate perturbation theory which requires large CI expansions to converge although often only a few low-lying electronic states contribute to the electronic properties at low temperature. Therefore, a procedure was implemented which includes spin-orbit interactions directly within the CAS-CI step [1].

The direct spin-orbit CAS-CI program uses a determinant-basis with spin-space separation [2] and the spin-string formalism proposed by Knowles and Handy [3]. Orbital relaxation effects in charge-transfer states are considered by means of the MCAS-CI approach [4]. For polynuclear systems, we developed and tested tailor-made starting vectors, constructed as direct products of subsystem wave functions for the individual sites.

First applications on magnetic properties of different Co(II) complexes comprising up to three magnetic centers, exhibiting first as well as second order spin-orbit coupling, are shown.

[1] D. Ganyushin, F. Neese, *J. Chem. Phys.* **138**, 104113 (2013).

[2] J. Olsen, B. Roos, P. Jørgensen, H. J. Å. Jensen, *J. Chem. Phys.* **89**, 2185 (1988).

[3] P. J. Knowles, N. C. Handy, *Chem. Phys. Lett.* **111**, 315 (1984).

[4] K. Fink, V. Staemmler, *Mol. Phys.* **111**, 2594 (2013).

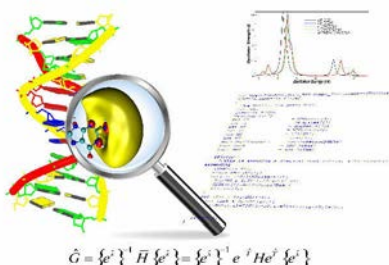
We thank the DFG for funding within the collaborative research center SFB/TRR88 “3MET”, project A1. T.B. thanks the Danish Research Council (FNU) for funding.

## A Lower Scaling Coupled Cluster Method for Excited States

Achintya Kumar Dutta<sup>1</sup>, Frank Neese<sup>1</sup>, Róbert Izsák<sup>1</sup>

<sup>1</sup>Max-Planck-Institut für Chemische Energiekonversion, Stiftstr. 34-36., 45470 Mülheim an der Ruhr, Germany

We present an efficient strategy to extend the equation of motion coupled cluster (EOM-CC) method for large molecules using pair natural orbitals. We use the domain based local pair natural orbital coupled cluster (DLPNO-CCSD) method for the ground state, while the EOM-CCSD calculation for excitation energy, ionization potential or electron affinity are performed in the canonical basis. A second similarity transformation (STEOM-CCSD) has been used to reduce the computational scaling of the excited states[1]. The most expensive external exchange term in the calculation is evaluated using the semi-numerical chain of spheres exchange (COSX) method, which gives nearly 10x speed up and removes the associated storage bottleneck [2]. We have devised a new scheme based on CIS natural orbital, which can automatically select active space for the STEOM-CCSD calculations [3]. An efficient scheme for calculation of transition properties has also been realised. Our new (back transformed) *bt*-PNO-STEOM-CCSD method has uniform accuracy for valence, Rydberg and charge transfer excited states and can be routinely applied to medium size molecules. For further speed up, we want to evaluate the expensive IP and EA calculation steps of *bt*-PNO-STEOM-CCSD method in pair natural orbital basis. A near-linear scaling IP-EOM-CCSD code, which can be applied for molecules with more 1000 atoms, has recently been implement for that purpose.



- [1] A. K. Dutta, F. Neese, and R. Izsák. *J. Chem. Phys.* **145**, 34102 (2016).
- [2] A. K. Dutta, F. Neese, and R. Izsák. *J. Chem. Phys.* **144**, 34102 (2016).
- [3] A. K. Dutta, M. Nooijen, F. Neese, and R. Izsák. *J. Chem. Phys.* **146**, 74103 (2017).
- [4] A. K. Dutta, F. Neese, and R. Izsák. *J. Chem. Phys.* **146**, 214111 (2017).

## QM modeling of organic-inorganic hybrid materials as heterogeneous catalysts for pharma industry

**Marta Corno, Ivana Miletto, Enrica Gianotti, Maurizio Cossi, Leonardo Marchese**

*Dipartimento di Scienze e Innovazione Tecnologica, Università degli Studi del Piemonte Orientale "Amedeo Avogadro", Viale T. Michel 11 - 15121 Alessandria, Italy*

Developing efficient heterogeneous catalysts for pharmaceutical industrial processes in the C-C coupling reactions is a current major challenge for material scientists, organic chemists, industrial engineers and other researchers. Recently, multifunctional organic-inorganic hybrid materials have become an attractive alternative class of catalysts, for applications in cascade, asymmetric, multi-step reactions. The idea of designing hybrid materials is originated by the observation of the success of nature developing enzymes in living organisms. Indeed, selectivity is a crucial factor for the survival of the species.

Organic-inorganic hybrid materials combine the advantages of inorganic solids (high mechanical, thermal, and structural stability) and organic molecules or macromolecules (flexibility and functionality), maximizing the chemical efficiency. Beside the different synthetic strategies, the covalent interactions among organic and inorganic units to synthesize class II hybrids allow to obtain more robust and stable functional solids. [1] Nevertheless, the family of Class II hybrid materials could suffer of low conversions and low selectivity because of a non-regular distribution of the different active centers.

In this context, also thanks to the recent evolutions in High Performance Computing (HPC) architectures, theoretical methods can be successfully applied to provide structural information and interface properties at an atomistic level to both guide and interpret experimental synthesis and measurements [2,3].

In this contribution, periodic and cluster models of silica-based frameworks, together with realistic models of hydroxylated amorphous silica surfaces, functionalized with organic catalysts, will be reported as reference for the synthesis and characterization of innovative porous organic-inorganic materials, with several active sites. The choice of the functional in the context of Density Functional Theory (DFT), inclusive of empirical corrections for dispersive interactions, compared to the use of low-cost quantum chemical methods, such as HF-3c [4], will be discussed. The advantages provided by the joint use of experimental and computational techniques will be also highlighted.

The present research activity is part of the HORIZON2020 European Project MULTI2HYCAT 'Multi-site organic-inorganic hybrid catalysts for multi-step chemical processes' (Grant Agreement n. 720783).

- [1] S. Newland, D. Xuereb, E. Gianotti, et al., *Catal. Sci. Technol.* **5**, 660 (2015).
- [2] V. Sacchetto, C. Bisio, D.F.O. Olivera, et al., *J. Phys. Chem C* **119**, 24875 (2015).
- [3] M. Delle Piane, M. Corno, P. Ugliengo, *Theor. Chem. Acc.* **135**, 53 (2016).
- [4] M. Cutini, B. Civalleri, M. Corno, et al., *J. Chem. Theory Comput.* **12**, 3340 (2016).

## Oxygen evolution reaction on pristine and nitrogen-doped carbon nanotubes

**Garold Murdachaew and Kari Laasonen**

*Department of Chemistry and Materials Science, School of Chemical Engineering,  
Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland*

A viable renewable energy ecosystem requires an energy carrier to store the often intermittent energy generated from carbon-free sources. Hydrogen obtained by electrochemical water splitting on a suitable catalyst can serve in this role. The ideal catalyst should be efficient, stable under operating conditions, and composed of abundant elements. Initial results obtained using density functional theory simulations of the more difficult half-reaction, the anodic oxygen evolution reaction (OER), with a carbon nanotube as catalyst, show that the presence of nitrogen reduces the required OER overpotential significantly. With graphitically-substituted nitrogen, the lowest obtained overpotential is 0.45 V, and is near the peak of the volcano plot with these materials. The OER mechanisms and the effects of coverage, explicit aqueous solvation, and defects will also be presented.

## Deactivation of Hazardous Chemicals at Oxide Surfaces

Tobias Klöffel<sup>1</sup>, Mariana Kozłowska<sup>2</sup>, Bernd Meyer<sup>1</sup>, Pawel Rodziewicz<sup>2</sup>

<sup>1</sup>*Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center,  
Friedrich-Alexander-Universität Erlangen-Nürnberg,  
Nägelsbachstr. 25, 91052 Erlangen, Germany*

<sup>2</sup>*Institute of Chemistry, University of Białystok, Hurtowa 1, 15-399 Białystok, Poland*

After World War I, large quantities of highly toxic chemical warfare agents were disposed in the Baltic Sea, where they now constitute a major environmental hazard. New fast, secure, and non-destructive methods are required for the decontamination of highly corroded containers, which are nowadays frequently found in fishing nets or at beaches of the Baltic sea.

A very promising approach is to use oxides as catalysts for the decomposition of the chemical warfare agents via hydrolysis reactions. In particular ZnO nanorods are promising candidates according to recent experimental work [1]. However, a detailed understanding of the chemical process of defunctionalization at the solid/liquid interface is mostly lacking, as it is close to impossible to perform standard surface science experiments due to the high toxicity of the materials. Yet, basic insights into the reaction mechanisms at the surface are crucial for improving the catalyst performance. For such hazardous materials *in silico* research can greatly reduce the number of required experiments.

In a previous study we analyzed the possible conformers of sulfur mustard (SM) in the gas phase [2] by means of the *ab initio* Car-Parrinello Molecular Dynamics (CPMD) method employing the CPMD code (see: [www.cpmd.org](http://www.cpmd.org)). The most stable gas phase conformers of SM, which were determined in these simulations, were used as starting point for our structural search of possible adsorbate structures of SM at two different ZnO surfaces: an ideal water-free and a water-covered ZnO termination. The structure search was conducted using a high throughput screening approach by performing *ab initio* geometry optimizations from snapshots of the MD simulations employing the Quantum Espresso software package (see: [www.quantum-espresso.org](http://www.quantum-espresso.org)) in order to obtain basic insights into the different types of interactions between the SM molecules and the ZnO surfaces. Furthermore, we will present first preliminary results of CPMD simulations on the full water/ZnO interface, which was created by embedding the ZnO prototype catalyst with adsorbed SM molecules in several layers of water.

- [1] G.K. Prasad, T.H. Mahato, B. Singh, K. Ganesan, P. Pandey, K. Sehhar, Detoxification reactions of sulphur mustard on the surface of zinc oxide nanosized rods, *J. Hazard. Mater.* 149 (2007).
- [2] J. Lach, J. Goclón, P. Rodziewicz, Structural flexibility of the sulfur mustard molecule at finite temperature from Car-Parrinello molecular dynamics simulations, *J. Hazard. Mater.* 306 (2016)

## Automated Multi-Configurational Calculations

Christopher J. Stein<sup>1</sup>, Markus Reiher<sup>1</sup>

<sup>1</sup>*Laboratorium für Physikalische Chemie, ETH Zürich, Vladimir-Prelog-Weg 2,  
8093 Zürich, Switzerland*

Quantum-chemical multi-configurational methods are indispensable for the calculation of electronic structures of molecules with close-lying frontier orbitals. Despite their importance, the necessity to manually select a subset of strongly correlated active orbitals renders the application of these methods error prone. Furthermore, the selected active orbital spaces have to be as compact as possible because subsequently applied methods for the calculation of dynamical correlation scale unfavourably with the number of active orbitals. This and the fact that empirical guidelines[1] for the manual active orbital selection require a phase of trial and error, often limit the application of these methods to experienced experts.

We recently proposed an automated active orbital space selection protocol based on orbital entropies that are calculated from partially converged density matrix renormalization group wave functions.[2] Converged complete active space wave functions from these automatically selected active orbitals were shown to be suitable reference wave functions for subsequently calculated dynamic correlation by means of multi-reference perturbation theory.[3]

Here, we demonstrate that extended active orbital selection protocols guarantee consistent active orbital spaces along reaction coordinates and for several excited states.[4] In addition, we present a graphical user interface that combines these protocols and enables automated multi-configurational calculations for various scenarios.

- [1] V. Veryazov, P.-Å. Malmqvist, B. O. Roos, *Int. J. Quantum Chem.* **111**, 3329 (2011).
- [2] C. J. Stein, M. Reiher, *J. Chem. Theory Comput.* **12**, 1760 (2016).
- [3] C. J. Stein, V. von Burg, M. Reiher, *J. Chem. Theory Comput.* **12**, 3764 (2016).
- [4] C. J. Stein, M. Reiher, *Chimia* **71**, 170 (2017).



## Photodissociation Dynamics and Spectroscopy in the Presence of Conical Intersections

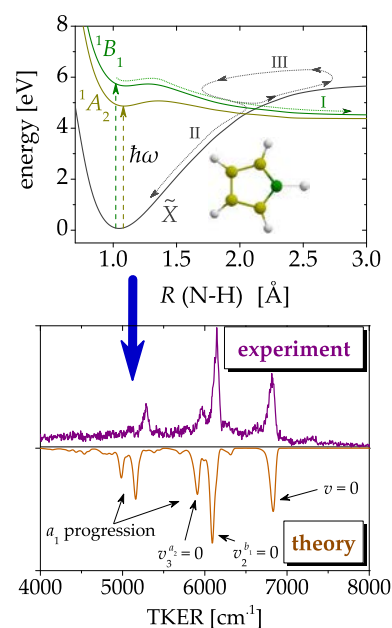
David Picconi<sup>1</sup>, Wolfgang Domcke<sup>1</sup>, Sergy Yu. Grebenshchikov<sup>1</sup>

<sup>1</sup>Department of Chemistry, Technische Universität München  
Lichtenbergstr. 4, 85747 Garching, Germany

Broad classes of photodissociation reactions proceed through conical intersections of excited electronic states.[1] The electronic degeneracy may affect the absorption spectra and the photofragment state distributions.[2] The latter are usually reconstructed from total kinetic energy release (TKER) spectra, in which the peaks correspond to vibrational states of the photoproducts, and the intensity gives the photon energy-dependent populations.[1]

In this contribution, the prototypical photodissociation pyrrole +  $h\nu \rightarrow$  pyrrolyl + H is analysed in detail. Under long-wavelength irradiation, pyrrole is excited to a low-lying repulsive  $\pi\sigma^*$  state. Upon N–H bond elongation, the potential energy surfaces (PES) of the  $\pi\sigma^*$  and  $S_0$  states cross.[3] The reaction is studied with wave packet simulations using new diabatic potential energy surfaces derived from CASPT2 calculations. The calculated absorption profile exhibits the ‘hallmark’ of the  $\pi\sigma^*/S_0$  intersection: Narrow Fano profiles on top of the continuous spectral envelope.[4] The simulations, performed with the MCTDH method, reproduce the experimental TKER spectra, and allow the complete assignment of the vibrational peaks of pyrrolyl. To our knowledge, this is the first quantum mechanical calculation of vibrationally-resolved TKER spectra of a polyatomic system.[5]

Approximate methods are also presented to compute the absorption spectrum and the final product distributions of dissociating molecules. These approaches allow a qualitatively correct estimate of spectroscopic observables with a minimum amount of *ab initio* calculations.[5]



- [1] M. N. R. Ashfold *et al.*, *Phys. Chem. Chem. Phys.* **12**, 1218 (2010)
- [2] D. Picconi and S. Yu. Grebenshchikov, *J. Chem. Phys.* **141**, 074311 (2014);  
*Phys. Chem. Chem. Phys.* **17**, 28931 (2015)
- [3] B. Cronin, M. G. D. Nix, R. H. Qadiri and M. N. R. Ashfold, *Phys. Chem. Chem. Phys.* **6**, 5031 (2004)
- [4] S. Yu. Grebenshchikov and D. Picconi, *Phys. Chem. Chem. Phys.* Advance Article, DOI: 10.1039/c7cp01401e (2017)
- [5] D. Picconi and S. Yu. Grebenshchikov, *in preparation*

## Adsorption of Graphene to Metal (111) Surfaces using the Exchange-Hole Dipole Moment Model

Matthew S. Christian<sup>1</sup>, A. Otero-de-la-Roza<sup>2</sup>, Erin R. Johnson<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Dalhousie University, 6274 Coburg Road, Halifax, Nova Scotia, Canada B3H 4R2*

<sup>2</sup>*Department of Chemistry, University of British Columbia, Okanagan, 3247 University Way, Kelowna, British Columbia, Canada V1V 1V7*

Graphene is a material that has unique electronic and tribologic properties. Understanding how graphene interacts with metals is important for advancing the use of graphene beyond the laboratory test environment to commercial manufacturing. Until recently, modeling graphene's interaction with metals using conventional density-functional theory (DFT) has been difficult because the lack of long-range, non-local correlation needed to calculate dispersion interactions. However, dispersion can be accounted for by adding a post-SCF correction to the DFT energy. We present a thorough study of graphene adsorption on metal surfaces using DFT, incorporating the exchange-hole dipole moment (XDM) dispersion model. Our results reproduce experimental observations of strong and weak graphene-metal interactions and demonstrate clear periodic trends. We also show that graphene typically prefers an aligned orientation with the metal surface and highlight how carbon-carbon bond strain affects monolayer formation.

- [1] A. O. de-la-Roza, E. R. Johnson, *J. Chem. Phys.* **136**, 174109 (2012).
- [2] M. S. Christian, A. O. de-la-Roza, E. R. Johnson, *J. Chem. Theory Comput.* **12**, 17953 (2016).
- [3] M. S. Christian, A. O. de-la-Roza, E. R. Johnson, *Carbon* **118**, 184 (2017).

## Adiabatic variational theory for anisotropic atom–diatom collisions at very low temperatures

Mariusz Pawlak<sup>1</sup>, Yuval Shagam<sup>2</sup>, Ayelet Klein<sup>2</sup>, Edvardas Narevicius<sup>2</sup>, Nimrod Moiseyev<sup>3</sup>

<sup>1</sup>*Faculty of Chemistry, Nicolaus Copernicus University in Toruń, Gagarina 7, 87-100 Toruń, Poland*

<sup>2</sup>*Department of Chemical Physics, Weizmann Institute of Science, Rehovot 76100, Israel*

<sup>3</sup>*Schulich Faculty of Chemistry and Faculty of Physics, Technion–Israel Institute of Technology, Haifa 32000, Israel*

We recently developed an adiabatic variational theory for low-temperature collisions between atoms and diatomic molecules [1, 2]. Within the framework of this theory, couplings between different angular momentum states (associated with diatomic and with atom-diatom relative rotations) and different angular momentum projection states during an experiment are taken into consideration. It provides us with physical insight into dynamics of reactions and enables us to study the role of anisotropy. Our approach reduces the dimensionality of the Hamiltonian under consideration without losing essential physics and significantly enhances the computational efficiency. The five degrees of freedom problem, where the bond length in the diatomic molecule is kept fixed, is replaced with a set of uncoupled one-dimensional subproblems. As an illustrative numerical example, the theory has been applied to calculate the Penning ionization reaction rate of the excited metastable helium atom and the molecular hydrogen for both configurations: *para* and *ortho*. The results are in very good agreement with the latest experimental findings [3].

- [1] M. Pawlak, Y. Shagam, E. Narevicius, N. Moiseyev, *J. Chem. Phys.* **143**, 074114 (2015).
- [2] M. Pawlak, Y. Shagam, A. Klein, E. Narevicius, N. Moiseyev, *J. Phys. Chem. A* **121**, 2194 (2017).
- [3] A. Klein, Y. Shagam, W. Skomorowski, P. S. Żuchowski, M. Pawlak, L. M. C. Janssen, N. Moiseyev, S. Y. T. van de Meerakker, A. van der Avoird, C. P. Koch, E. Narevicius, *Nature Phys.* **13**, 35 (2017).

## Cation- $\pi$ interactions in CREBBP inhibition: an electrostatic model for small-molecule binding affinity and selectivity

Kiran Kumar<sup>1</sup>, Wilian A. Cortopassi<sup>1</sup>, Robert S. Paton<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of Oxford, 12 Mansfield Road, Oxford, U.K.*

CREBBP bromodomain containing proteins are epigenetic readers that have received increasing attention in recent years as promising cancer drug targets [1]. To aid in inhibitor design, we utilized computational chemistry techniques, such as classical molecular dynamics (MD) and quantum mechanics (QM), to analyse key interactions that drive selectivity for CREBBP by a series of fifteen 5-isoxazolyl-benzimidazole inhibitors (IBIs) [2] via the formation of a key cation- $\pi$  interaction with a conserved arginine residue unique to CREBBP [3].

100 ns MD simulations with explicit solvation were performed with an initial inhibitor template bound to a CREBBP protein. Cation- $\pi$  interactions were critical for binding and present for more than 70% of simulation time, although not initially observed in crystal structures. Given the importance of this interaction for the stability of the inhibitor, we performed additional binding free energy calculations on fifteen IBIs using molecular mechanics/Poisson-Boltzmann (PB) and generalized Born (GB) surface area (MM-PBSA, MM-GBSA) scoring functions. We also performed QM-complexation energies for an accurate prediction of cation- $\pi$  interactions. A third technique analysing the Electrostatic Potential Surface Area (ESPs) of the substituted benzenes demonstrated that consideration of only the surface above the  $\pi$  system is enough for a quantitative ( $R^2 = 0.84$ ,  $n = 15$ ) and qualitative prediction of these interactions.

Results from our three methodologies correlated well with experimental binding affinities for prediction of cation- $\pi$  interactions with CREBBP inhibitors. However, ESP is significantly faster without compromising accuracy. Applications of these MM, QM, and ESP calculations can be easily extended to other small molecule protein complexes in which cation- $\pi$  interactions are necessary for driving selectivity.

- [1] P. Filippakopoulos, S. Knapp, *Nat. Rev. Drug Discov.* **13**, 337–356 (2014).
- [2] D. A. Hay, O. Fedorov, S. Martin, D. C. Singleton, C. Tallant, C. Wells, S. Picaud, M. Philpott, O. P. Monteiro, C. M. Rogers, S. J. Conway, T. P. Rooney, A. Tumber, C. Yapp, P. Filippakopoulos, M. E. Bunnage, S. Muller, S. Knapp, C. J. Schofield and P. E. Brennan, *J. Am. Chem. Soc.* **136**, 9308–9319 (2014).
- [3] K. Kumar, W. A. Cortopassi, R. S. Paton, *Org. Biomol. Chem.* **14**, 10926-10938 (2016).

## A Generalized Empirical Potential to Describe Halogen Bonds.

**Lucas A. Santos, Daniela R. Silva, Elaine F. F. da Cunha, Teodorico C. Ramalho**

*Department of Chemistry, Federal University of Lavras, Campus Universitário, Lavras, Brazil*

The Halogen Bonds have proved to be very relevant to understand phenomena in materials science, organic, medical, and biochemistry fields [1]. Recent works have shown strong evidences that orbital interactions lead to formation of halogen bonded systems, putting in doubt another approach used to understand these interactions, the  $\sigma$ -hole model [2,3]. In fact, the accurate description of the electronic structure of Halogen Bonds is highly necessary. However, large systems are still a great challenge to electronic structure methods. In this perspective, simpler techniques such as molecular mechanics force fields are plausible approaches to obtain good results over these systems, once they are carefully parameterized [4].

In this work, a new empirical potential has been developed to describe Halogen Bonds, considering the F, Cl and Br atoms, in function of the quantum parameters  $\delta$  and  $\gamma$ , as showed in equation (1) [3].

$$E_{mod} = \varepsilon \left\{ \left( \frac{r_{e+\delta\cos\theta/6}}{r} \right)^{10} - 2 \left( \frac{r_e}{r+\gamma} \right)^6 \right\} \quad (1)$$

S-triazine...Ar/NC<sub>2</sub>H<sub>3</sub> have been used as a model to fit  $E_{mod}$  regarding quantum calculations [3]. A crucial factor to design  $E_{mod}$  was to show the straight relationship between the maximum ESP value on  $\sigma$ -Hole ( $V_{max}$ ) and the energies of LUMOs that contains the  $\sigma^*_{C-X}$  orbital. This feature has allowed us to build parameters in function of  $V_{max}$  to describe the orbital interactions, that were the main responsible to lead the Halogen Bonds [3]. The new empirical potential  $E_{mod}$  have also demonstrated a great performance to describe systems out of the training set [3]. In this scenario, we believe this study will be helpful to improve the force fields description of large systems containing Halogen Bond.

We would like to thank FAPEMIG, CAPES and CNPq for the financial support.

### References:

- [1] G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo, *Chem. Rev.*, **116**, 2478-2601 (2016).
- [2] L. P. Wolters, P. Schyman, M. J. Pavan, W. L. Jorgensen, F. M. Bickelhaupt, *Wiley Interdiscip Rev Comput Mol Sci*, **4**, 523-540 (2014).
- [3] L. A. Santos, E. F. F. da Cunha, T. C. Ramalho, *J. Phys. Chem. A*, **121**, 2442-2452 (2017).
- [4] L. A. Santos, E. F. F. da Cunha, M. P. Freitas, T. C. Ramalho, *J. Phys. Chem. A*, **118**, 5808-5817 (2014).

## The Role of Intramolecular Interactions on the Bioactive Conformation of Epinephrine

Daniela R. Silva, Lucas A. Santos, Josué M. Silla, Matheus P. Freitas

*Laboratory of Molecular Modelling, Department of Chemistry, Federal University of Lavras, Campus Universitário, Lavras, Brazil*

Molecular structure plays a critical role in the physical and chemical properties of compounds. The bioactive conformation of epinephrine deposited in the Protein Data Bank (PDB ID: 4LDO [1]) adopts a gauche arrangement along the O-C-C-N dihedral angle. The nature of the gauche effect, i.e. the preference of electronegative groups to assume the more sterically hindered gauche rather than the anti orientation, has been attributed to intramolecular interactions, such as hyperconjugation, hydrogen bond and electrostatics [2]. Therefore, in order to better understand the relative influence of intramolecular interactions on the bioactive structure, this work aims to quantum-chemically analyze the conformational isomerism of epinephrine both in gas phase and implicit water.

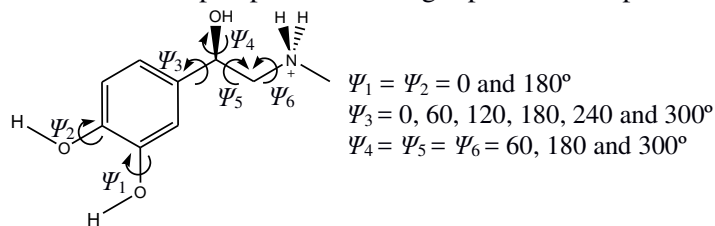


Figure 1: Structure of *N*-protonated epinephrine and dihedral angles evaluated.

Thirty energy minima were found for epinephrine in the gas phase and ninety-two in implicit water. The most stable conformers in the gas phase are also highly populated in implicit solvent. These conformers adopted a gauche orientation regarding the O-C-C-N torsional angle. The results from natural bond orbital analysis and quantum theory of atoms in molecules indicated the formation of an intramolecular hydrogen bond. However, the replacement of the amino hydrogens by methyl groups did not disrupt the gauche arrangement, thereby indicating that the electrostatic gauche effect takes place.

The authors are grateful to CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior), CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico), and FAPEMIG (Fundação de Amparo à Pesquisa do Estado de Minas Gerais) for supporting this research.

[1] A.M. Ring, A. Manglik, A.C. Kruse, M.D. Enos, W.I. Weis, K.C. Garcia, et al., *Nature*. **502**, 575 (2013).

[2] L.A.F. Andrade, J.M. Silla, M.P. Freitas, *J. Mol. Struct.* **1072**, 203 (2014).

## Oganesson: Rare Gas or not? Monte-Carlo Melting Simulations of Heavy and Super-heavy Group-18 Elements

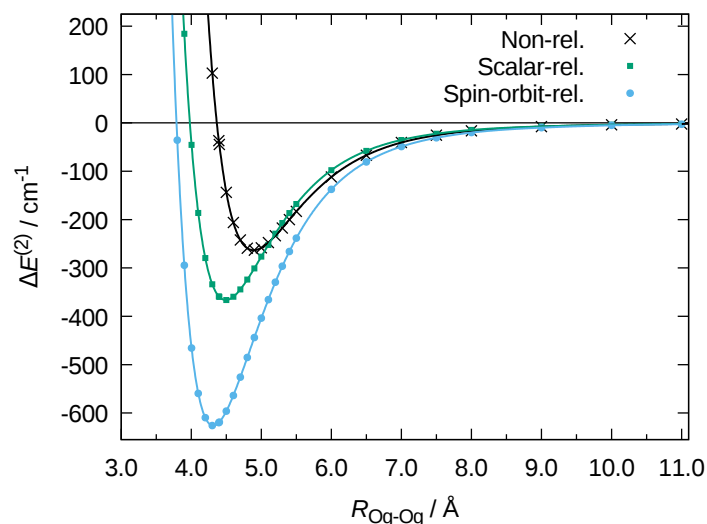
Paul Jerabek<sup>1</sup>, Odile Smits<sup>1</sup>, Kirk A. Peterson<sup>2</sup>, Elke Pahl<sup>1</sup>, Peter Schwerdtfeger<sup>1</sup>

<sup>1</sup>Centre for Theoretical Chemistry and Physics, Massey University, Auckland, New Zealand

<sup>2</sup>Department of Chemistry, Washington State University, Pullman, Washington, USA

We are presenting Monte-Carlo simulations of thermodynamical properties for heavy and super-heavy noble gas elements based on interatomic potentials from accurate *ab-initio* calculations. The Extended-Lennard-Jones type two-body potentials [1] were obtained by performing Coupled-Cluster calculations up to the CCSDTQ level of theory. Spin-orbit relativistic effects were taken into account and included the Gaunt term as an approximation to the Breit interaction. Three-body interactions were considered in the form of Extended-Axilrod-Teller potentials.

One of most interesting quantities to obtain from our Parallel Tempering Monte-Carlo (PTMC) simulations are reliable predictions for melting temperatures.[2] Especially for the experimentally elusive oganesson (Element 118) it is of great interest to see if it is still a gas at ambient conditions or not.



A comparison of two-body interatomic potentials for oganesson computed at non-relativistic, scalar-relativistic and spin-orbit-relativistic levels revealed the importance of spin-orbit effects in this element and the influence on the melting behavior.

[1] P. Schwerdtfeger *et. al*, *Phys. Rev. B* **2006**, 73, 064112.

[2] E. Pahl, P. Schwerdtfeger *et. al.*, *Angew. Chem. Int. Ed.* **2008**, 43, 8207–8210.

## Importance of local exact exchange potential in hybrid functionals for accurate excited states

**Jaewook Kim<sup>1</sup>, Kwangwoo Hong<sup>1</sup>, Sungwoo Kang<sup>1</sup>, Jaechang Lim<sup>1</sup>,  
Sang-Yeon Hwang<sup>1</sup>, Seongok Ryu<sup>1</sup>, Sunghwan Choi<sup>1</sup>, and Woo Youn Kim<sup>1</sup>**

*<sup>1</sup>Department of Chemistry, Korean Advanced Institute of Science and Technology, 291  
Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea*

Nowadays, DFT has become an essential analysis tool in diverse scientific fields. More than 25,000 papers used DFT every year since 2011.[1] Such tremendous success of DFT especially in chemistry cannot be made without the development of hybrid functionals, as is exemplified by the fact that the famous hybrid functional, B3LYP, has been cited more than 55,000 times.

Standard hybrid functionals utilize the Hartree-Fock exchange operator to obtain Kohn-Sham orbitals. Without losing accuracy for ground state properties, we can replace the exchange operator in the hybrid functionals with local exact exchange potential. This local potential can be made by using the optimized effective potential method, or its approximated version, such as Krieger-Li-Iafrate(KLI) method.[2-3]

In this presentation, we will present the formalism of the localized version of hybrid functional, which incorporates a KLI approximated hybrid potential, and its applications. The Kohn-Sham orbital obtained from the local version of hybrid functionals shows distinct properties to conventional one, and it makes the DFT represent optical excitation more precisely. Also, we performed a benchmark calculation using the Caricato set[4] for excited states. The KLI approximated hybrid method even with an LDA kernel gives a surprisingly small mean absolute error of 0.25eV which outperformed all other pure, global hybrid, and long-range-corrected hybrid functionals encompassing 61 well-known functionals. In particular, it shows good performance for Rydberg excitations.

[1] A. Pribram-Jones, D. A. Gross, and K. Burke, *Annu. Rev. Phys. Chem.* **66**, 283 (2015).

[2] J. Kim, K. Hong, S.-Y. Hwang, S. Ryu, S. Choi, and W. Y. Kim, *Phys. Chem. Chem. Phys.* **19**, 10177 (2017).

[3] J. Kim, K. Hong, S. Choi, and W. Y. Kim, *Bull. Korean Chem. Soc.* **36**, 998 (2015).

[4] M. Caricato, G. W. Trucks, M. J. Frisch, and K. B. Wiberg, *J. Chem. Theory Comput.* **6**, 370 (2010).



## Non-Adiabatic Molecular Dynamics Simulations for elucidating high photoluminescence (PL) efficiency of dual chromophores material

Jiwon Moon and Joonghan Kim\*

*Department of Chemistry, The Catholic University of Korea, Bucheon 14662, Republic of Korea*

1-anthracen-9-yl-pyrene derivatives, namely dual core derivatives, which were highly efficient blue emitting materials were synthesized in the previous study [1, 2]. Most of blue emitter materials have been known to have low efficiency as organic light emitting diode (OLED) device. But, the novel dual core materials have nearly twice the PL efficiency of single core materials. To understand the optical properties of dual core materials, non-adiabatic molecular dynamics simulations [3] based on the time-dependent density functional theory (TDDFT) were performed. The two lowest excited singlet states were involved in the dynamics, and there were competing relaxation paths. On the basis of our simulated results, the decay from the  $S_2$  state to the  $S_1$  state via conical intersection plays a key role in high PL efficiency. This study would help to understand good PL efficiency of the dual core chromophore materials.

[1] B. Kim, Y. Park, J. Lee, D. Yokoyama, J.-H. Lee, J. Kido, J. Park, *J. Mater. Chem. C*, **1**, 432 (2013)

[2] H. Lee, B. Kim, S. Kim, J. Kim, J. Lee, H. Shin, J.-H. Lee, J. Park, *J. Mater. Chem. C*, **2**, 4737 (2014)

[3] M. Barbatti, M. Ruckebauer, F. Plasser, J. Pittner, G. Granucci, M. Persico, H. Lischka, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, **4**, 26 (2014).

### ACKNOWLEDGMENT

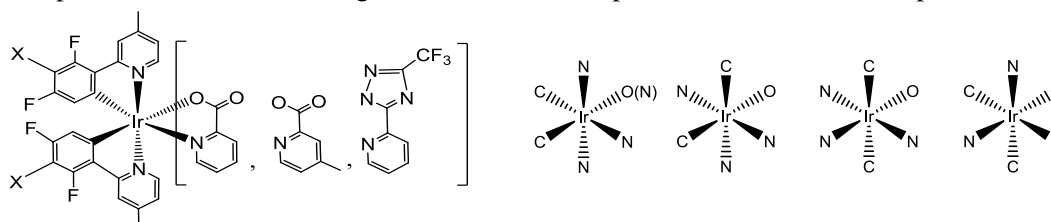
This research was also supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (NRF-2016R1D1A1B03933120). This work was also supported by the National Institute of Supercomputing and Network/Korea Institute of Science and Technology Information with supercomputing resources including technical support (KSC-2016-C1-0002).

## Phosphorescent lifetimes of perfluoro-substituted Iridium complexes as deep-blue OLED materials

**Kiyull Yang<sup>1</sup>, Soon-Ki Kwon<sup>2</sup>, Yun-Hi Kim<sup>3</sup>**

<sup>1</sup>Department of Chemistry Education, <sup>2</sup>School of Materials Science and Engineering Research Institute, <sup>3</sup>Department of Chemistry  
Gyeongsang National University, Republic of Korea

Time-dependent density functional theory (TD-DFT) calculations were performed to examine electronic properties, excitation energies and phosphorescent lifetimes of the perfluoro-substituted iridium (Ir) complexes which were newly synthesized for applications in deep-blue phosphorescent organic light emitting diodes (OLEDs). All the calculations for phosphorescent lifetimes of the compounds were done by Amsterdam Density Functional (ADF) package based on the zeroth-order regular approximation (ZORA). The electrons in the HOMO of the compounds were mostly distributed over the phenyl group of the main ligand, with there being a large contribution from the *d* atomic orbital of iridium as well, suggesting the introduction of the strong electron-withdrawing perfluoro carbonyl group led to a decrease in HOMO level: perfluoro alkyl group more strongly affects the HOMO level than the LUMO level. The phosphorescent lifetimes of the non-carbonyl perfluoro compounds were shorter than those of the perfluoro carbonyl compounds. The shortest phosphorescent lifetime is estimated up to 2.5  $\mu$ s for the compound with trifluoromethylated triazole (fptz) as the ancillary ligand, indicative of good triplet harvesting. We also estimated the degree of the metal-to-ligand charge transfer (MLCT) transition in the triplet transition: the contribution of the MLCT for the iridium complexes was found to be higher than 34% for all perfluoro-substituted compounds.



X = COCF<sub>3</sub>, COCF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>, CF<sub>3</sub>, and CF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>

Figure 1. Structure of perfluoro-substituted iridium (Ir) complexes (left) and their isomers (right).

[1] S. Lee, S.-O. Kim, H. Shin, H.-J. Yun, K. Yang, S.-K. Kwon, J.-J. Kim, and Y.-H. Kim, *J. Am. Chem. Soc.*, **135**, 14321 (2013).

[2] J.-B. Kim, S.-H. Han, K. Yang, S.-K. Kwon, J.-J. Kim, and Y.-H. Kim, *Chem. Comm.*, **51**, 58 (2015).

## A theoretical study of the recognition of a neutralizing antibody to the HIV-1 envelope glycoprotein

Kaori Ueno-Noto<sup>1</sup>

<sup>1</sup> College of Liberal Arts and Sciences, Kitasato University,  
1-15-1 Kitasato, Minamiku, Sagamihara, Kanagawa, Japan

Human Immunodeficiency Virus type 1 (HIV-1) envelope glycoprotein gp140 has been a target protein for the development of HIV-1 vaccines. It is a trimeric antigen based upon glycoprotein gp120 linked to a portion of the transmembrane glycoprotein gp41. Human PGT antibodies have shown to bind directly to the glycoprotein via high mannose glycans on the gp120. Two crystal structures of the PGT antibody (PGT128) and gp140 complex have been recently reported (PDB ID: 5C7K and 5JSA, Fig. 1), whose structures of gp41 were slightly different each other. [1,2] In these complex, four glycans of 16 glycans on the gp120 are found in the region between gp120 and the antibody. Details of the recognition mechanisms of the antibody to the glycoprotein as basic knowledge toward the vaccine development have not been elucidated so far. In this study, the interaction between the glycans and the antibody PGT128 in the antibody-envelope protein complexes were analyzed theoretically to elucidate general recognition mechanisms of PGT antibodies.

MP2 level of large-scale quantum mechanical calculations employing fragment molecular orbital method was applied to the crystal structures of PGT128-gp140 complexes. In both crystal structures, a glycan-glycan interaction between Asn301-glycan and Asn262-glycan was observed, suggesting to play a role in the recognition of the antibody to the glycoprotein. In 5C7K, significant pair interaction energies were found between the antibody and Asn332-glycan as well as Asn301-glycan. On the other hand, in 5JSA, the Asn332-glycan dominantly interacted with the antibody. Molecular dynamics simulations on these complexes were performed to compare the contributions of the glycans on the antibody-glycoprotein interactions. The role of glycans in the antibody's recognition with the antigen will be discussed at the upcoming meeting.

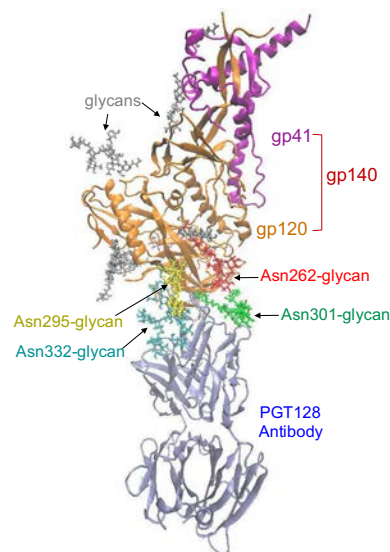


Fig.1 The crystal structure of PGT128 antibody and HIV-1 envelope glycoprotein gp140 (PDB ID: 5JSA[2])

- [1] Kong, L *et. al. Acta Crystallogr. D Biol. Crystallogr.* **D71**, 2099, (2015).  
[2] Kong, L *et. al. Nat. Commun.* **7**, 12040, (2016).

## Comparison Se-Se bond in $\text{SeHCl}\cdots\text{SeHCl}$ and cyclic $\text{SeHCl}\cdots\text{SeHCl}\cdots\text{X}$ ( $\text{X} = \text{SHCl}, \text{ClCl}, \text{SeHCl}, \text{BrCl}$ ) complexes

Lixin. Mo<sup>1,2</sup>, Yanli Zeng<sup>1</sup>, Xiaoyan Li<sup>1</sup>, Lingpeng Meng<sup>1,\*</sup>

<sup>1</sup> College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang, P. R. China

<sup>2</sup>Huihua College of Hebei Normal University, Shijiazhuang, P. R. China

\*Contact author: menglp@hebtu.edu.cn

**Abstract:** The changes in the strength and characteristic of Se-Se bond in dimer  $\text{SeHCl}\cdots\text{SeHCl}$  and cyclic trimer  $\text{SeHCl}\cdots\text{SeHCl}\cdots\text{X}$  ( $\text{X} = \text{SHCl}, \text{ClCl}, \text{SeHCl}, \text{BrCl}$ ) were investigated by calculations at the MP2/aug-cc-pVTZ level. Based on the analysis of molecular electrostatic potential, the dimer and cyclic trimer were constructed and optimized. Compared with the Se-Se bond in the  $\text{SeHCl}\cdots\text{SeHCl}$  dimer, all cyclic trimers have shorter Se-Se bond lengths, negative three-body interaction energies, greater electron densities at the bond critical points, and larger second-order perturbation energies. These results suggest that the Se-Se bond in the cyclic trimer is enhanced. That is, the addition of molecule X strengthens the Se-Se bond. The absolute values of interaction energies and electron densities increase in the order of  $\text{X} = \text{ClCl} < \text{SHCl} < \text{BrCl} < \text{SeHCl}$ , which are in line with the  $V_{\text{S,max}}$  of  $\sigma$ -hole in molecule X. This means that the Se-Se bond in the  $\text{SeHCl}\cdots\text{SeHCl}\cdots\text{X}$  cyclic trimers becomes stronger in the same order. Furthermore, the greater the  $V_{\text{S,max}}$  of  $\sigma$ -hole in molecule X, the greater the enhancing impact on Se-Se bond. In addition, the topological analysis of electron density shows that  $\text{Se}\cdots\text{Se}$  interactions in the cyclic trimers have more covalent character than that in the dimers.

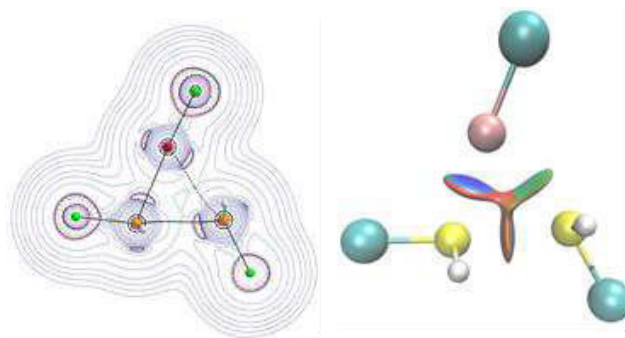


Fig 1 Contour map of the Laplacian of the electron density (left) and surfaces of reduced density gradient in the intermolecular region (right) of  $\text{SeHCl}\cdots\text{SeHCl}\cdots\text{BrCl}$  cyclic trimer.

This project was supported by the National Natural Science Foundation of China (Contract Nos: 21373075, 21371045, 21372062) and the Natural Science Researching Programs in Higher Education Institutions of Hebei Province (Contract No: Z2017006).

## Electrochemical properties of anatase-type TiO<sub>2</sub> nanoparticles – a theoretical approach.

Gergely Juhasz<sup>1,2</sup>

<sup>1</sup>*Dpt. Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo, Japan*

<sup>2</sup>*CREST, JST, Japan*

The electrochemical reduction of organic acids on anatase-type TiO<sub>2</sub> electrode was recently reported by Yamauchi [1]. Such an electrochemical reaction has a potential to produce alcohol products with high selectivity and Faraday efficiency, which then can be used as alternative fuel. However, only electrochemical reduction oxalic acid reported so far, and experiments with other acids like acetic acid were unsuccessful.

There are several questions were raised about this reaction, including the mechanism or the role of the anatase electrode. We used Density Functional Tight Binding (DFTB) method to study the behavior of organic acids (oxalic acid, acetic acid) on anatase surface. For the simulation, slab models of the 101 surface of anatase and nanoparticle model with 101 faces were used.

On 101 surface, a dissociative type absorption is the strongest for carboxylic acid molecules, according to both the calculations and experimental data. While the geometry of the interacting carboxyl group and absorption energy is very similar to oxalic acid and acetic acid (-114 and -118 kJ / mol, respectively), there is a difference in electronic structure: the LUMO orbital of oxalic acid is strongly interacting with the lower edge of the conducting band of the electrode, this cannot be seen in the case of acetic acid. Since the reduction of the molecules on the surface is due to the extra electrons coming from the conducting band levels of the electrode to LUMO orbitals, this explains why acetic acid cannot be reduced on anatase electrodes.

The nanoparticles, unlike surface slab models, always have an uncompensated dipole moment, as well as Ti ions with low coordination numbers. The calculations showed an approx. 0.5 eV smaller band gap for the nanoparticles, which was also influence by the morphology of the nanoparticle. This decrease of the gap were mostly due to the significantly lower LUMO energy levels, which play an important role in the electrochemical reduction over these nanoparticles.

[1] R. Watanabe, M. Yamauchi, M. Sadakiyo, R. Abe and T. Takeguchi, *Energy Environ. Sci.*, **8**, 1456 (2015).

## Nature of MH...X bond in Cp<sub>2</sub>Mo(L)H ...I-C≡C-R Complexes

Yaru Dang, Weihua Wang, Xiaoyan Li\*

College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang, P. R. China

\*Contact author: lixiaoyan@hebtu.edu.cn

**Abstract:** The metallocene compounds with sandwich structure are important organometallic catalysts and play an important roles in the fields of organic synthesis, medicine and bio-organic chemistry.<sup>[1,2]</sup> For all of the studied compounds, the DFT/M06-L calculations were performed with the Gaussian 09 program package. The aug-cc-pVDZ-pp basis set for Mo atom and the aug-cc- pVDZ basis set for all other atoms were used. The nature of H...I bond in the Cp<sub>2</sub>Mo(L)H [L=H, CO, P(OMe)<sub>3</sub>]...I-C≡C-R (R=NO<sub>2</sub>, Cl, Br, H, OH, CH<sub>3</sub>, NH<sub>2</sub>) have been investigated using the electrostatic potential analysis, energy decomposition analysis and natural bond orbital analysis. The calculated results show that H...I interactions in the title complexes are belong to halogen bonds, not hydrogen bonds. Different to others normal halogen bonds, not only the electrostatic interaction, but also the orbital interaction play important roles in this kind of halogen bonds, the steric interaction is small. The interaction energies are determined by the most positive electrostatic potential of I atom, not the most negative electrostatic potential of the H atom of Mo-H bond. With the increasing of electron withdrawing ability of the substituent R in the alkyne, the electrostatic potential maximum of the I atom increases, which enhances the strength of the H...I halogen bond and the electron transfer.

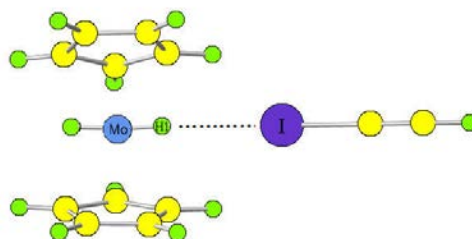


Figure 1: Geometry of the title compounds

[1] M. Maschke, M. Lieb, N. Metzler-Nolte, *Eur. J. Inorg. Chem.*, **36**, 5953(2012).

[2] H. Y. Zhu, Y. Z. Chen, S. Li, X. D. Yang, Y. N. Liu. *Int. J. Hydrogen Energ.*, **36**, 11810(2011).

This work was supported by the National Natural Science Foundation of China (Contract NO. 21372062) and the Natural Science Foundation of Hebei Province (Contract NO. B2016205042).

## SMASH: Massively Parallel Quantum Chemistry Program

Kazuya Ishimura

*Department of Theoretical and Computational Molecular Science, Institute for Molecular Science, 38 Nishigo-naka, Myodaiji, Okazaki, Aichi, Japan*

The performance of computer systems continues to be improved by the use of numbers of nodes and CPU cores or the attachment of accelerators because of heat and power problems. On the other hand, nano-sized molecular systems are one of the attractive and promising targets, for example catalysts, electric and fuel cells, self-assembled materials, and biological materials. Therefore, parallel computing is a significant approach to treat large molecular systems using present and future computers.

Scalable Molecular Analysis Solver for High-performance computing systems (SMASH) is a massively parallel program for quantum chemistry calculations and released under the Apache License 2.0 [1]. The SMASH program is written in the Fortran90/95 language with MPI and OpenMP standards for parallelization, and supports Hartree-Fock, DFT, and MP2 energy and geometry optimization calculations. Frequently used routines, such as one- and two-electron integral calculations, are modularized to make program developments simple as shown in Figure 1. The computational time and speed-up of the DFT (B3LYP) energy calculation for  $(C_{150}H_{30})_2$  with the cc-pVDZ basis set (4500 basis functions) are 154.2 sec and 50,499 (Figure 2) on 98,304 cores of the K computer (SPARC64 VIIfx 2.0GHz, 8cores/node), respectively.

```
subroutine calc2elec(twoeri,exijkl,coijkl,xyzijkl,
nprimijkl,nangijkl,nbfijkl,maxdim,mxprsh,
threshex)
twoeri : Two-electron integrals (Output)
exijkl : Exponents of basis functions (Input)
coijkl : Coefficients of basis functions
xyzijkl : XYZ components of four centers
nprimijkl : Numbers of primitive basis functions
nangijkl : Degrees of angular momenta of basis
functions (s=0, p=1, d=2,...)
nbfijkl : Numbers of basis functions of shells
(s=1, p=3, d=5 or 6, ...)
maxdim : Maximum number of dimension for
twoeri array
mxprsh : Maximum number of primitive basis
functions for exijkl and coijkl
threshex : Threshold of  $\exp(-x^2)$  function
```

Figure 1. Arguments of two-electron integral routine.

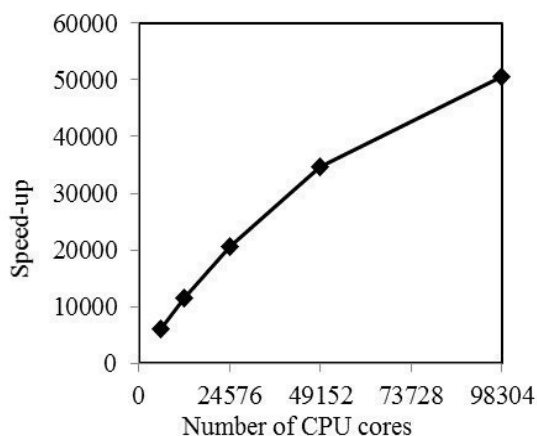


Figure 2. Speed-up of B3LYP calculation.

[1] <http://smash-qc.sourceforge.net/>.



## Theoretical Approaches on Isothermal Crystallization Behavior of $\beta$ -Nucleating Agent Filled Glass Fiber/Polypropylene Composites

Jong Sung Won<sup>1</sup>, Chun Su Kim<sup>1</sup>, Jong Hyun Park<sup>1</sup>, Young-Koan Ko<sup>2</sup>, and Seung Goo Lee<sup>1\*</sup>

<sup>1</sup>Department of Advanced Organic Materials and Textile System Engineering, Chungnam National University, 99 Daehak-ro, Daejeon 34134, Republic of Korea

<sup>2</sup>Lotte Chemical, 115 Gajeonbuk-ro, Daejeon 34110, Republic of Korea

\* lsgoo@cnu.ac.kr

Fiber reinforced thermoplastic composites are widely used in various industries because of their many advantages of excellent mechanical properties, low cost, and simple molding processes for various product. Especially, in an area of automotive materials which aims to reduce weight, cost and improve fuel efficiency, glass fiber (GF) reinforced polypropylene (PP) composites have been used for above advantages with recyclability. Because stress transfer in the GF/PP composites is influenced by the interphase crystallization of PP, the optimization of the mechanical properties of composites requires an extensive knowledge of the crystalline behavior of the PP. Among various parameters about crystallization, nucleating agent has an important role to the crystallization behaviors of the GF/PP composites. In this study, the  $\beta$ -nucleating agent filled GF/PP composites were prepared using a melt compounding process employing a twin screw extruder. The isothermal crystallization behaviors of  $\beta$ -nucleating agent filled GF/PP composites according to were measured using a differential scanning calorimetry and analyzed with Avrami's kinetic theory. There was a significant dependence of  $\beta$ -nucleating agent on the crystallization behavior of the PP matrix. The incorporation of  $\beta$ -nucleating agent improved effectively the crystallization rate of the GF/PP composites through heterogeneous nucleation. The nucleating effect of the GF surface related to the trans-crystallization was observed using a polarized optical microscopy. Great changes in the microstructure and mechanical properties of the GF/PP composites occurred by incorporating  $\beta$ -nucleating agent. Further effects of inclusion of the  $\beta$ -nucleating agent on the GF/PP composites were discussed and analyzed with theoretical approaches.

- [1] H. D. Wagner, *Compos. Sci. Technol.* **48**, 181 (1993).



## Relationship between Open-Shell Character and Third-Order Nonlinear Optical Properties in Rectangular-Shaped Tetraradical Model Systems

Hiroshi Matsui<sup>1</sup>, Shota Takamuku<sup>1</sup>, Ryohei Kishi<sup>1</sup>, Benoît Champagne<sup>2</sup>,  
Masayoshi Nakano<sup>1</sup>

<sup>1</sup>Department of Material Engineering Science, Graduate School of Engineering Science,  
Osaka University, Machikaneyama-cho 1-3, Toyonaka, Osaka 560-8531, Japan

<sup>2</sup>Department of Chemistry, Faculty of Science, University of Namur, Rue de Bruxelles 61 -  
5000 Namur, Belgium

Our previous studies have revealed that systems with intermediate diradical character ( $y_0$ ) exhibit remarkably larger second hyperpolarizability  $\gamma$ , which is the molecular property at the origin of third-order nonlinear optical (NLO) responses, than closed-shell ( $y_0 = 0$ ) and pure open-shell ( $y_0 = 1$ ) systems of similar size [1]. This novel design principle is also valid for one-dimensional multiradical systems [2]. In contrast, for rectangular-shaped tetraradical systems such as dimer of diradical molecules [3], comprehensive relationship between open-shell character and  $\gamma$  is still veiled due to their multi-configurational nature and the related difficulty in evaluating the NLO responses. In this study, therefore, we analyze the relationship between the open-shell character and  $\gamma$  of rectangular-shaped tetraradical systems using the extended-Hubbard model.

Dimensionless model Hamiltonian for dimer of diradicaloids is expressed as

$$H/U_0 = 1/U_0 \left[ \sum_i U_0 n_{i\uparrow} n_{i\downarrow} + \sum_{j>k} \sum_{\sigma} t_1 (a_{k\sigma}^{\dagger} a_{j\sigma} + a_{j\sigma}^{\dagger} a_{k\sigma}) + \sum_{l>m} \sum_{\sigma} t_2 (a_{m\sigma}^{\dagger} a_{l\sigma} + a_{l\sigma}^{\dagger} a_{m\sigma}) \right] \quad (1)$$

where  $U_0$ ,  $t_1$  and  $t_2$  denote on-site Coulomb repulsion, intramolecular transfer integral and intermolecular transfer integral, respectively. The intramolecular longitudinal component of dimensionless  $\gamma$  ( $\gamma_{\text{intra}}$ ) is shown in Figure 1 to depend on the intramolecular  $y_{\text{intra}} = 1 - \frac{4(t_1/U_0)}{\sqrt{1+16(t_1/U_0)^2}}$  and intermolecular  $y_{\text{inter}} = 1 - \frac{4(t_2/U_0)}{\sqrt{1+16(t_2/U_0)^2}}$  diradical characters. A novel

enhanced  $\gamma_{\text{intra}}$  region for open-shell systems with small diradical character  $y_{\text{intra}}$  is found at  $y_{\text{intra}} \sim y_{\text{inter}}$ . Other cases including inter-site Coulomb repulsion and exchange integral will be also presented.

[1] M. Nakano et al., *Phys. Rev. Lett.* **99**, 033001 (2007); M. Nakano et al., *J. Phys. Chem. Lett.* **6**, 3236 (2015). [2] K. Yoneda et al., *Chem. Phys. Chem.* **12**, 1697 (2011). [3] C. Bryan et al., *J. Chem. Soc., Chem. Commun.* **131**, 1447 (1994).

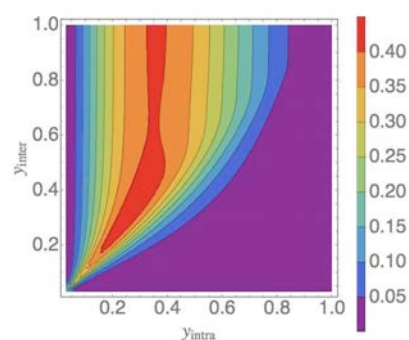


Figure 1.  $y_{\text{intra}}$  and  $y_{\text{inter}}$  dependences of  $\gamma_{\text{intra}}$ .

## Modelling the LCST Behaviour of Tactic poly(PEGMA)

Brad A. Wells<sup>1</sup>, Amanda S. Barnard<sup>1</sup>

<sup>1</sup>*Molecular and Materials Modelling Laboratory, Data6/CSIRO, Village Street,  
Docklands, Melbourne, Australia*

Thermoresponsive polymers have rapidly changing physical properties, such as solubility, with changing temperature. One such behaviour is the lower critical solution temperature (LCST), above which the solvated polymer go through a phase separation, reversibly forming agglomerated microstructures. In this work the LCST behaviour in water of the thermoresponsive polymer poly[poly(ethylene glycol) methacrylate] (PEGMA) was investigated.[1] Initial molecular dynamics simulations at different temperatures showed that the single solvated polymer chain exists predominately in a linear configuration at lower temperatures, but converted to a self-folded configuration at higher temperature. These configurations are shown in Figure 1. These different configurations are indicative of more pronounced water-polymer interactions at lower temperature and therefore the greater solubility of the polymer chain. Metadynamics calculations were then used to determine the relative free energy of each configuration at different temperatures. In these simulations the radius of gyration was used as a collective variable to sample the configuration space. The simulations also reveal some of the molecular mechanisms behind the thermoresponsive behavior of the polymer and the impact of different tacticities.

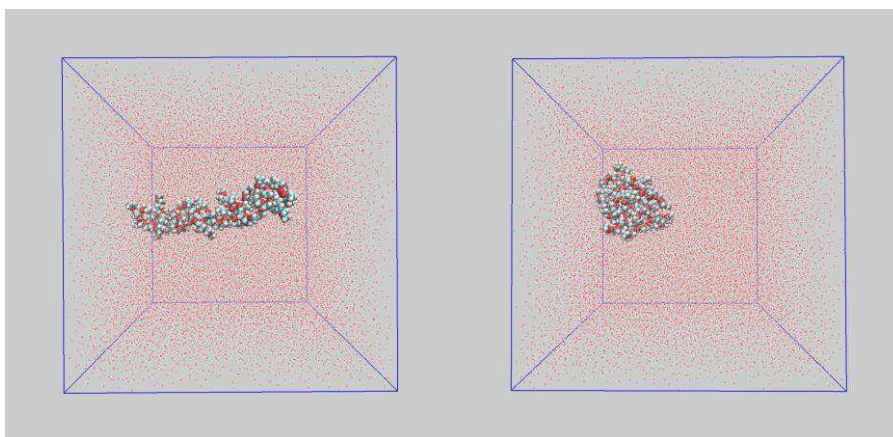


Figure 1 poly(PEGMA) at low (left) and high (right) temperature

[1] T. Terashima, T. Sugita, K. Fukae, and M. Sawamoto, *Macromolecules*, **47**, 589 (2014).

## Semiempirical OMx/MRCI methods: comprehensive benchmarks of electronically excited states and surface-hopping dynamics of a biomolecule

Deniz Tuna<sup>1\*</sup> and Walter Thiel<sup>1</sup>

<sup>1</sup>Max-Planck-Institut für Kohlenforschung, 45470 Mülheim an der Ruhr, Germany

\*Current affiliations: Department of Chemistry and The PULSE Institute, Stanford University, Stanford, California 94305, United States; SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States

The semiempirical OMx methods[1] perform well for many ground-state properties.[2] Coupled with an MRCI formalism they can also be applied to electronically excited states. We present OMx/MRCI results on extensive benchmarks for energies, geometries and properties of electronically excited states of CHNOF organic molecules.[3] These benchmarks reveal that OM2/MRCI is a particularly useful tool for performing many types of excited-state computations at almost instantaneous speed, but they also pinpoint current weaknesses that need to be addressed in ongoing developments.[3] OM2 parameters are now also available for the element sulfur. We demonstrate their performance for the computation of vertical excitation energies of a large set of sulfur-organic compounds and for the simulation of the surface-hopping dynamics of thiophene.[4]

Finally, we present a comprehensive application study of OM2/MRCI adaptive-timestep[5] surface-hopping dynamics simulations for the photoinduced dynamics of urocanic acid, a UV filter found in human skin.[6] Our study covers all 32 possible tautomers, isomers and conformers of the isolated neutral form. We ran almost 6000 excited-state trajectories, thereby gaining an unprecedentedly detailed insight into the tautomer- and isomer-resolved photoinduced dynamics of this molecule. The main photochemical process, *E/Z* photoisomerization, is analyzed in detail, but rare side processes have also been found. This study demonstrates the value of the OM2/MRCI method for performing very fast and comprehensive excited-state dynamics simulations.

[1] P. O. Dral, X. Wu, L. Spörkel, A. Kosłowski, W. Weber, R. Steiger, M. Scholten, W. Thiel, *J. Chem. Theory Comput.* **12**, 1082 (2016).

[2] P. O. Dral, X. Wu, L. Spörkel, A. Kosłowski, W. Thiel, *J. Chem. Theory Comput.* **12**, 1097 (2016).

[3] D. Tuna, Y. Lu, A. Kosłowski, W. Thiel, *J. Chem. Theory Comput.* **12**, 4400 (2016).

[4] D. Tuna, X. Wu, D. Fazzi, W. Thiel, *in preparation*.

[5] L. Spörkel, W. Thiel, *J. Chem. Phys.* **144**, 194108 (2016).

[6] D. Tuna, M. Barbatti, W. Thiel, *in preparation*.

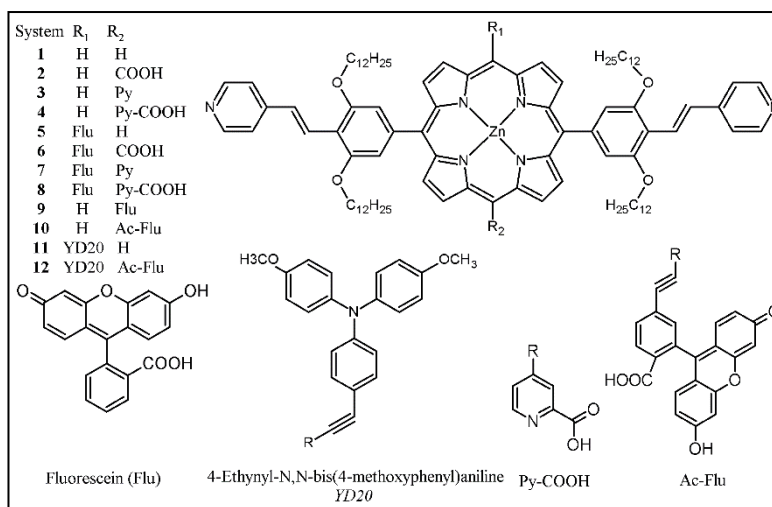
## Modulating Charge-Transfer Between Fluorescein-Porphyrin-based Chromophores and TiO<sub>2</sub> in Dye-Sensitized Solar Cells

M. Saavedra-Torres<sup>1</sup>, G. Cárdenas-Jirón<sup>1</sup>, R. López<sup>2</sup>

<sup>1</sup>Laboratorio de Química Teórica, Facultad de Química y Biología, Universidad de Santiago de Chile (USACH), Casilla 40, Correo 33, Santiago, Chile

<sup>2</sup>Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo. C/ Julián Clavería 8, 33006 Oviedo, Asturias, Spain.

The porphyrins have been highly used as part of the dye sensitized solar cells (DSSC) and photoconversion research, used to broad the range of TiO<sub>2</sub> absorption region, and to improve the efficiency of electron transfer. In this work we propose to use two bonded chromophores as DSSC candidates; a porphyrin using as reference the spider structure to prevent aggregation of molecules [1] and fluorescein, a dye belonging to the xanthene's family. We studied a set of *meso*-substituted zinc spider-porphyrins, by considering the substitutions described in Figure 1 and anchoring with TiO<sub>2</sub> clusters, evaluating energetic, electronic and structural aspects. Under the Density Functional Theory (DFT) and Time Dependent-DFT frameworks, several functionals were evaluated, comparing with experimental data. Preliminary results suggest that the best chromophores include fluorescein in R<sub>2</sub>, with important red-shift absorption and charge transfer. Secondarily, we note the importance of the linkage with the porphyrin, which is noted mainly over charge transfer effects between R<sub>1</sub> and R<sub>2</sub>. Finally, we noted that the adsorption to TiO<sub>2</sub> favors the absorption to the near-infrared region.



**Figure 1.** Structure view of the molecular structures studied.

**Acknowledgments.** We acknowledge the financial support given by FONDECYT/CONICYT Projects 1131002 and 1171719 (GCJ) and thank to MECESUP Project USA1555 by Research Assistant position (MST).

[1] C. Stangel et al. *Inorg. Chem* **22**, 11871 (2014).

## TDDFT Investigation of Manipulation of the Electronic and Optical Properties of Phosphorus Containing Heteroacenes

Heehyun Baek and Joonghan Kim\*

*Department of Chemistry, The Catholic University of Korea, Bucheon 14662, Republic of Korea*

Phosphorus containing heteroacenes have attracted a great deal of attention because their electronic and optical properties such as HOMO–LUMO gap, UV–vis absorption, and fluorescence emission can be altered by the addition of various substituents to acene rings.[1]–[3] Recently, 2,7-Ph<sub>2</sub>-naphtho[1,2-d:5,6-d']bi-(soxaphosphole)s [Ph<sub>2</sub>-NBOP] has been synthesized and their electronic and optical properties have been characterized.[4] However, systematic quantum chemical calculations are still absent. In this work, DFT and TDDFT calculations with CAM-B3LYP long-range corrected functional were performed to clarify the alterations of optical properties with respect to substitutions to heteroacenes. We identified that those alterations are originated from the size of p orbital of heteroatoms that could hinder effective  $\pi$  interaction of acene rings.

- [1] J. E. Anthony, *Chem. Rev.* **106**, 5028 (2006).
- [2] T. Agou; J. Kobayashi; T. Kawashima, *Org. Lett.* **8**, 2241 (2006).
- [3] T. Agou; J. Kobayashi; T. Kawashima, *Chem. Commun.* **30**, 3204 (2007).
- [4] F. L. Laughlin; N. Deligonul; A. L. Rheingold; J. A. Golen; B. J. Laughlin; R. C. Smith; J. D. Protasiewicz, *Organometallics*, **32**, 7116 (2013).

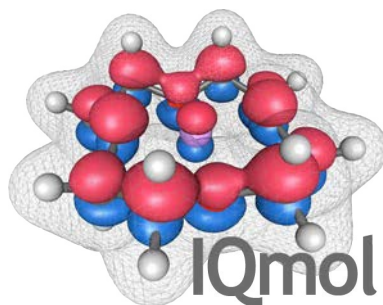
### ACKNOWLEDGMENT

This research was also supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (NRF-2016R1D1A1B03933120). This work was also supported by the National Institute of Supercomputing and Network/Korea Institute of Science and Technology Information with supercomputing resources including technical support (KSC-2016-C1-0002).

## IQMOL - The Smart Choice in Molecular Visualization Software

Andrew T. B. Gilbert<sup>1</sup>

<sup>1</sup>*QChem Inc. 6601 Owens Dr, Pleasanton, CA 94588, USA*



Quantum chemistry is becoming more mainstream thanks, in large part, to the increased availability of easy-to-use software and graphical interfaces that make the software more accessible and appealing to students and newcomers.

IQMOL is an open-source molecular editor and visualization package that runs on the OS X, Windows and Linux platforms. It supports the usual range of functionality such as surface plotting (orbitals, densities), animations (frequencies, reaction pathways) and spectra prediction (UV, IR). However, unlike other free molecular editors, IQMOL allows the user to directly tap into the power of a commercial quantum chemistry package - QCHEM - via a public, freely accessible server. Calculations on this server are time-limited, but offer access to the full functionality of QCHEM and provide a low-barrier entry point to undergraduate computational chemistry laboratories.

## MDbox: a cloud-based repository for molecular dynamics simulations

Karmen Condic-Jurkic<sup>1</sup>, Mark Gregson<sup>2</sup>, Steven De Costa<sup>2</sup>

<sup>1</sup>*Research School of Chemistry, The Australian National University, Canberra,, Australia*

<sup>2</sup>*Link Digital, Canberra, Australia*

Computational modelling has become an integral tool in almost every branch of science, including chemistry and biology. Computational chemistry methods are now widely used to provide better understanding of molecular processes at the atomistic level, complementing experimental findings. The majority of molecular dynamics (MD) simulations are computationally costly, often requiring supercomputer access and significant scientific input. Unfortunately, the original trajectories generated in the process are rarely made publicly available beyond the analysis presented in publications and supporting information. The simulations remain locally stored on hard drives or private servers without public access. Considering the human and computational resources used to generate these trajectories, they present a very valuable asset in molecular studies, especially biomolecular and materials sciences. Currently, there are general repositories that allow hosting of research data, like Figshare or Zenodo, but to the best of our knowledge, there is no publicly available repository dedicated exclusively to hosting and managing data generated by MD simulations, that is available to everyone. iBIOMES platform offers a solution for distributed environment [1], but there are many benefits of having a specialised and localised repository, including better control of data availability and access to large scale data analysis.

We are currently developing MDbox – a prototype for a specialised open access repository for MD simulation datasets. MDbox aims to provide a platform for storing and sharing trajectories and their corresponding input files, which should improve documentation of commonly used protocols and enhance the replicability and reproducibility of simulations [2]. In addition, the aim is to make collaboration and data exchange easier, and provide an alternative for making research publicly available and citable.

In our information-driven era, the open data approach is of great value for further development of computational modelling and for cross-disciplinary researchers in both academia and industry. The growing movement to make data produced by publicly funded research open provides an additional incentive. However, the most exciting prospects for MDbox comes in the form of new research opportunities and the advancement of molecular modelling, ranging from developing new analytics tools for large datasets to machine learning (AI) techniques.

[1] J. C. Thibault, J. C. Facelli, T. E. Cheatham III, *J. Chem. Inf. Model* **53**(3), 726 (2013).

[2] K. Hinsén, *Procedia Comput. Sci.* **4**, 579 (2011).



## Electronic Properties of Bilayer Gallium

**Dani Z. Metin<sup>1</sup>, Lukas Hammerschmidt<sup>1</sup>, Nicola Gaston<sup>1</sup>**

<sup>1</sup>*The MacDiarmid Institute for Advanced Materials and Nanotechnology, Department of Physics, The University of Auckland, Level 7, Building 303, 38 Princes Street, Auckland*

Melting point depression is a normal consequence when moving from bulk materials to the nanoscale, due to the increasing surface area to volume ratio. Gallium clusters behave anomalously, exhibiting superheating in clusters with less than 95 atoms.[1] Two-dimensional nanomaterials give insight into the nature of cluster properties, as they represent an extreme case where the ratio of surface area to volume is virtually infinite. A two-dimensional gallium structure has been demonstrated in molecular dynamics simulations to explain anomalous melting temperature of gallium nanoclusters.[2] 2-dimensional gallium has been recently synthesized through mechanical exfoliation.[3]

Here, we present the electronic structure of bilayer gallium with the use of density functional theory. Changes in densities of states and band structure as a consequence of variation of the interplanar distance, as well as variation of the metallic plane distance are investigated. We then consider substrate effects in order to further investigate the electronic properties of bilayer gallium.

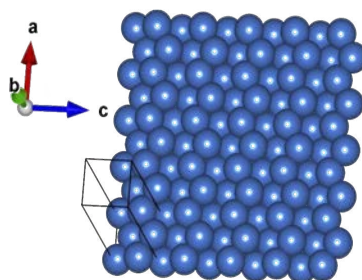


Figure 1: Bilayer gallium, derived from (010) surface of  $\alpha$ -gallium

- [1] K.L. Pyfer, J.O. Kafader, A. Yalamanchali and M.F. Jarrold, *J. Phys. Chem. A* **18**, 4900 (2014).
- [2] K. G. Steenbergen, N. Gaston, *Nano Lett.* **16**, 21 (2015).
- [3] V. Kochat, A. Samanta, Y. Zhang, S. Bhowmick, P. Manimunda, S. A. Asif, A. Stender, R. Vajtai, A. K. Singh AK, C. S. Tiwary, P. M. Ajayan *arXiv preprint arXiv:1704.08371* (2017).



## Probing supramolecular self-assembly with molecular dynamics simulations

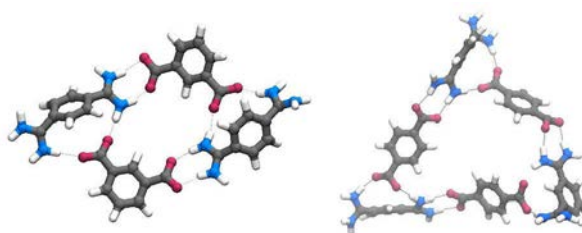
Michael Thomas<sup>1</sup>, Thomas Anglim Lagones<sup>1</sup>, Martyna Judd<sup>1</sup>, Mahbod Morshedi<sup>1</sup>, Megan L. O'Mara<sup>1</sup>, Nicholas G. White<sup>1</sup>

<sup>1</sup>*Research School of Chemistry, The Australian National University, Canberra, Australia*

Supramolecular chemistry, at its core, is concerned with the construction of large, non-covalently bound assemblies from smaller molecular constituents. The structure of solid state supramolecules can be determined using various X-ray techniques. Solution phase supramolecular structures are much more difficult to determine as traditional structure determination techniques, like NMR, provide limited information about molecular interactions.

Molecular dynamics (MD) is a modelling technique that is frequently used to explore the self-assembly and interactions of a range of solvated systems, including micelles, bilayers and membrane proteins. In this study, we used MD to probe the potential self-assembly and interactions of simple charge-assisted hydrogen bonded assemblies [1]. We are unaware of MD being used to aid structure determination in this type of supramolecular system. Para- or meta-bis(amidinium) compounds and para-, meta- or ortho-dicarboxylates were simulated in a variety of solvents in which a range of intermolecular interactions were observed and quantified. Some combinations of chemical species and solvents lead to the formation of interesting structures, such as 1-D tapes, 2-D sheets and various cycles. Interactions described by MD simulations were in good agreement with results from <sup>1</sup>H and DOSY NMR spectroscopy. Qualitatively, MD data were in agreement with ability of experimental systems to aggregate or crystallize out of solution.

To produce interesting solution state structures, supramolecular chemistry looks to balance the complex interplay between the macromolecular building blocks, and between these building blocks and the solvent. Analysis of hydrogen bond formation in MD simulations suggests a simple metric to determine if particular building blocks in a particular solvent will produce interesting structures - the number of hydrogen bonds per acceptor or donor group between building blocks.



- [1] M. Thomas, T. A. Lagones, M. Judd, M. Morshedi, M. L. O'Mara, N. G. White, *Chem. Asian J.*, DOI: 10.1002/asia.201700406, (2017)

## Computational results for the cobalt and platinum paired single-atom catalysis of the oxygen reduction reaction

**Julia Melisande Theresa Agatha Fischer<sup>1</sup>, Marlies Hankel<sup>1</sup>, Debra J. Searles<sup>1,2</sup>**

<sup>1</sup>*Centre for Theoretical and Computational Molecular Science, Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Queensland 4072, Australia.*

<sup>2</sup>*School of Chemistry and Molecular Biosciences, The University of Queensland, Queensland 4072, Australia.*

A single-atom catalyst (SAC) refers to an isolated single metal atom, stabilized in a solid substrate, which functions as an active centre for heterogeneous catalysis.[1] The main advantage of using these catalysts is that they reduce the amount of expensive, rare metals required. Paired SAC refers to the combined effect of two single atoms adjacent to each other.

It is widely known that the best electrochemical catalyst for the oxygen reduction reaction (ORR) is Pt. In collaboration with Yao's experimental group,[2] we have shown that the Co and Pt paired SAC outperforms the Pt metal catalyst for the ORR. In experimental studies, the distribution of metal distances and the chemical environment were determined for high performance paired SACs. Based on this information, model structures were constructed and density functional theory (DFT) calculations carried out on these systems. Nitrogen doped graphene with different sized vacancies were used to vary the metal-metal distances of the Co and Pt atoms. The free energies of intermediate species of the OOR were calculated to determine the likely mechanism of the reaction on these systems. Further, to compare the results to the experiments, the overpotentials were determined from the difference in voltage for the reaction to occur experimentally and the thermodynamically expected value. Both calculations and experiments show that enhancement of the ORR can be obtained with a lower overpotential using a combined CoPt system rather than a Pt paired SAC. The charge density differences and the density of states show that the enhancement is due to an increased electron density around Co, leading to a d-orbital contiguous to the Fermi level.

[1] X. F. Yang, A. Wang, B. Qiao, J. Li, J. Liu, and T. Zhang, *Acc. Chem. Res.* **46**, 8 (2013).

[2] L. Zhang, J. M. T. A. Fischer, Y. Jia, X. Yan, W. Xu, X. Wang, J. Chen, M. Hankel, D. J. Searles, S. Feng and X. Yao, manuscript in preparation.

**$L_a$  or  $L_b$ , that is the question! –  
Quantum Dynamical and Semi-classical Studies of Pyrene**

**Matthias K. Roos, Sebastian Reiter, Regina de Vivie-Riedle**

*Department of Chemistry, Ludwig-Maximilians-Universität, Butenandtstr. 5-13,  
Munich, Germany*

Pyrene, the textbook example for the formation of excimers, is nowadays a widely used fluorescence marker, sensing molecule and building block in organic semiconductors useful for organic light emitting diodes (OLEDs) or organic photovoltaic cells (OPV). Nonetheless, the basic mechanism behind its exceptional photophysics is not well understood.

Pyrene is excited by UV light to the  $S_2$  state, a  $\pi\pi^*$  state labeled  $L_a$  according to Platt's notation. The  $S_1$  or  $L_b$  has a negligible contribution to the absorption. Yet, emission occurs exclusively from the  $L_b$  state according to experiments. Therefore, an ultrafast relaxation pathway like a conical intersection between these two states must exist.

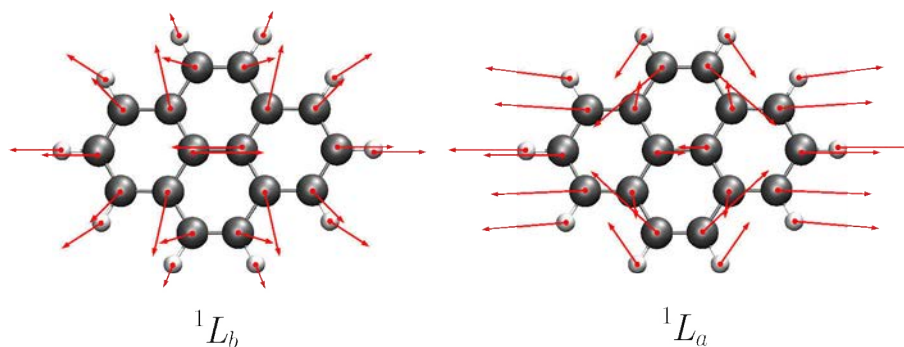


Figure 1: Displacement vectors for the  $L_b$  and  $L_a$  state.

To simulate this photophysical process we use both quantum dynamical and semi-classical on-the-fly methods, the former on a two dimensional grid built from displacement vectors between the minimum structures. Therefore, we employ the Wilson G-Matrix method for the kinetic energy operator. In both cases CASSCF(4,4) is used as quantum chemical method. This small active space includes only the necessary excitations to describe both  $L_a$  and  $L_b$  and prevents one-sided stabilization of either one. The choice of method and active space will be discussed in depth for this molecule, which is highly challenging due to its partial loss of symmetry.

We discuss the results for both dynamical simulations focussing on the transfer times through the conical intersection and on the comparison with time-resolved experiments. Furthermore, we talk about the implications of our simulations.

## Energy transfer in Fenna-Matthews-Olson complex with a realistic all-atom interpolated potential model

Chang Woo Kim<sup>1</sup> and Young Min Rhee<sup>2</sup>

<sup>1</sup>*Department of Chemistry, Pohang University of Science and Technology (POSTECH),  
Pohang 37673, Korea*

<sup>2</sup>*Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST),  
Daejeon 34141, Korea*

Due to the importance in solar energy conversion, energy transfer dynamics in light harvesting complexes has been a topic of interest over the last decade. Light energy migrates between the aggregate of pigments in the form of electronic excitation after being absorbed by the antenna complex. This process is influenced by constant thermal fluctuations at ambient temperature. Therefore, modeling the environmental perturbations on the pigment excitation energy is a key element for related simulations. One of the important yet still elusive aspect of the energy transfer process is the effect of interplay between electronic excitation and intramolecular pigment vibrations. Reliably considering such an aspect in atomistic simulation is however very challenging, especially because extensive quantum chemical calculations are conventionally required. For bacteriochlorophyll pigments in the Fenna-Matthews-Olson (FMO) light-harvesting complex, our group has recently achieved this goal and constructed a potential energy model with the density functional theory (DFT) level reliability [1]. Even with this level of reliability, molecular dynamics simulations can be performed almost as cheaply as with traditional force fields. Directly pursuing the energy transfer dynamics in the complex is also feasible after combining this model with a quantum dynamics method suitable for semi-classical atomistic simulations [2]. Based on the simulation results, we briefly characterize the environmental perturbations by visualizing the motions related to the strong modes in the spectral density and also discuss how exciton delocalization affect the complex's characteristics. We then present the results of actual energy transfer simulations for the complex and show that the energy transfer is promoted when the pigment vibration is included in the simulation. Finally, by tuning our pigment potential energy model in a computational way, we try to investigate how the different parts of the spectral density affect the energy transfer process.

[1] C. W. Kim; Y. M. Rhee, *J. Chem. Theory Comput.* **12**, 5235–5246 (2016).

[2] H. W. Kim; Y. M. Rhee, *J. Chem. Phys.* **140**, 184106 (2014).

## Density functionals in the studies of dipole moment and polarizability of the spatially confined molecules

Marta Chołuj<sup>1</sup>

<sup>1</sup>*Department of Physical and Quantum Chemistry, Wrocław University of Science and Technology, Wyb. Wyspiańskiego 27, Wrocław, Poland*

Over the past few decades, there has been a growing interest in theoretical and experimental studies of the spatial confinement phenomenon. This is strongly connected with the fact that confining environments can significantly modify various physical and chemical properties of atomic and molecular systems [1]. Therefore, the investigations of spatially restricted chemical objects are of pivotal importance for development of many fields of science. In particular, a considerable amount of scientific effort in theoretical chemistry has been devoted to the analysis of the influence of confining environment on the electric properties of atoms, molecules and molecular complexes [2-5].

The quantum chemical studies of molecular electric properties under spatial confinement are usually performed using the highly correlated wave function based methods and extended basis sets, because it is well established that such formalism has to be applied in order to obtain accurate results. However, in this work, we examine a performance of numerous density functionals (e.g. B3LYP, CAM-B3LYP, PB0,  $\omega$ B97X-D, M06, M06-L, BLYP, OLYP, M11, M11-L) in the calculations of dipole moment and polarizability of the spatially restricted molecules. The set of studied molecules includes, *inter alia*, CO, BF, LiH, LiF, HF, HCl. The obtained results are compared with CCSD(T) reference values. The external spatial confinement is modeled by applying the harmonic oscillator potential of cylindrical symmetry:

$$V(r_i) = \frac{1}{2} \omega^2 r_i^2 = \frac{1}{2} \omega^2 (x_i^2 + y_i^2)$$

where the  $\omega$  parameter describes the strength of spatial restriction. Such potential, included in the Hamiltonian of an isolated systems in the form of one-electron operator, allows to model effects arising from the Pauli exclusion principle and mimics a nanotube-like confining cages.

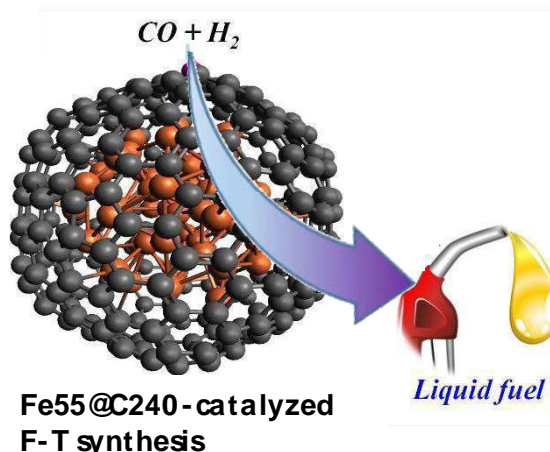
- [1] W. Jaskólski, *Phys. Rep.* **271**, 1 (1996).
- [2] J. Lo, M. Klobukowski, *Chem. Phys.* **328**, 132 (2006).
- [3] M. Chołuj, W. Bartkowiak, P. Naciążek, K. Strasburger, *J. Chem. Phys.* **146**, 194301 (2017).
- [4] M. Chołuj, W. Bartkowiak, *Chem. Phys. Lett.* **663**, 84 (2016).
- [5] R. Zaleśny, R. Góra, J. Kozłowska, J. Luis, H. Ågren, W. Bartkowiak, *J. Chem. Theory Comput.* **9**, 3463 (2013).

## Computational insight into Fe@C-catalyzed Fischer-Tropsch Synthesis

Geraldine Cilpa-Karhu and Kari Laasonen

*Department of Chemistry and Materials Science, COMP Centre of Excellence in Computational Nanoscience, Aalto University, Kemistintie 1, Finland*

A new generation of Fe-based catalysts for Fischer-Tropsch synthesis (FTS) has emerged. In these catalysts, iron under various forms (carbide/iron/iron oxide) is confined in carbon materials. These catalysts have shown enhanced activity for FTS as well as enhanced durability [1]. Single-shell carbon-encapsulated iron nanoparticles (SCENs) have been studied in our group both computationally and experimentally and the results have demonstrated that they are electron-donor-acceptor complexes that can act as effective catalysts for the hydrogen evolution reaction [2,3]. Recent studies have also shown the SCENs's catalytic ability for the oxygen evolution reaction [4]. Thus, we explored further the ability of our realistic SCEN model system Fe55@C240 for FTS using density functional theory and investigated the known Fe-based FTS mechanisms [5] on our novel catalyst.



- [1] S. Y. Hong et al., *Nanoscale* **7**, 16616 (2015).
- [2] S. Taubert et al., *Phys. Chem. Chem. Phys.* **16**, 3648 (2014).
- [3] M. Tavakkoli et al., *Angew. Chem. Int. Ed.* **54**, 4535 (2015).
- [4] X. Cui et al., *Energy Environ. Sc.* **9**, 123 (2016).
- [5] E. de Smit et al., *Chem. Soc. Rev.* **37**, 2758 (2008).

## Pseudo $\pi$ -hole Interactions vs $\pi$ -hole Interactions

Bo Lu, Wei Li, Lingpeng Meng, Yanli Zeng\*

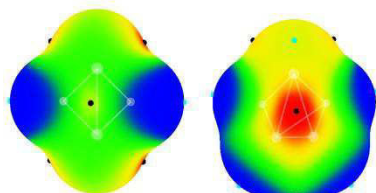
College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang  
050024, P. R. China

Contact author: yanlizeng@mail.hebtu.edu.cn

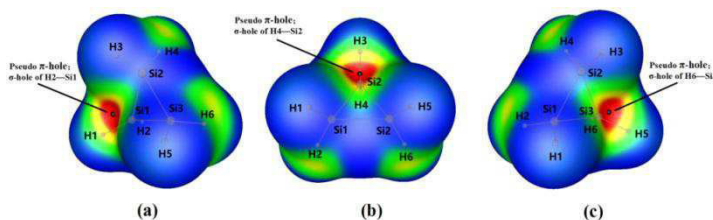
Noncovalent interactions between molecules play an important role in supramolecular chemistry, molecular biology, and materials science<sup>1</sup>. In recent years, interest in new types of  $\pi$ -hole<sup>2</sup> interactions has increased. A region of low electronic density that are perpendicular to portion of a molecular framework instead of being along the extensions of bonds (as are  $\sigma$ -holes) is termed as the positive " $\pi$ -hole" (Fig. 1).

For cyclopropane and its derivatives  $M_3H_6$  ( $M = C, Si, Ge, Sn, Pb$ ), the "pseudo  $\pi$ -hole" regions have been discovered above and below the M-M-M three-membered ring. To rationalize the origin of the pseudo  $\pi$ -hole, taking  $Si_3H_6$  as an example, the three  $\sigma$ -holes on the extension orientations of H2-Si1 bond, H4-Si2 bond, and H6-Si3 bond are shown in Fig. 2a, 2b and 2c, respectively. The three  $\sigma$ -holes could be converged to one positive electrostatic potential region -- the pseudo  $\pi$ -hole region. On the other side of the Si-Si-Si three-membered ring, the three  $\sigma$ -holes on the extension orientations of H1-Si1 bond, H3-Si2 bond, and H5-Si3 bond also converge to the pseudo  $\pi$ -hole region.

In this work, the  $\pi$ -hole interactions in  $SN_2P_2 \cdots NH_3$  and  $SN_2P_2 \cdots PH_3$  have been studied. The pseudo  $\pi$ -hole interactions have been designed and investigated between  $M_3H_6$  and F-CN. The termolecular and tetramolecular complexes  $M_3H_6 \cdots (NCF)_n$  ( $n = 2, 3$ ) were constructed to investigate the enhancing effects of  $F \cdots N$  halogen bonds on the pseudo  $\pi$ -hole interaction. Also, the pseudo  $\pi$ -hole interactions are compared with the  $\pi$ -hole interactions.



**Fig. 1** Electrostatic potentials on the 0.001 a.u. contour of the molecular electron density of  $S_2N_2$  and  $SN_2P_2$ .



**Fig. 2** Electrostatic potentials on the 0.001 a.u. contour of the molecular electron density of  $Si_3H_6$  to show the three  $\sigma$ -holes on the extension orientations of three H-Si bonds: (a) H2-Si1; (b) H4-Si2; (c) H6-Si3.

### References:

- 1 K. Müller-Dethlefs and P. Hobza, *Chem. Rev.* **100**, 143 (2000).
- 2 L. Gao, Y. L. Zeng, X. Y. Zhang and L. P. Meng, *J. Comput. Chem.* **37**, 1321(2016).

This project was supported by the National Natural Science Foundation of China (21371045, 21373075) and the Natural Science Foundation of Hebei Province (B2015205045). Thanks are also due to Education Department of Hebei Province of China through innovative hundred talents support program (SLRC2017041).

## Consistent interpretation of coarse-grained peptide kinetics using Markov state models biased with external information

Joseph F. Rudzinski<sup>1</sup>, Kurt Kremer<sup>1</sup>, Tristan Bereau<sup>1</sup>

<sup>1</sup>*Max Planck Institute for Polymer Research, 55128 Mainz, Germany*

Simple, physics-based coarse-grained (CG) models have provided tremendous insight into the essential features of the protein folding process. Recent advancements in CG methodologies allow increased chemical detail and accuracy, while retaining the sampling efficiency to address problems intractable for atomically-detailed models. This beneficial speed-up, attained through a combination of reduced molecular friction and softer interaction potentials, comes at the cost of obscuring the connection to the true dynamical properties of the underlying system. Although it is possible to rescue the dynamics via a generalized Langevin formalism, this approach offers a daunting computational and conceptual challenge for complex biological molecules that give rise to hierarchical dynamics, i.e., kinetic processes coupled over various timescales. As an alternative, this work considers a Markov state modeling framework for characterizing and correcting the hierarchy of slow kinetic processes generated from CG simulations. In particular, the proposed Bayesian scheme identifies essential adjustments to a Markov state model, generated from CG simulations, in order to achieve consistent kinetics, with respect to given reference data for the system.[1] We test the method on two CG peptide models and demonstrate that the resulting information may be directly and effectively employed for model reparametrization.[2] In both cases, the reparametrization results in an improved hierarchy of slow kinetic processes, while retaining the fundamental properties of the original model. Finally, to better characterize the utility of the proposed methodology in the context of combining CG protein folding simulations with experimental reference data, we perform a detailed investigation of structure-kinetic relationships for CG helix-coil transitions.

[1] J. F. Rudzinski, K. Kremer, T. Bereau *J. Chem. Phys.* **144**, 051102 (2016).

[2] J. F. Rudzinski, T. Bereau *Eur. Phys. J. Spec. Top.* **225**, 1373 (2016).



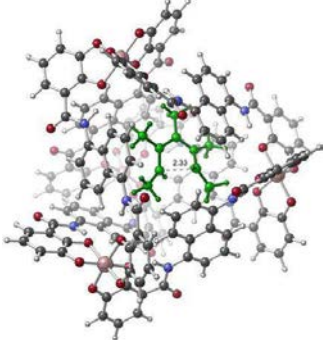
## How Does Ga<sub>4</sub>L<sub>6</sub> Supramolecular Cage Help Carbocation Cyclizations?

Q. Nhu N. Nguyen<sup>1</sup>, Robert G. Bergman<sup>2</sup>, Kenneth N. Raymond<sup>2</sup>, F. Dean Toste<sup>2</sup>, Dean J. Tantillo<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of California-Davis, Davis, CA 95616, USA*

<sup>2</sup>*Department of Chemistry, University of California-Berkeley, Berkeley, CA 94720, USA*

As supramolecular cavities provide various ways to mimic enzymes' activities, understanding how these supramolecular cages work will help navigate future research and contribute to the study of natural enzymes [1]. This study focused on the cyclization reactions of pentamethylpentadienyl alcohols catalyzed by polyanionic Ga<sub>4</sub>L<sub>6</sub> cage (net minus 12 charge), and the rate accelerations were observed to be about 1-2 million folds in previous experimental studies [2]. All quantum mechanical calculations were done with *Gaussian09*[3] software package, using various DFT methods and water implicit continuum solvation model (CPCM)[4] as water was the main experimental solvent. Full optimizations with frequency calculations were performed for the systems catalyzed by the gallium cage, allowing all the substrates' and cage's atoms to relax.



Background reactions were calculated and compared to catalyzed systems in the absence of explicit solvent water molecules, as well as in the presence of 1 to 4 solvent waters. Various single-point calculations on the truncated cage configurations were performed to examine how various features of the cage contributed to the catalytic effects. Quantum mechanical calculations suggested that the negative 12 charged gallium-based cages accelerated the cyclization reactions by altering the basicity of the substrates' hydroxyl groups. This also led to an investigation of the change in basicity of alcohol-based, amine-based, phosphorus-based substrates.

[1] a) S. I. Stupp, L. C. Palmer, *Chem. Mater.* **26**(1), 507 (2014); b) D. W. Christianson, *Chem. Rev.* **106**, 3412 (2006); c) D. J. Tantillo, *Nat. Prod. Rep.* **28**, 1035 (2011).

[2] a) C. J. Hastings, M. D. Pluth, R. G. Bergman, K. N. Raymond, *J. Am. Chem. Soc.* **132**, 6938 (2010); b) C. J. Hastings, R. G. Bergman, K. N. Raymond, *Chem. Eur. J.* **20**, 3966 (2014).

[3] *Gaussian09*, Revision B.01, M. J. Frisch, et al., Gaussian, Inc., Wallingford CT (2009).

[4] a) V. Barone, M. J. Cossi, *Phys. Chem. A* **102**, 1995 (1998); b) M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comp. Chem.* **24**, 669 (2003).

## Towards accurate description of weak and strong correlations via spin-projection

Takashi Tsuchimochi<sup>1</sup>, Seiichiro Ten-no<sup>1, 2</sup>

<sup>1</sup>*Graduate School of Science, Technology, and Innovation, Kobe University, Kobe, Japan*

<sup>2</sup>*Graduate School of System Informatics, Kobe University, Kobe, Japan*

Recently, there has been tremendous interest in understanding strongly correlated electronic structures appeared in open-shell systems such as transition metal complexes. However, compared to single-reference methods, it is much more challenging to develop multi-reference theories in general, due to complications in derivation and implementation as well as a large computational cost. Among several multi-configuration approaches, symmetry-projected Hartree-Fock (PHF) has been shown to be a simple and attractive mean-field model, residing in between single- and multi-reference domains. PHF itself was proposed several decades ago by Löwdin in his series of papers, but its complicated formulation has long hindered the developments of post-PHF theories that can handle, for example, excited states and weak (dynamical) correlation. The Scuseria group has recently reformulated the PHF equation in a dramatically simpler way, and opened a new frontier for multi-reference methods that are less extensive than the conventional ones. This enabled us to propose correlation methods using PHF as a reference wave function, such as perturbation theory and spin-extended configuration interaction singles and doubles (ECISD)[2]. The latter has been shown to be promising especially when the size-consistent correction due to Davidson is introduced, accurately describing the potential energy curves of several small molecules with near FCI results.

In this presentation, we will report two important extensions on ECISD. First, the analytical gradient of the ECISD energy is derived, which makes it possible to perform geometry optimization and computations of molecular properties[3]. It is shown that the geometries and dipole moments obtained by ECISD and MRCI are comparable. We will discuss how the size-consistent correction can be incorporated into the ECISD equation without resorting to the Davidson correction. One way to achieve this is to employ and extend the formalism of coupled electron pair approximation (CEPA) for ECISD[4]. This way, linearized coupled-cluster based on PHF can be also obtained. We will show the CEPA variants are in many cases more reliable than ECISD.

- [1] C. A. Jiménez-Hoyos, T. M. Henderson, T. Tsuchimochi, and G. E. Scuseria, *J. Chem. Phys.* T. Tsuchimochi and T. Van Voorhis, *J. Chem. Phys.* **141**, 164117 (2014).
- [2] T. Tsuchimochi and S. Ten-no, *J. Chem. Phys.* **144**, 011101 (2016); *J. Chem. Theory Comput.* **12**, 1741 (2016).
- [3] T. Tsuchimochi and S. Ten-no, *J. Chem. Phys.* **146**, 074104 (2017).
- [4] T. Tsuchimochi and S. Ten-no, *J. Chem. Theory Comput.* **13**, 1667 (2017).

## On the use of Gaussian Process Regression in Geometry Optimizations

Gunnar Schmitz<sup>1</sup>, Ove Christiansen<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Aarhus University, Langelandsgade 140, Aarhus DK-8000, Denmark*

For many high level methods like for example CCSD(F12\*)(T\*) yet no analytical geometrical gradients are available. And due the required man hours for deriving the required working equations and implementing them in an efficient fashion this gap won't probably be filled in the recent future. Therefore one has in geometry optimizations at the moment to rely on numerical derivatives if one aims to use this kind of methods. For small molecules this might even be more efficient, but for larger and larger molecules this becomes more and more a bottle neck since for each gradient step at least  $2 \cdot (3N - 6)$  single point calculations (SPs) are required if central differences are used.

With means of Gaussian Process Regression (GPR) – a procedure related to the field of machine learning – we explore how these SPs can be recycled to reduce their over all number in the end. GPR was already very recently successfully applied for constructing potential energy surfaces (PESs) and showed promising results by for example reducing the number of required SPs by one order of magnitude or by factorizing the PES matrix elements in a useful format.[1, 2]

In the context of geometry optimizations the GPR generates from the already computed SPs a potential on which the geometry is optimized. Overall convergence is achieved if both the potential and the geometry is converged.

[1] J. Cui, R. V. Krems, *J. Phys. B: At., Mol. Opt. Phys.* **49**, (2016).

[2] J. P. Alborzpour, D. P. Tew, and S. Habershon, *J. Chem. Phys.* **145**, (2016).

## Anharmonic Vibrational Spectra from Double Incremental Potential Energy Surfaces and Dipole Surfaces.

Diana Madsen<sup>1</sup>, Carolin König<sup>1, 2</sup>, Ove Christiansen<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark*

<sup>2</sup>*Division of Theoretical Chemistry and Biology, KTH Royal Institute of Technology, Roslagstullsbacken 15, S-106 91 Stockholm, Sweden*

Linearly scaling potential energy- and dipole surfaces have been generated by a so-called double incremental approach[1] and applied to calculate anharmonic vibrational spectra for different molecules. In the double-incremental approach, the surfaces are expressed as an expansion including up to a certain number of vibrational modes coupling simultaneously and an incremental evaluation of the energy or dipole. The incremental evaluation is made by dividing the molecules into fragments and including combinations of these fragments in an incremental fashion. In order to get computational savings, coordinates with well-defined locality have been applied. These coordinates are either local to one fragment or spanning multiple fragments. By introducing auxiliary coordinates for the spanning coordinates, new coordinates spanning only some fragments can be obtained. In this way, a linear scaling of both the number of single points and accumulated cost of single points can be obtained. However, the auxiliary coordinates require an extra transformation, which leads to an extra error. Consequently, there have been two kinds of errors to investigate the impact of: 1) the fragmentation error and 2) the transformation error. The results have shown that for some systems like para tetra-phenyl the calculated spectra show insignificant fragmentation and transformation errors. The double incremental approach is potentially a game-changer regarding pushing the limits of molecular sizes for which accurate anharmonic vibrational spectra can be calculated.

[1] C. König and O. Christiansen, *The Journal of Chemical Physics* **145**, 064105 (2016).

## Simulating rare events with the Adaptive Multilevel Splitting method

Laura J. Silva Lopes<sup>1</sup>, Jérôme Hénin<sup>2</sup>, Tony Lelièvre<sup>1</sup>

<sup>1</sup>*CERMICS, Ecole des Ponts ParisTech, 77455 Marne La Vallée, France*

<sup>2</sup>*Laboratoire de Biochimie Théorique, Institut de Biologie Physico-Chimique, 75005 Paris, France*

Simulation of rare events has been an important field of research in biophysics for nearly two and a half decades now. The goal is to obtain kinetics information for processes like protein (un)folding or ligand-protein (un)binding. A usual quantity of interest is the transition rate, or equivalently its inverse, the transition time. However, these events generally involves transitions between metastable states, namely regions where the system remains trapped for very long times. This makes brute force computations unpractical. The Adaptive Multilevel Splitting (AMS) method is a powerful and versatile method for the simulation of rare events[1]. It has been recently adapted to the sampling of reactive trajectories and its is currently implemented in Tcl for NAMD[2]. From an AMS simulation, it is possible to obtain the transition time. Some interesting properties of the AMS method were already emphasized in previous works, like its unbiasedness[3]. The goal of this work is to numerically exhibit some properties of the algorithm, obtain transition times for different systems and compare them to experimental results. We applied the method to  $\beta$ -cyclodextrine-ligand systems[4] (Figure 1).

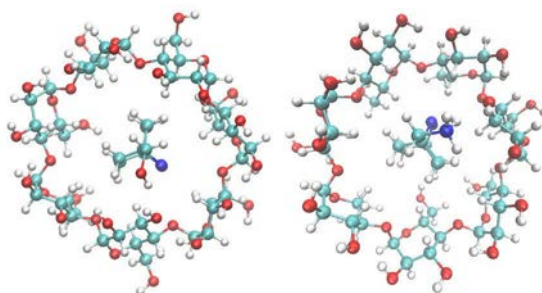


Figure 1:  $\beta$ -cyclodextrine with two ligands for which we calculated the unbinding time.

- [1] F. Cérou, F., A. Guyader, *Stoch. Anal. Appl.* **25**, (2007).
- [2] T. Ivan, C. G. Mayne, K. Schulten, T. Lelièvre, *J. Chem. Theory Comput.* **12**, (2016).
- [3] C.-E. Bréhier, M. Gazeau, L. Goudenège, T. Lelièvre, M. Rousset, *Ann. Appl. Probab.* **6**, (2016).
- [4] X. Zhang, G. and Gramlich, X. Wang, W. M. Nau, *J. Am. Chem. Soc.* **124**, (2002).

## Catalyzed Decomposition of Alkyl Hydroperoxides to Ketones – A Mechanistic Investigation

**Marko Hermesen<sup>1,2</sup>, Jessica Hamann<sup>1</sup>, Anna-Corina Schmidt<sup>1</sup>, Ansgar Schäfer<sup>2</sup>, Peter Comba<sup>3</sup>, Thomas Schaub<sup>1,4</sup>**

<sup>1</sup>*Catalysis Research Laboratory, Im Neuenheimer Feld 584, 69120 Heidelberg, Germany*

<sup>2</sup>*BASF SE, Quantum Chemistry & Molecular Simulation, Carl-Bosch-Str. 38, 67056 Ludwigshafen, Germany*

<sup>3</sup>*Institute for Inorganic Chemistry & IWR at Heidelberg University, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany.*

<sup>4</sup>*BASF SE, Synthesis & Homogeneous Catalysis, Carl-Bosch-Str. 38, 67056 Ludwigshafen, Germany*

Several vanadium(V)dipicolinato complexes were identified as promising candidates for the decomposition of hydroperoxides to corresponding ketones and water. As hydroperoxide decomposition is currently the main industrial route to cyclohexanone, but also inevitably forms the corresponding alcohol, we set out to explain the formation of ketone in a radical-free mechanism that has so far not been reported. The insight gained will be of interest for development of ketone-selective decomposition catalysts. This poster will focus on the computational investigation of different possible mechanisms and the identification of an intramolecular hydrogen transfer to the metal catalyst that is key to the observed reactivity [1].

[1] A.-C. Schmidt, M. Hermesen, F. Rominger, R. Dehn, J. H. Teles, A. Schäfer, O. Trapp, T. Schaub, *Inorg. Chem.*, **56**, (2017).

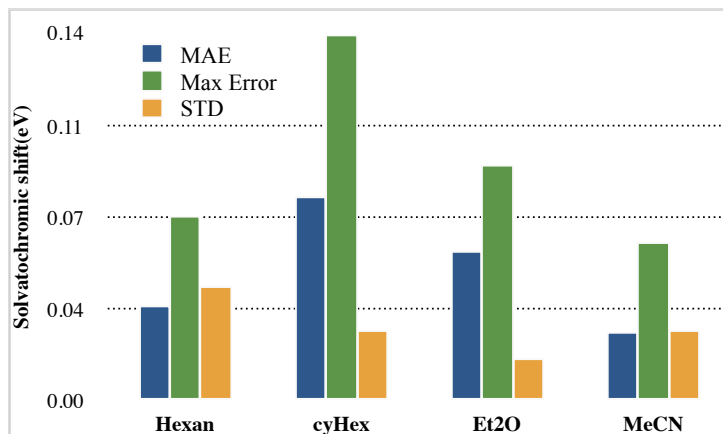
## COSMORI-CC2: A polarizable continuum RI-CC2 method for calculation of vertical excitation energies and analytic gradients

Sarah K. Khani , Christof Hättig

*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum,  
Germany*

We represent an implementation of the conductor-like screening model (COSMO) in combination with the resolution of identity implementation of the approximate coupled-cluster singles and doubles method CC2 in the TURBOMOLE package [1]. The central idea of the COSMORI-CC2 approach is to place the solute in a cavity within a polarizable continuum and use the solvated Hartree-Fock (HF) orbitals for the CC2 calculation [2]. The performance of the implemented approach is tested for a set of experimental benchmark data for solvatochromism in molecules containing 42 gas-phase to solvent shifts for 15 molecules [3].

Along with the COSMORI-CC2 implementation for calculation of vertical excitation energies, the gradient theory of COSMORI-CC2 has been developed and implemented in the TURBOMOLE package [4,5].



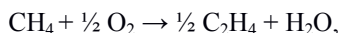
- [1] C. Hättig, A. Köhn, *J. Chem. Phys.* **117**, 6939 (2002).
- [2] A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin Trans 2*, **799** (1993).
- [3] A. Dreuw, *J. Phys. Chem. A* **119**, 5446 (2015).
- [4] C. Hättig, *J. Chem. Phys.* **118**, 7751 (2003).
- [5] A. Köhn, C. Hättig, *J. Chem. Phys.* **119**, 5021 (2003).

## The Oxidative Coupling of Methane: First-principles Micro-kinetic Modeling

Matthias Baldofski<sup>1</sup> and Joachim Sauer<sup>1</sup>

<sup>1</sup>*Institut für Chemie, Humboldt-Universität zu Berlin, Unter den Linden 6, 10099 Berlin, Germany*

Transformation of hydrocarbons, especially methane into more beneficial or value added products (VAP) is of great chemical interest. A possible route to C<sub>2</sub> products is the oxidative coupling of methane (OCM),



which is highly exothermic,  $\Delta_r H(800^\circ\text{C}) = -139 \text{ kJ mol}^{-1}$ ,  $\Delta_r G(800^\circ\text{C}) = -153 \text{ kJ mol}^{-1}$ . Despite many proposals, an efficient catalyst still needs to be found. The widely accepted mechanism by Wang and Lunsford [1] involves Li induced O<sup>•</sup> radicals as active sites. Hydrogen abstraction from CH<sub>4</sub> at this site is considered as a crucial step [2] for generation of CH<sub>3</sub> radicals. Recent experimental and computational studies have shown that this mechanism needs to be revised [3]. Interestingly, pristine MgO has been found to be also active at the same temperature [4]. Here, we present a new mechanism of OCM based on DFT calculations. Methane binds heterolytically on Mg<sup>2+</sup>O<sup>2-</sup> sites at steps and corners. Methyl radicals are released into the gas phase when O<sub>2</sub> is present on the surface. The role of the catalyst surface is to bind CH<sub>4</sub> and O<sub>2</sub> which exchange a redox equivalent directly among themselves, but not with the surface. A detailed micro-kinetic model for OCM has been developed based on the new reaction mechanism. This micro-kinetic model has been implemented in a one-dimensional plug flow reactor model, which includes explicitly the interaction between gas phase species and the catalyst surface. This allows direct comparison between our theoretical simulation and experiment [5]. We also make the connection to recent experimental findings of Freund [6] and Schlögl *et al.* [7].

### References

- [1] J. X. Wang, J. H. Lunsford, *J. Phys. Chem.*, **90**, 5883, 1986.
- [2] N. W. Cant *et al.*, *J. Chem. Soc. Chem. Commun.*, 766, 1988.
- [3] P. Myrach *et al.* *ChemCatChem.*, **2**, 854, 2010.
- [4] K. Kwapien *et al.* *Angew Chem Int Edit*, **53**, 1-6, 2014.
- [5] P. Schwach *et al.*, *J. Catal.*, 2015, **329**, 560-573.
- [6] Y. Cui *et al.*, *Angew. Chem. Int. Edition*, **52**, 11595, 2013.
- [7] P. Schwach *et al.*, *Angew. Chem. Int. Edition*, **52**, 4, 2013.



## Accurate calculation of alkali metal peroxides and superoxides dissociation

A. Zaichenko, D. Mollenhauer

*Institute of Physical Chemistry, Justus-Liebig University Giessen, Heinrich-Buff-Ring 17,  
D-35392 Giessen, Germany*

The understanding of the dissociation of alkali metal-oxygen compounds to the free metal and oxygen is crucial to improve metal-air batteries, which have particularly high energy density [1, 2]. Peroxides and superoxides act as products and intermediates in reduction and oxidation processes in lithium, sodium and potassium/oxygen batteries [3]. The most precise theoretical consideration of the reactions can be performed at level of small molecular model systems:  $\text{LiO}_2$ ,  $\text{NaO}_2$ ,  $\text{KO}_2$ ,  $\text{Li}_2\text{O}_2$  and  $\text{Na}_2\text{O}_2$ . The geometric and electronic structure of the model systems have been studied by the SA-CASSCF/CASPT2 approach. Dissociation energies and potential energy surfaces for different spin states provide a deep insight into dissociation mechanism and reaction products [4]. The chemical character of the electronic states is analyzed in a systematic way. Coupling between excited states in reagents and products is discussed. In Figure 1 the dissociation of  $\text{LiO}_2$  to the Li atom and  $\text{O}_2$  molecule is shown. Crossing between states explains formation of active oxygen forms.

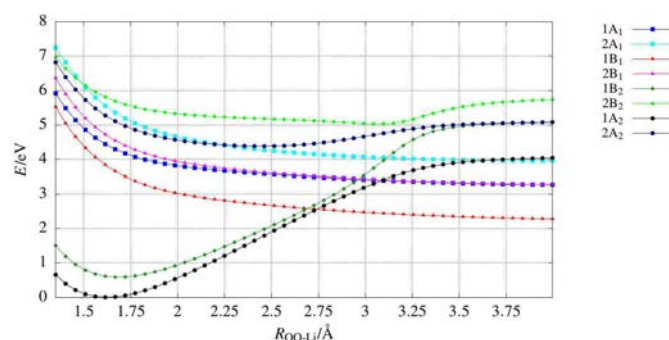


Figure 1: Potential energy curves for different electronic states of the molecular lithium superoxide dissociation calculated at CASSCF(13,12)/CASPT2 level of theory. The cc-pV5Z basis set has been applied.

Financial support is provided by the DFG via the GrK (Research training group) 2204 "Substitute Materials for sustainable Energy Technologies".

- [1] Xin Zhang, Xin-Gai, Zhaojun Xie, Zhen Zhou, *Green Energy & Env.* **1**, 4-17 (2016).
- [2] Philipp Adelhelm, Pascal Hartmann, Conrad L. Bender, Martin Busche, Christine Eufinger and Juergen Janek, *Beilstein J. Nanotechnol.* **6**, 1016–1055 (2015).
- [3] Maria del Pozo, Walter R. Torres, Santiago E. Herrera, and Ernesto Julio Calvo. *Chem-ElectroChem*, **3**(10), 1537–1540 (2016).
- [4] Aleksandr Zaichenko, Doreen Mollenhauer, *Manuscript to be submitted* (2017).

## Light-triggered CO Release in Novel Manganese Complexes – a Quantum Chemical Investigation

J. Steinmetzer<sup>1</sup>, S. Gläser<sup>2</sup>, S. Kupfer<sup>1</sup>, A. Schiller<sup>2</sup>, S. Gräfe<sup>1</sup>

<sup>1</sup>*Institute of Physical Chemistry, Abbe Center of Photonics, Friedrich-Schiller-University Jena, Helmholtzweg 4, 07743 Jena, Germany*

<sup>2</sup>*Institute of Inorganic and Analytical Chemistry, Friedrich-Schiller-University Jena, August-Bebel-Straße 2, 07743 Jena, Germany*

The recognition of CO as a key actor in the human physiology led to its emerging use as a therapeutic agent. Smart design of CO-releasing molecules (CORMs) offers control over the release trigger and specificity towards a desired target tissue. A promising approach are photoCORMs, where the release is initiated by irradiation. To facilitate the further design of CORMs it is of utmost importance to understand the relationship between its electronic structure and its release properties. The present work is concerned with the study of several novel manganese-photoCORMs based on a tridentate coligand synthesized by Schiller et al. and their resulting photoproducts.[1] Excited state properties such as electronic spectra were obtained with the TDDFT and SA-CASSCF/MS-CASPT2 approaches. The influence of counterions, solvent and the systems redox state on the CO-release were unraveled. The computational analysis revealed that the lowest excitations correspond to ligand field transitions between orbitals with mainly manganese  $t_{2g}$  character into orbitals with  $e_g$  character that are antibonding towards the CO-ligands. These transitions are verified as CO-releasing through relaxation in these states using the minimum energy path method. The arising vacant coordination site at the CORM can be filled through coordination of the former counterion or a solvent molecule. Both options lead to a destabilization of the occupied frontier orbitals and a strong redshift in the absorption spectrum of the photoproducts. Consequently, metal-to-ligand charge transfer transitions in coligand- $\pi^*$  orbitals can induce further CO-release.

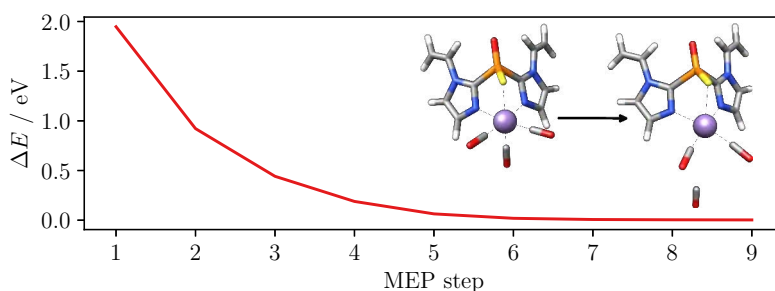


Figure 1: Minimum energy path (MEP) in the  $S_2$  of the photoCORM leading to photorelease of CO.

[1] A. Schiller et al., *Inorg. Chem.* **44**, 6482 (2005).

## Rational design of single molecule magnets

Matija Zlatar<sup>1</sup>, Maja Gruden<sup>2</sup>

<sup>1</sup>*Department of Chemistry, Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, Belgrade, Serbia*

<sup>2</sup>*Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, Belgrade, Serbia*

In recent years, there has been a growing interest in the single molecule magnets (SMM) that display a bistable (up/down) magnetic spin state below certain critical temperature because of their potential applications. Obtaining SMMs working at room temperature is reduced to understanding Zero-Field-Splitting (ZFS) parameters that determines the magnetic anisotropy of isolated transition metal complex. In this work, computational study of the magnetic anisotropy in series of transition metal complexes when changing the metal ion or the ligands in a controlled way will be presented. In order to achieve this goal, first, it was necessary to correctly determine the spin-ground state of transition metal ions, not straightforward task [1]. We performed detailed density functional based calculations probing the spin-state of these systems using variety of density functional approximations (DFAs). OPBE, SSB-D and S12g emerged to be one of the best DFAs for this task. In a second step, LF-DFT [2] is applied for the calculations of ZFS parameters. In addition to accurate prediction of magnitude, sign of the ZFS parameters, and orientation of the principal magnetic axes, we can pin-point the excitations that control magnetic anisotropy. In this way, we rationalize the connection between the structure, spin-ground state, excited states and magnetic properties of transition-metal complexes. The present approach will be illustrated by discussion of the magnetic anisotropy in trigonal-bipyramidal complexes of Ni(II) [3], scorpionate complexes [4], and octahedral complexes of Mn(IV) [5].

**Acknowledgments:** This work was supported by the Serbian Ministry of Science (Grant No. 172035) and COST Action CM1305 ECOSTBio (Explicit Control Over Spin-states in Technology and Biochemistry).

- [1] M. Swart, M. Gruden, *Acc. Chem. Res.*, **49**, 2690 (2016).
- [2] M. Atanasov, C.A. Daul, C. Rauzy, *Chem. Phys. Lett.* **367**, 737 (2003). 367, 737.
- [3] M. Gruden-Pavlović, M. Perić, M Zlatar, P. García-Fernández, *Chem. Sci.* **5**, 1453 (2014).
- [4] M. Perić, A. García-Fuente, M. Zlatar, C. Daul, S. Stepanović, P. García-Fernández, M. Gruden-Pavlović, *Chem. -Eur. J.* **21**, 3716 (2015).
- [5] M. Zlatar, M. Gruden, O. Y. Vassilyeva, E. A. Buvaylo, A. N. Ponomarev, S. A. Zvyagin, J. Wosnitza, J. Krzystek, P. García-Fernández, C. Duboc, *Inorg. Chem.* **55**, 1192 (2016).

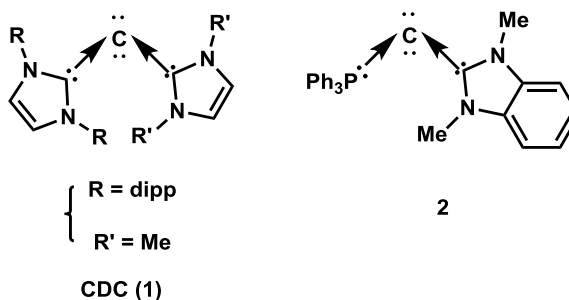
## Theoretical Study on Analog of Carbodicarbene: NBO and Mechanism of Addition Reaction

Yusuke Kuroda<sup>1</sup>, Chao-Ping Hsu<sup>2</sup>, Tiow-Gan Ong<sup>2</sup>, Masato Kobayashi<sup>3</sup>, and Tetsuya Taketsugu<sup>3</sup>

<sup>1</sup>Graduate School of Chemical Sciences and Engineering, Hokkaido University, N10-N8, Kita-ku, Sapporo, Japan, <sup>2</sup>Institute of Chemistry, Academia Sinica, Academia Rd., Nankang, Taipei, Taiwan, <sup>3</sup>Faculty of Science, Hokkaido University, N10-W8, Kita-ku, Sapporo, Japan.

y-kuroda@cse.hokudai.ac.jp

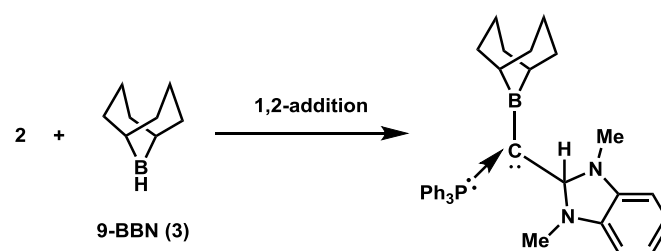
N-heterocyclic carbenes (NHCs) are known as a stable carbene compounds[1]. Carbodicarbenes (CDCs; compound **1**, Scheme1), in which two NHCs coordinate to the central divalent carbon (0), can be stably isolated. In addition, the coordination bonds are considered as a bent allene structure[2], so we are interested in the electronic states of these bonds. In this study, we investigated the mode of the coordination bonds for CDC and compound **2** by the NBO calculation, in which one NHC is replaced to triphenylphosphine.



Also, compound **1** and **2** react with 9-borabicyclo[3.3.1]nonane (9-BBN; compound **3**) to obtain 1,2-adducts.

Scheme 1 Carbodiarylene Compounds

On the other hands, compound **2** reacts with small boron compound (i.e. phenylborane), and the central divalent carbene (0) coordinate to the boron atom. We analyze this reaction mechanism and report it.



Scheme 2 1,2-addition reaction of compound **2** and **3**

[1] D. P. Curran, *et al.*, *Angew. Chem. Int. Ed.* **50**, 10294 (2011).

[2] R. Tonner and G. Frenking, *Angew. Chem. Int. Ed.* **46**, 8695 (2007).

[3] W.-C. Chen, *et al.*, *Angew. Chem. Int. Ed.* **54**, 15207 (2015).

## Towards understanding strong electron correlation in molecular complexes on surfaces

M. P. Bahlke<sup>1</sup>, P. Wahl<sup>2,3</sup>, L. Diekhöner<sup>4</sup>, C. Herrmann<sup>1</sup>

<sup>1</sup>*Institute for Inorganic and Applied Chemistry, University of Hamburg,  
Martin-Luther-King-Platz 6, 20146 Hamburg, Germany*

<sup>2</sup>*Max Planck Institute for Solid State Research, Heisenbergstrasse 1, 70569 Stuttgart, Germany*

<sup>3</sup>*SUPA, School of Physics and Astronomy, University of Saint Andrews, North Haugh, Saint Andrews, Fife KY16 9SS, Scotland, United Kingdom*

<sup>4</sup>*Department of Physics and Nanotechnology, Aalborg University, Skjernvej 4A, 9220 Aalborg, Denmark*

The interaction of conduction band electrons with localized unpaired electrons can cause the formation of a singlet state at sufficiently low temperature. This effect is known as the Kondo effect [1] and can be observed in many experimental setups such as break junctions [2] and in scanning tunneling microscopy (STM) experiments [3].

Our goal is to understand the Kondo effect from a chemical perspective, to allow for a systematic manipulation of molecules (e.g. via ligand substitution) that in turn controls the Kondo effect. As a first step in this direction, we investigated a series of cobaltcarbonyl complexes adsorbed on Cu(100), as reported by P. Wahl *et al.* [4], concerning the Kondo effect in the scope of a combination of density functional theory and the single impurity Anderson model (DFT++).

We found that hybridization of the Co 3d shell strongly depends on the number of CO ligands attached to cobalt, which is potentially the reason for the increasing Kondo temperature with an increased number of Co ligands.



Figure 1:  $\text{Co(CO)}_4$  and  $\text{Co(CO)}_2$  on Cu(100) as obtained by PBE.

- [1] L. Kouwenhoven, L. Glazman, *Physics World* **14**, 33 (2001).
- [2] J. J. Parks *et al.*, *Phys. Rev. Lett.* **99**, 026601 (2007).
- [3] J. Li, W.-D. Schneider, R. Berndt and B. Delley, *Phys. Rev. Lett.* **80**, 2893 (1998).
- [4] P. Wahl, L. Diekhöner, G. Wittich, L. Vitali, M. A. Schneider and K. Kern, *Phys. Rev. Lett.* **95**, 166601 (2005).

## Strong-Scaling Parallelization of Ab Initio Calculations on Massively Parallel Architectures

**Jörg Kussmann<sup>1,2</sup>, Christian Ochsenfeld<sup>1,2</sup>**

<sup>1</sup>*Chair of Theoretical Chemistry, Department of Chemistry, University of Munich (LMU),  
Butenandtstr. 7, D-81377 Munich, Germany*

<sup>2</sup>*Center for Integrated Protein Science (CIPSM) at the Department of Chemistry, University of  
Munich (LMU), Butenandtstr. 5–13, D-81377 Munich, Germany*

The development of linear-scaling ab initio methods in the last two decades has significantly extended their range of applicability, so that nowadays systems with more than 1000 atoms can be treated on a single compute-node [1]. Considering Moores law (doubling transistor count every 18-24 months), linear-scaling methods ensure that an increase in computing power directly translates into increasing treatable system sizes. In the last decade, however, the speed of a single CPU-core did not grow accordingly and Moores law is only upheld in form of an increasing number of computing-cores in, e.g., multi-core CPUs or graphics processing units (GPUs).

Recent developments by several groups have shown that the use of GPUs can strongly improve the performance of ab initio methods [2-5]. In this presentation we discuss parallelization strategies implemented in our program package FERMIOns++ [4, 5] with a particular focus on two-electron integrals. Our recently developed hybrid integral engine [6] allows for an efficient and strong-scaling parallelization on different platforms, supporting MPI-connected CPU/GPU compute-nodes (employing CUDA for NVIDIA and OpenCL for AMD-GPUs [7]). This not only allows the efficient application of ab initio methods to large molecular systems, but also opens a path to ab initio molecular dynamics (MD) simulations. First examples of Born-Oppenheimer and Ehrenfest molecular dynamics calculations are presented.

- [1] J. Kussmann, M. Beer, and C. Ochsenfeld, *WIREs Comput. Mol. Sci.* **3**, 614 (2013).
- [2] I. S. Ufimtsev and T. J. Martínez, *J. Chem. Theor. Comput.* **4**, 222 (2008).
- [3] I. S. Ufimtsev and T. J. Martínez, *J. Chem. Theor. Comput.* **5**, 1004 (2009).
- [4] J. Kussmann and C. Ochsenfeld, *J. Chem. Phys.* **138**, 134114 (2013).
- [5] J. Kussmann and C. Ochsenfeld, *J. Chem. Theory Comput.* **11**, 918 (2015).
- [6] J. Kussmann and C. Ochsenfeld, *J. Chem. Theory Comput.*, in press (2017).
- [7] J. Kussmann and C. Ochsenfeld,  
*J. Chem. Theory Comput.*, DOI: 10.1021/acs.jctc.7b00515 (2017).

# Full-Dimensional Excited-State Intramolecular Proton Transfer Dynamics of Salicylic Acid

Tim Raeker, Bernd Hartke

*Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel,  
Olshausenstraße 40, D-24098 Kiel, Germany*

Salicylic acid (SAC) and its excited-state intramolecular proton transfer (ESIPT) capabilities have been extensively studied both experimentally and theoretically by static calculations. However, to our knowledge, no radiationless pathway has been proposed so far, but instead excited-state deactivation was only investigated *via* fluorescence.

In this contribution, we will present full-dimensional photodynamics of SAC using the floating-occupation configuration-interaction (FOCI) treatment with single and paired double excitations based on the semiempirical RM1 Hamiltonian. To clarify mechanistic details, the potential energy surface (PES) is scanned along the proton transfer coordinates in one and two dimensions. The time-evolution of relevant degrees of freedom, quantum yields and isomer populations are evaluated from 200 surface-hopping trajectories.

It was found that a non-radiative deactivation pathway from the excited state to the ground state is indeed accessible through a conical intersection (CoIn), *via* rotation of the carboxyl group (Fig. 1). Together with the ESIPT process, this rotation also allows the interchange of the protons ( $H_1$  and  $H_8$ ) of the two (formal) OH groups, which makes the overall dynamics still more complex. A comprehensive overview of all these entangled steps will be given in this study.

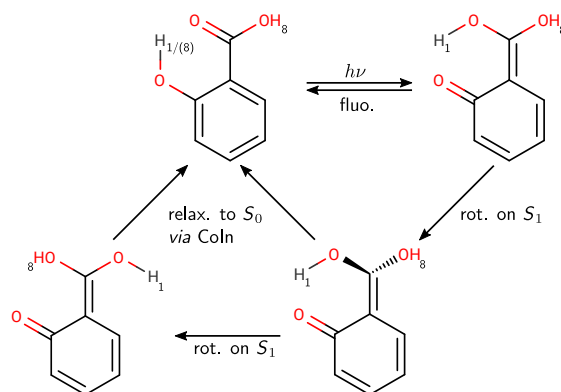


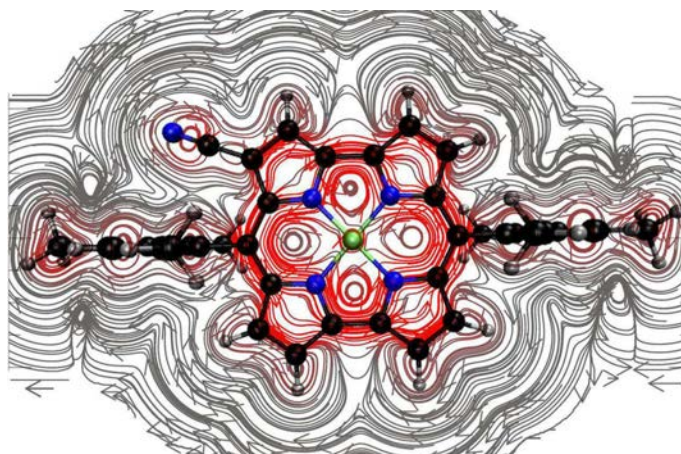
Figure 1: Reaction scheme of the excited-state dynamics of SAC.

## New insights on aromatic pathways in porphyrinoids by calculations of magnetically induced currents

Heike Fliegl<sup>1</sup>

<sup>1</sup>*Centre for Theoretical and Computational Chemistry (CTCC), Department of Chemistry, University of Oslo, P.O.Box 1033 Blindern, 0315 Oslo, Norway.*

When aiming at systematically synthesizing porphyrinoids with distinct properties knowledge about electron mobility pathways is essential. Experimentally, these pathways are not easily accessible, which makes complementary theoretical studies necessary. It is possible to determine reliable aromatic pathways in porphyrinoid macrocycles by studying magnetically induced current densities.[1] An overview of different ways to calculate and analyse the magnetically induced current density in such molecules is given. The computational approach used is the gauge including magnetically induced current density method (GIMIC), which is an independent, free available program.[2, 3] New features of the GIMIC program will be presented [4, 5] and very recent results obtained for various porphyrinoids such as Ni(II)cyanonorcorrole (see below) will be highlighted illustrating the potential and challenges of the method.



- [1] D. Sundholm, H. Fliegl and R. J. F. Berger, *WIREs*, **6**, 639 (2016).
- [2] J. Jusélius, D. Sundholm and J. Gauss, *J. Chem. Phys.*, **121**, 3952 (2004).
- [3] H. Fliegl, S. Taubert, O. Lehtonen and D. Sundholm, *Phys. Chem. Chem. Phys.*, **13**, 20500 (2011). [ <https://github.com/qmcurrents/gimic> ]
- [4] H. Fliegl, J. Jusélius and D. Sundholm, *J. Phys. Chem. A*, **120**, 5658 (2016).
- [5] C. Kumar, T. Kjærgaard, T. Helgaker and H. Fliegl, *J. Chem. Phys.*, **145**, 234108 (2016).

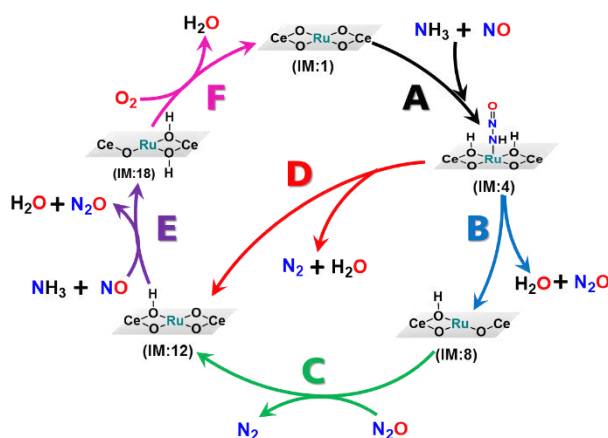


## Selective Catalytic Reduction of NO with NH<sub>3</sub> over Ru-doped CeO<sub>2</sub> investigated by DFT method

Chirawat Chitpakdee<sup>1</sup>, Anchalee Junkaew<sup>1</sup>, Supawadee Namuangruk<sup>1</sup>

<sup>1</sup>National Nanotechnology Center, National Science and Technology Development Agency,  
111 Thailand Science Park, Paholyothin Rd., Klongluang, Pathumthani 12120, Thailand

Reaction mechanism of the selective catalytic reduction of nitric oxide (NO) by ammonia (NH<sub>3</sub>-SCR) on the Ru doped CeO<sub>2</sub>(111) were investigated using density functional theory (DFT) calculation, corrected by on-site Coulomb interactions (DFT+*U*). The roles of Lewis and Brønsted acid sites on the reaction mechanism were examined. Our results suggest that the Lewis acid of Ru dopant on RuCeO<sub>2</sub>(111) enhances the NH<sub>3</sub> adsorption compared with the clean CeO<sub>2</sub>(111) surface. The catalytic cycle consists of two consecutive steps of NO reduction followed by the surface regeneration. The first NO reduction occurs at Ru Lewis acid site via NHNO intermediate to produce N<sub>2</sub>, H<sub>2</sub>O, and the Brønsted acid site. The NH<sub>3</sub> adsorption and dissociation are facile on RuCeO<sub>2</sub>(111) catalyst. The second NO reduction occurs over the Brønsted acid site, which is slightly more difficult than the first NO reduction in terms of NH<sub>3</sub> adsorption and dissociation. However, the calculations reveal that Brønsted acid site promotes the H<sub>2</sub>O formation. At the final step, the clean RuCeO<sub>2</sub>(111) surface is regenerated by healing the oxygen vacancy by O<sub>2</sub> with low activation energy. For the whole catalytic cycle, the Lewis active sites of RuCeO<sub>2</sub>(111) tend to be poisoned by water due to its high desorption energy. Based on the complete reaction mechanism achieved from this work, RuCeO<sub>2</sub> is predicted as one of the promising catalysts for the NO reduction by SCR-NH<sub>3</sub> at moderate temperature.



**Scheme 1.** The catalytic cycles of NH<sub>3</sub>-SCR of NO on RuCeO<sub>2</sub>

## Structure optimization of temporary anions with CAP-EOM-CC methods using analytic gradients

Zsuzsanna Benda<sup>1</sup>, Kerstin Rickmeyer<sup>1</sup>, Thomas-Christian Jagau<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of Munich (LMU), D-81377 Munich, Germany*

Temporary anions play an important role in various biological and chemical processes that involve electron-molecule collisions, as for example DNA damage by slow electrons or interstellar reactions [1]. They can be formed by electron attachment to neutral molecules with negative electron affinity, thus are not stable with respect to electron loss. These metastable states can be observed in electron impact experiments as resonances in the spectrum, with the spectral width corresponding to the inverse lifetime of the state. The theoretical investigation of these resonances is, however, difficult, as they are not discrete states in the usual Hermitian description. A solution to this problem is to employ a complex absorbing potential (CAP) that transforms the resonance into a discrete state with complex energy, which gives the position and the lifetime of the resonance. The CAP can be integrated in coupled cluster (CC) methods to have a high-level description of electron correlation effects, and the electron attachment variant of the equation-of-motion (EOM-EA) method can be used to ensure a balanced description of neutral and anionic states [2].

To explore decay routes and understand experimental findings, structural studies of resonances are essential. By deriving and implementing analytic gradients for CAP-EOM-CC methods, we could for the first time carry out geometry optimizations of temporary anions with a method that accounts for the finite lifetime of the state [3].

In this study, the general theory and implementation of analytic gradients for CAP methods is presented, and the CAP-EOM-EA-CCSD and CAP-EOM-EA-CCSD(2) methods are applied to geometry optimization of several temporary anions. The performance of the two methods and the basis set effects are investigated for small to medium sized molecules.

Finally, the methods are used to investigate the experimentally observed substantial difference in lifetimes of the A'' anionic resonances of acrylonitrile and methacrylonitrile [4], and the trends in the energies and lifetimes of the temporary anions of ethylene, butadiene and hexatriene [5].

- [1] T.-C. Jagau, K. B. Bravaya, A. I. Krylov, *Annu. Rev. Phys. Chem.* **68**, 525 (2017).
- [2] D. Zuev, T.-C. Jagau, K. B. Bravaya, E. Epifanovsky, Y. Shao, E. Sundstrom, M. Head-Gordon, A. I. Krylov, *J. Chem. Phys.* **141**, 024102 (2014).
- [3] Z. Benda, T.-C. Jagau *J. Chem. Phys.* **146**, 031101 (2017).
- [4] K. Regeta, M. Allan, *J. Chem. Phys.* **142**, 184307 (2015).
- [5] K. Jordan, P. Burrow, *Chem. Rev.* **87**, 557 (1987).

## Environmental effects on the UV-Vis spectra of chlorophyll in the LHCII protein complex

Souloke Sen<sup>1</sup>, Pablo López-Tarifa<sup>1</sup>, Nicolleta Ligouri<sup>2</sup>, Roberta Croce<sup>2</sup>, Lucas Visscher<sup>1</sup>

<sup>1</sup>*Amsterdam Center for Multiscale Modeling, Dep. Theoretical Chemistry, Faculty of Sciences, VU University, De Boelelaan 1083, 1081HV Amsterdam, The Netherlands*

<sup>2</sup>*Laboratory of Biophysics of Photosynthesis, Dep. Physics and Astronomy, Faculty of Sciences, VU University Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands*

The major light-harvesting complex of photosystem II (LHCII) serves as the principal solar energy collector in the photosynthesis of green plants. It captures and converts light into chemical energy, which is further used to oxidise water in the light reactions of photosynthesis. Classical dynamics simulations have recently shown that the solubilized form of LHCII [1] differs from its crystal structure [2], showing signatures of a light-harvesting state that matches with experimental observations. During the microsecond dynamics, also a shortening of inter-chromophores distances was observed, highlighting some potential quenching sites.

In this work, using Density Functional Theory (DFT) and its time-dependent extension, TDDFT (as implemented in the ADF software package [3]), we study the effect of the protein chain on the UV vis spectrum of one of the putative quenching sites that involves the chlorophyll alpha 612 (CHLA612). Taking the LHCII crystal structure as test case, we select all the protein residues within a 7 Å sphere around the Mg atom of the porphyrin ring. By gradually releasing the constraints in the geometry optimization of the structure, we find that the Q<sub>x</sub> absorption band of the CHLA612 is heavily affected by the interaction with electronegative surrounding atoms, especially with a S atom of a nearby methionine residue, with which the Mg atom forms an antibonding interaction between the p orbitals on S and  $\pi$  orbital of the porphyrin. These insights will be used in the near future to systematically study a classical trajectory of the solubilized form of LHCII, where natural thermal oscillations of both protein environment and CHLA are taken into account.

### References :

- [1] Liguori, N. et al. *Sci. Rep.* **5**, 15661; doi: 10.1038/srep15661 (2015).
- [2] Liu, Z. et al. *Nature* **428**, 287–92 (2004).
- [3] ADF, ([www.scm.com](http://www.scm.com))

## Theoretical analyses of solid electrolyte interphase film formation in secondary batteries via Red Moon method

Norio Takenaka<sup>1,2</sup>, Takuya Fujie<sup>2</sup>, Bouibes Amine<sup>2,3</sup>, Masataka Nagaoka<sup>1,2,3</sup>

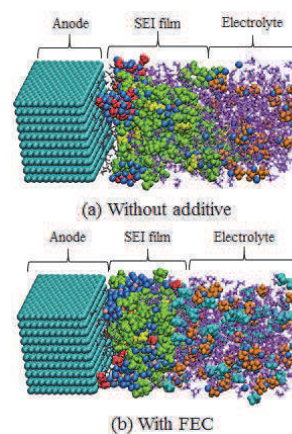
<sup>1</sup>ESICB, Kyoto University, Kyodai Katsura, Nishikyo-ku, Kyoto 615-8520, Japan

<sup>2</sup> Graduate School of Informatics, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan

<sup>3</sup>Core Research for Evolutional Science and Technology, Japan Science and Technology Agency, Honmachi, Kawaguchi 332-0012, Japan

The rechargeable secondary batteries such as lithium-ion battery (LIB) are expected to be utilized as not only ubiquitous electric power sources such as mobile phones but also large-scale electricity storage devices. Their lifetime and stability are found to be strongly dependent on the nature of passivation film called solid electrolyte interphase (SEI) film formed on the anode surface. However, since it is difficult to directly observe the film formation processes in experiment, its microscopic mechanism is still not found. Under the circumstances, we have proposed a new atomistic reaction simulation method, which is a Red Moon method (or hybrid Monte Carlo (MC)/molecular dynamics (MD) reaction method) [1], and applied it to the investigation of SEI film formation in secondary batteries [2-4].

In this study, by using a Red Moon method, we were able to simulate for the first time the SEI film formation processes on the anode surface at the atomistic level [2]. Then, we clarified the microscopic mechanism of the additive effect on the SEI film formation [3], where the addition of the fluoroethylene carbonate (FEC) leads to the smaller irreversible capacity and smoother SEI film (see Fig. 1). Further, we also investigated the salt concentration effect [4]. These research findings are expected to provide a guiding principle for developing high-performance secondary batteries.



**Figure 1.** Typical snapshots of SEI films without and with FEC.

[1] M. Nagaoka, Y. Suzuki, T. Okamoto, N. Takenaka, *Chem. Phys. Lett.*, **583**, 80 (2013)

[2] N. Takenaka, Y. Suzuki, H. Sakai, M. Nagaoka, *J. Phys. Chem. C*, **118**, 10874 (2014)

[3] N. Takenaka, H. Sakai, Y. Suzuki, P. Uppala, M. Nagaoka, *J. Phys. Chem. C*, **119**, 18046 (2015)

[4] N. Takenaka, T. Fujie, B. Amine, M. Nagaoka, to be submitted.

## Bridging Time Scales with Variationally Enhanced Sampling

Omar Valsson<sup>1</sup>

<sup>1</sup>*Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128, Mainz, Germany*

The usefulness of atomistic simulations is generally hampered by the presence of several metastable states separated by high free energy barriers leading to kinetic bottlenecks. Transitions between metastable states are thus rare events that occur on much longer time scales than one can simulate in practice. Numerous enhanced sampling methods have been suggested to alleviate this time scale problem, including methods based on identifying a few crucial order parameters or collective variables and enhancing their fluctuations through the introduction of an external biasing potential [1].

Here we will discuss Variationally Enhanced Sampling [2], a generally applicable enhanced sampling method which is based on a rigorous variational principle [2]. In this approach an external bias potential that acts in the space spanned by the collective variables is constructed by minimizing a convex functional. The underlying free energy landscape as a function of the selected collective variables can be obtained directly from the bias that minimizes this functional. We present numerous examples which show the flexibility, practicality, and usefulness of the method. We will furthermore discuss how the variational property of the method can be used to extend the method in novel and innovative ways, including for example: to obtain kinetics of rare events from atomistic simulations [3]; to accelerate nucleation events by employing a physical model from classical nucleation theory [4]; and to parameterize coarse-grained phenomenological models from microscopic simulations [5].

We will also introduce the VES code (<http://www.ves-code.org>), an open-source library for the PLUMED 2 plugin (<http://www.plumed.org>) that implements methods based on Variationally Enhanced Sampling. The VES code can be used with a wide range of molecular dynamics codes. The code is furthermore designed in modular way to allow for a quick implementation of new features within Variationally Enhanced Sampling.

- [1] O. Valsson, P. Tiwary, and M. Parrinello, *Annu. Rev. Phys. Chem.* **67**, 159 (2016).
- [2] O. Valsson and M. Parrinello, *Phys. Rev. Lett.* **113**, 090601 (2014).
- [3] J. McCarty, O. Valsson, P. Tiwary, and M. Parrinello, *Phys. Rev. Lett.* **115**, 070601 (2015).
- [4] P. Piaggi, O. Valsson, and M. Parrinello, *Faraday Discuss.* **195**, 557 (2016).
- [5] M. Invernizzi, O. Valsson, and M. Parrinello, *Proc. Natl. Acad. Sci. USA* **114**, 3370 (2017).

## Performance of Range-Separated Hybrid Functional with Krieger-Li-Iafrate Potential for Molecular Excitation Energies

**Sungwoo Kang<sup>1</sup>, Jaewook Kim<sup>1</sup>, Sunghwan Choi<sup>1</sup>, Jaechang Lim<sup>1</sup>, Sang-Yeon Hwang<sup>1</sup>, Seongok Ryu<sup>1</sup> and Woo Youn Kim<sup>1\*</sup>**

<sup>1</sup>*Department of Chemistry, Korean Advanced Institute of Science and Technology, 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea*

Density functional theory is widely used for electronic structure calculations in chemical systems, especially with the Hartree-Fock (HF) hybrid exchange-correlation functionals. We reported the accuracy of optical spectra using hybrid functionals with local exact exchange potential under the Krieger-Li-Iafrate(KLI) approximation instead of the non-local Hartree-Fock exchange on the grid basis, and showed that the KLI hybrid outperforms the HF hybrid even with a simple local density approximation kernel.[1]

In this research, we implemented a range-separated LC- $\omega$ PBE(2Gau) developed by Hirao et. al.[2] with its long-range exchange operator replaced from HF to KLI [LC- $\omega$ PBE(2Gau, KLI)]. The computational cost of calculations using global KLI hybrid and LC- $\omega$ PBE(2Gau, KLI) was compared. We applied the LC- $\omega$ PBE(2Gau, KLI) functional to computing various excitation energies incorporating charge-transfer excitation characters, including metal-to-ligand or ligand-to-metal charge transfers. Optical spectra calculations are performed using various methods, including the time-dependent HF method with exact-exchange orbitals developed by Görling et al.[3] and time-dependent density functional theory with various exchange-correlation kernels.

[1] J. Kim, K. Hong, S.-Y. Hwang, S. Ryu, S. Choi and W. Y. Kim, *Phys. Chem. Chem. Phys.* **19**, 10177-10186 (2017).

[2] J.-W. Song and K. Hirao, *J. Chem. Phys.* **143**, 144112 (2015).

[3] A. Heßelmann and A. Görling, *J. Chem. Phys.* **134**, 034120 (2011).

## Computational NMR Spectroscopy for Host-Guest Hemicarcerands

**Abril C. Castro<sup>1</sup>, Adrià Romero<sup>1</sup>, Sílvia Osuna<sup>1</sup>, Kendall N. Houk<sup>2</sup>, Marcel Swart<sup>1,3</sup>**

<sup>1</sup>*Institut de Química Computacional i Catàlisi (IQCC), Departament de Química, Universitat de Girona, Campus de Montilivi, 17071 Girona, Spain.*

<sup>2</sup>*Dept. Chemistry and Biochemistry, Univ. California Los Angeles (UCLA), 607 Charles E. Young Drive East, Los Angeles, CA 90095-1569, USA.*

<sup>3</sup>*ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Spain.*

One of the most exciting and challenging research fields in chemistry emerged in 1985 with Cram's synthesis of a molecule capable of trapping other molecules in its interior. Since then, the chemistry of molecular container compounds has become a challenging and rewarding field of organic chemistry.[1] In this project, the incarceration of *o*-benzyne and other 27 guest molecules within hemicarcerand **1** (see Figure 1a), studied experimentally by Warmuth,[2] and Robbins and co-workers,[3] respectively, has been studied via density functional theory (DFT). The possible incarceration of *o*-benzyne within a second hemicarcerand **2** (see Figure 1b) as synthesized by Cram and co-workers has also been additionally explored. Full structure optimization and determination of the <sup>1</sup>H-NMR chemical shift was performed. In addition, the rotational mobility and the conformational preference of the guest molecules inside the hemicarcerand structures were explored, providing intriguing correlations of the chemical shifts with structural parameters of the host-guest system. Our proton NMR chemical shifts at the KT2/ET-pVQZ level indicate a direct correlation between theoretical calculations and experimental measurements, and provide a new strategy to characterize these challenging host-guest complexes.

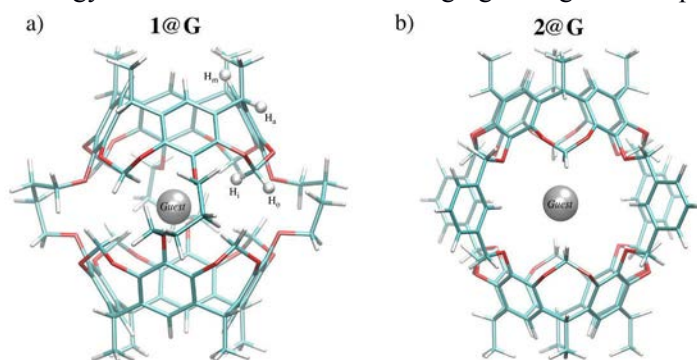


Figure 1. Hemicarcerands **1** and **2** with a guest **G** in its interior.

- [1] K. N. Houk, K. Nakamura, C. Sheu, A. E. Keating, *Science*, **273**, 627 (1996).
- [2] R. Warmuth, *Angew. Chem. Int. Ed.*, **36**, 1347 (1997).
- [3] T. A. Robbins, et al., *J. Am. Chem. Soc.*, **116**, 111 (1994).

**When 2 is better than 1: variational Geminal theory**

**Stijn De Baerdemacker<sup>1</sup>, Pieter Claeys<sup>1,2</sup>, Jean-Sébastien Caux<sup>2</sup>, Dimitri Van Neck<sup>1</sup>, Paul Ayers<sup>3</sup>**

<sup>1</sup>*Center for Molecular Modeling, Ghent University, Belgium*

<sup>2</sup>*Institute for Theoretical Physics, University of Amsterdam, The Netherlands*

<sup>3</sup>*Department of Chemistry and Chemical Biology, McMaster University, Canada*

The resonances and interplay between bonding/antibonding orbitals are the main culprit for the strong static quantum correlations in molecular systems [1]. This resonance provides the basis building block for Geminal theory, which starts from the assumption that the electronic degrees of freedom are organised as a mean-field of (Lewis) pairs, rather than single electrons [2]. Due to the symmetric nature of electron pairs, opposed to the antisymmetric character of single electrons, Geminal theory has proven to be computationally intractable, until very recently [3]. In this presentation, I will present a computationally tractable version of Geminal theory [4], based on the premises of Richardson-Gaudin integrability [5], a method known from mathematical physics.

- [1] T. Helgaker, P. Jorgenson and J. Olsen, *Molecular Electronic Structure*, Wiley (2000)
- [2] P. R. Surjan, *An introduction to the theory of geminals*, Springer (1999)
- [3] P. A. Limacher, P. W. Ayers, P. A. Johnson, S. De Baerdemacker, D. Van Neck, and P. Bultinck, *J. Chem. Theor. Comp.* **9** 1394 (2013)
- [4] P. W. Claeys, S. De Baerdemacker, D. Van Neck and J-S. Caux *in preparation*
- [5] J. Dukelsky, S. Pittel, and G. Sierra *Rev. Mod. Phys.* **76**, 643 (2004)



## Computational Insights into Dispersion Interactions in Self-Assembled Supramolecular Host-Guest Systems

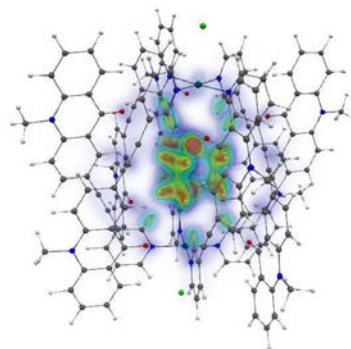
A. Wuttke<sup>1</sup>, R. A. Mata<sup>1</sup>

<sup>1</sup>*Institute of Physical Chemistry, Georg-August-University Göttingen, Tammannstr. 6, Göttingen, Germany*

A halide-triggered metallocupramolecular host was systematically studied for the uptake of small neutral molecules. Binding of chloride anions in the outer two pockets of the interpenetrated double-cage activates guest uptake in its central pocket [1]. This compound and the process of binding is related to a previously published double cage system, but one which was limited to anion binding. The newly synthesised compound quite remarkably is able to bind uncharged and apolar guests.

A computational study was carried out on these host-guest systems, with a particular focus on the interactions taking place in the inner pocket. Dispersion Interaction Density (DID) plots [2] show how the whole compound structure contributes to the stabilisation of the apolar guests (FIG 1).

In order to build a bridge between theory and experiment, binding affinities were calculated through a composite approach. The latter consists of systematic guest conformational screening, DFT optimisations and truncated Hessian calculations for thermodynamical corrections. The electronic energies are corrected with SCS-LMP2 calculations using D-COSMO-RS [3]. Our calculated affinities are generally found to be within 3 kcal/mol compared of the experimentally measured values (NMR, double mutant cycle and isothermal calorimetry).



**FIG. 1** DID plot of DABCO in the supramolecular host

- [1] S. Löffler, A. Wuttke, R. A. Mata, G. H. Clever, *to be published*.
- [1] A. Wuttke, R. A. Mata, *JCC* **38.1**, 15-23 (2017).
- [1] S. Sinnecker, A. Rajendran, A. Klamt, M. Diedenhofen, F. Neese, *J. Phys. Chem. A* **110(6)**, 2235 (2006).

## Macrocycle Conformational Sampling by DFT-D3/COSMO-RS Methodology

**Ondrej Gutten<sup>1</sup>, Daniel Bím<sup>1</sup>, Jan Řezáč<sup>1</sup>, Lubomír Rulíšek<sup>1</sup>**

<sup>1</sup>*The Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences,  
Gilead Sciences Research Center & IOCB, Prague, Czech Republic*

The poster presents the endeavour of optimizing and evaluating several computational protocols for exploration of conformational space of small molecules using combination of force-field/semi-empirical and DFT-D3/COSMO-RS [1] methods. The selection of systems focuses on macrocyclic compounds as a promising class of molecules for drug development, as well as challenging systems for empirical description of energy-structure relationship.

The optimal protocol consists of an exploratory part, based on MD/LLMOD [2] search, and a refining part, based on accurate free energy calculations obtained from DFT, COSMO-RS and gas-phase frequency analysis. The workflow enables minimizing the computational cost by providing multiple checkpoints for discarding high-energy conformers.

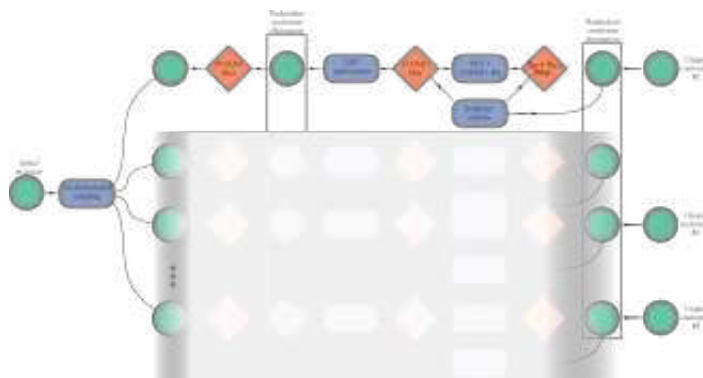


Fig.1 Roadmap of conformational sampling protocol.

The study examines 8 systems of varying size and provides a wealth of QM data about more than 8,000 different conformers and structural data for more than 30,000 conformers, available for further analysis. Understanding the relations between individual components of energy and structure is essential for estimation of error associated with the protocol and, hence, proper interpretation of sampling procedures.

[1] A. Klamt, *J. Phys. Chem.* **99**, 2224 (1995)

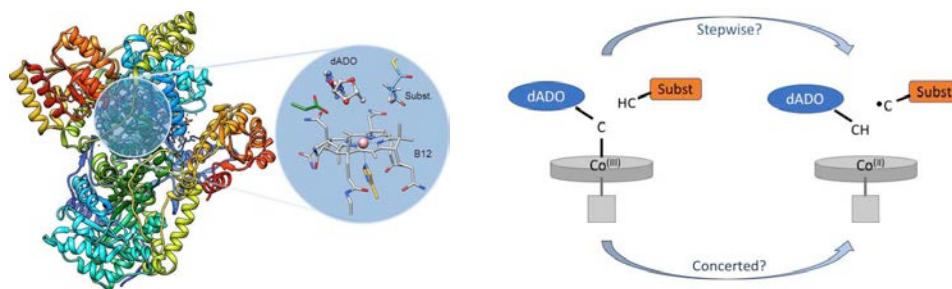
[2] I. Kolossvary; G. M. Keseru, *J. Comput. Chem.* **22**, 21 (2001)

## Modelling the reactions catalysed by coenzyme B<sub>12</sub> dependent enzymes: Accuracy and cost-quality balance

Christian R. Wick<sup>1</sup> and David M. Smith<sup>1</sup>

<sup>1</sup> Division of Physical Chemistry, Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia

Coenzyme B<sub>12</sub> (5'-deoxyadenosylcob(III)alamin, dAdoCbl) is one of the most prominent organometallic cofactors due to the presence of a carbon-cobalt (Co-C) bond, which is the key to enzymatic reactions utilizing coenzyme B<sub>12</sub> as a cofactor: The homolytic cleavage of the Co-C bond, which leads to the formation of a 5'-dAdo radical, is highly encouraged in the enzymatic environment compared to the nonenzymatic reaction. In a (subsequent or concerted) second step, the 5'-dAdo radical is involved in an H-atom transfer reaction, generating a substrate radical and 5'-dAdo. However, the accurate theoretical description of both elementary reactions is challenging. More recently, the Co-C cleavage was investigated with dispersion-corrected DFT and LPNO-CCSD calculations utilising the full coenzyme.[1] This and another study[2] have elucidated the importance of the model system design and, especially, the inclusion of dispersion and solvent corrections. Concomitantly, the accurate description of the H-atom transfer reaction is known to be very sensitive to the level of theory applied.[3–5] Our goal is to find a model chemistry that ensures an accurate description of both reactions, Co-C cleavage and H-atom transfer. We discuss the differences between typical model systems, the effects of dispersion and solution corrections and finally present a suitable ONIOM(QM/MM) setup that simultaneously reduces the computational costs and retains the accuracy of non-approximate calculations on the full coenzyme system. All these efforts help us to tackle the decades-long controversy about the actual mechanism among the different classes of coenzyme B<sub>12</sub> dependent enzymes.



- [1] Z. Qu, A. Hansen, S. Grimme, *J. Chem. Theory Comput.* **11**, 1037, (2015).
- [2] K. P. Kepp, *J. Phys. Chem. A* **118**, 7104, (2014).
- [3] D. J. Henry, C. J. Parkinson, P. M. Mayer, L. Radom, *J. Phys. Chem. A* **105**, 6750, (2001).
- [4] M. L. Coote, *J. Phys. Chem. A* **108**, 3865, (2004).
- [5] B. Durbeej, G. M. Sandala, D. Bucher, D. M. Smith, L. Radom, *Chemistry* **15**, 8578, (2009).

## Why do Novel Mo-Alkylidene Catalysts Facilitate Olefin Metathesis in the Presence of Functional Groups?

**Maren Podewitz,<sup>1</sup> Leonard C. Pasqualini,<sup>1</sup> Michael R. Buchmeiser,<sup>2</sup>  
Klaus R. Liedl<sup>1</sup>**

<sup>1</sup> *Institute of General, Inorganic and Theoretical Chemistry/Theoretical Chemistry and Center for Molecular Biosciences (CMBI), University of Innsbruck, Austria*

<sup>2</sup> *Institute of Polymer Chemistry, University of Stuttgart, Germany*

Synthesis of highly functionalized polymers is an ultimate goal in chemistry because it allows for design of materials with tailored properties. Molybdenum catalysts (e.g. of the Schrock type) have successfully been used for polymerization of olefins but these catalysts are very sensitive to functional groups at the monomers. However recently, an N-heterocyclic carbene Mo-alkylidene catalyst has been reported that does tolerate functional groups and polymerizes olefins with hydroxyl, carboxyl, or carbonyl functionalities. [1]

DFT is employed to investigate the reaction mechanism of this catalyst and to explore the origin of its functional group tolerance at the example of the bicyclo[2.2.1]hept-5-en-2-carbaldehyd monomer. Energetics of the polymerization reaction as well as of the deactivation reaction are presented and regional selectivity of the polymer formation is explained. Compared to Schrock type catalysts, this novel Mo-alkylidene catalysts shows significantly reduced reactivity towards carbonyl coordination.

[1] M. R. Buchmeiser, S. Sen, J. Unold, W. Fey, *Angew. Chem Int. Ed.* **53**, 9384 (2014).

## Database of Benchmark Interaction Energies Mapping Repulsive Contacts in Organic Molecules

V. M. Miriyala<sup>1</sup>, J. Řezáč<sup>1,2</sup>

<sup>1</sup>*Department of Computational Chemistry, Institute of Organic Chemistry and Biochemistry,  
Academy of Sciences of the Czech Republic, Flemingovo Náměstí  
542/2, 16610 Prague, Czech Republic*

<sup>2</sup>*Email: rezac@uochb.cas.cz*

Recent years have witnessed the evolution of new and promising approximate QM methods that depend on parameterization to benchmark results obtained with highly accurate calculations. Among the most important areas is the study of non-covalent interactions, which plays a vital role in understanding lot of chemical, biological, biochemical and physical properties. Although highly efficient SQM methods such as SCC-DFTB and PM6 with corrections for dispersion and hydrogen bonding[1, 2] are known to out perform many of the currently available semi empirical methods, they underestimate the repulsion, which leads to substantial overbinding at short distances. To correct this issue, it is necessary to develop new set of benchmark data that would systematically cover the repulsive region of the intermolecular potential, and use it in the reparameterization of the methods or corrections for them. The benchmark must be constructed using higher order wavefunction methods, for these interactions are often influenced by strong correlation effects. In this work we present the data for 161 molecular complexes for which we systematically constructed their dissociation curves up to the repulsive region (6 points per system). Totally the dataset contains 966 points mapping all combinations of the organic elements (H, C, N, O) in different chemical context. We present the detailed methodology of constructing the complexes and the benchmark CCSD(T)/CBS results along with the results of testing multiple DFT and SQM methods.

[1] J. Řezáč, P. Hobza, *J. Chem. Theory Comput.* **8**, (2012).

[2] V. M. Miriyala, J. Řezáč, *J. Comput. Chem.* **38**, 688 (2017).

## Extended single-reference vibrational coupled cluster for the description of molecular double-well systems

Mads Bøttger Hansen<sup>1</sup>, Ove Christiansen<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark*

In vibrational coupled cluster (VCC) theory the vibrational state has an exponential parametrization based on a single-configuration reference state, oftenmost obtained from a mean-field vibrational self-consistent field (VSCF) calculation;

$$|\text{VCC}\rangle = \exp(\hat{T})|\text{VSCF}\rangle$$

Here  $\hat{T}$  is the cluster operator, the effect of which is to generate a superposition of configurations for which some of the modes have been excited w.r.t. the reference state. By truncating  $\hat{T}$  at a certain level  $n$ , i.e. by only allowing up-to- $n$ -mode excitations, a hierarchy of VCC[ $n$ ] methods are achieved that converge towards the full vibrational configuration interaction (FVCI) solution which is exact within the chosen one-mode basis but is much too costly to compute for anything but the smallest molecules.

Due to the ansatz VCC works very well when the reference state is dominant in the FVCI solution, and fortunately this is oftenmost the case for the ground states of molecules vibrating around a well-defined electronic energy minimum. Excited state energies can subsequently be accurately obtained from response theory. Molecules possessing double-wells, on the other hand, can have several dominant configurations due to the near-degeneracy of the bound double-well states – our goal is then to adapt VCC to describe vibrational correlation efficiently also in these cases.

Instead of making a full-blown multi-reference VCC formulation, the theory of which would be both hard to develop, implement and apply, we have introduced an extended single-reference model where *certain* higher-than- $n$ -mode excitations are allowed in  $\hat{T}$  by allowing the double-well modes not to count towards the  $n$ -mode limit. By doing so all one-mode states for the double-well mode(s) have the same excitation space and are thus described equivalently in practice even though a certain reference is singled out in the ansatz.

We will look at how this model performs when calculating ground and excited state energies for small and medium-sized molecules containing amino and hydrogen transfer groups.

## Open-shell character from experimental and calculated bond lengths

B. Alexander Voigt<sup>1</sup>, C. Herrmann<sup>1</sup>

<sup>1</sup>*Institute for Inorganic and Applied Chemistry, University of Hamburg,  
Martin-Luther-King-Platz 6, 20146, Hamburg, Germany*

Determining the open-shell character of singlet molecules is a challenging task. Experimentally, diamagnetic behavior is measured making the distinction between open-shell singlets and closed-shell singlets difficult. Yet, there is a connection between open-shell singlet character and measurable nonlinear optical properties.[1] Molecules with a singlet ground state and small singlet-triplet gaps (i.e. thermally accessible triplet states) are usually attributed with a larger open-shell character than those with larger singlet-triplet gaps.[2] Theoretically, the open-shell character may be quantified by the diradical character, which can be defined in several ways.[3]

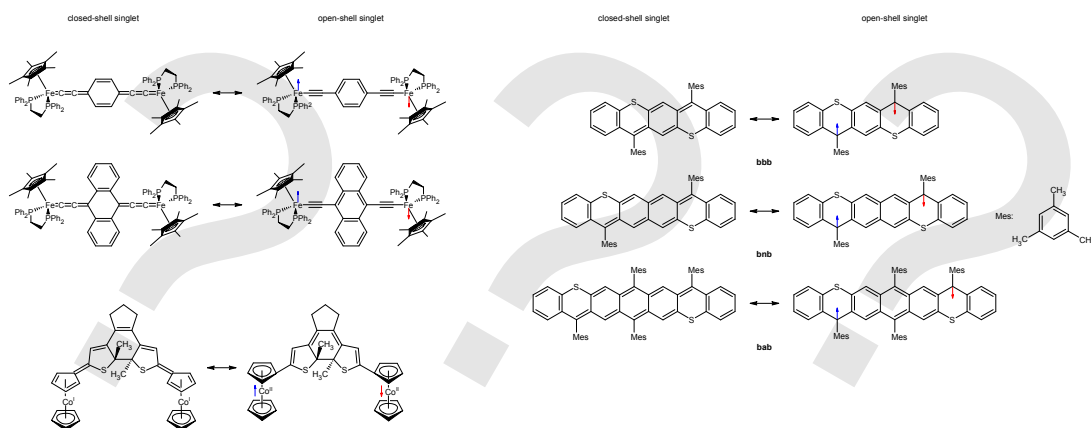


Figure 1: Structural formulas of dinuclear iron [4] and [5] and cobalt complexes (left) and organic bisbenzothiaquinodimethanes [2] (right)

We investigated experimental and calculated (BP86/def2-TZVP, B3LYP/def2-TZVP) structures (see Figure) looking for correlations between open-shell character and bond-length patterns.

- [1] K. Kamada *et al*, *J. Phys. Chem. Lett.* **1**, 937-940 (2010).
- [2] S. Dong *et al*, *Angew. Chem.* **128**, 9462-9466 (2016).
- [3] E. Ramos-Cordoba *et al*, *Phys. Chem. Chem. Phys.* **16**, 9565 (2014).
- [4] F. Paul *et al*, *Inorg. Chem.* **48**, 10608-10624 (2009).
- [5] F. de Montigny *et al*, *Organometallics* **24**, 4558-4572 (2005).

## Chemical bonding and adsorption dynamics of cyclooctynes in the creation of organic/inorganic interfaces

Lisa Pecher, Fabian Pieck, Ralf Tonner

*Fachbereich Chemie and Material Sciences Center, Philipps-Universität Marburg,  
Hans-Meerwein-Straße 4, 35032 Marburg, Germany*

The creation of hybrid organic/inorganic interfaces is important for the development of new materials and devices, because it can lead to an enhanced application range. Cyclooctyne is a potential candidate for building such interfaces on silicon, as it forms dense and ordered structures upon adsorption on Si(001).[1] Understanding the structural selectivity in this system might allow to design molecules that lead to any desired interface structure. Selectivity is often governed by intermediates in the adsorption process, however, experiments on the adsorption of cyclooctyne on Si(001) showed it to proceed directly into the final state.[2] Our density functional theory calculations imply that there might be two competing adsorption pathways: Direct and, alternatively, via an ultra-short-lived intermediate not detectable under usual lab conditions. By combining bonding analysis methods (Periodic Energy Decomposition Analysis[3]) and *ab-initio* molecular dynamics (AIMD), we investigated the relevance and properties of this intermediate. The results show (i) why it can emerge in the adsorption process, (ii) how it would determine structural selectivity and (iii) why it would not be observable in experiment. This highlights the importance of computational chemistry for the field of material science.

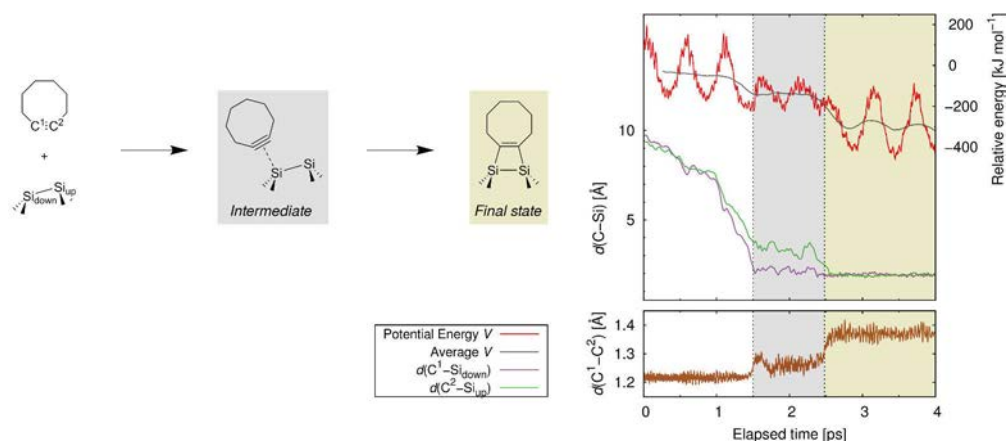


Figure 1: Left: Schematic representation of the adsorption process of cyclooctyne on Si(001). Right: Selected data from an AIMD simulation which allows distinguishing between the separated system (white), intermediate (grey) and final state (yellow).

- [1] G. Mette *et al.*, *Chem. Phys. Lett.* **556**, 70 (2013).
- [2] M. Reutzel *et al.*, *J. Phys. Chem. C* **120**, 26284 (2016).
- [3] M. Raupach, R. Tonner, *J. Chem. Phys.* **142**, 194105 (2015).

This work was funded by Deutsche Forschungsgemeinschaft (DFG) within SFB 1083.



## Exciton dynamics in Light Harvesting Complexes: From ab initio TDDFT calculation towards Open System models

Joaquim Jornet-Somoza<sup>1</sup>, Robert Biele<sup>1</sup>, Angel Rubio<sup>2,1</sup>

<sup>1</sup>Nano-Bio Spectroscopy Group and ETSF Scientific Development Center, Departamento de Física de Materiales, Centro de Física de Materiales CSIC-UPV/EHU and DIPC, University of the Basque Country UPV/EHU, Avenida Tolosa 72, 20018 Donostia San Sebastián, Spain

<sup>2</sup>Max Planck Institute for the Structure and Dynamics of Matter, Luruper Chaussee 149, 22761 Hamburg, Germany

The current increase in energy demands across the world makes fossil-fuel based energy resources unsustainable. Solar energy conversion is one alternative to produce green renewable energy. However, the efficiency of modern organic photovoltaic cells is still low (<10%) compared to biological systems (~100%).

Although many theoretical and experimental investigation has been done to study the mechanisms involved in the natural Light Harvesting Complexes (LHCII), many questions are still open: i) specific role of the individual chromophores ii) importance of the environment modifying the exciton pathways iii) relevance of coherence in the exciton energy transfer.

In this work we present how excitonic properties for complex systems can be obtained from real-time propagation TDDFT and how this properties fit into the exciton models used to simulate the energy transfer when the system is coupled to the environment (e.g. Förster approximation to Hierarchical Equation of Motion)

Based on our local density decomposition analysis [1], we study exciton dynamics on LHCII to understand time-scales and possible energy pathways towards the reaction center.

Our results are in good agreement with the recently obtained molecular structure of the Photosystem II [2], and reveal the crucial relevance of the protein environment to modulate the exciton pathway toward an efficient energy transport.

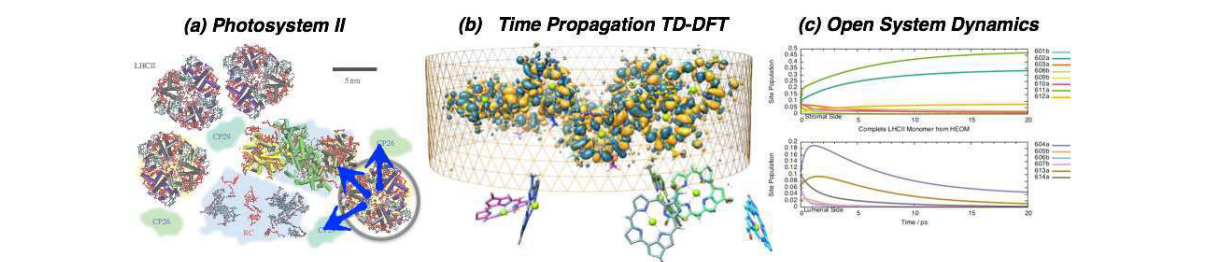


Figure 1: (a) Molecular structure of the Photosystem II in higher plants. (b) Real-time TDDFT simulation of a laser induced exciton transport during  $\sim 100$ fs, (c) Exciton dynamics using HEOM reveals 4 time-scales as observed experimentally

- [1] J. Jornet-Somoza et al, *Phys. Chem. Chem. Phys.* **17**, 26599 - 26606 (2015)
- [2] X. Wei et al., *Nature* **534**, 69 (2016)

## How to describe quantum interferences to separate nuclear spin isomers

Sandra Gómez<sup>1</sup>, Markus Oppel<sup>1</sup>, Christopher Symonds<sup>2</sup>, Dmitrii Shalashilin<sup>2</sup>,  
Graham Worth<sup>3</sup>, Leticia González<sup>1</sup>

<sup>1</sup>*Institute of Theoretical Chemistry, University of Vienna, Währinger Straße 17, 1090 Vienna, Austria*

<sup>2</sup>*School of Chemistry, University of Leeds, LS2 9JT Leeds, United Kingdom*

<sup>3</sup>*Dept. of Chemistry, University College London, 20, Gordon St., WC1H 0AJ London, United Kingdom*

The existence of nuclear-spin isomers was reported for the first time in 1927 by Heisenberg and Hund to explain anomalous properties of molecular hydrogen [1,2]. However, the experimental separation and/or conversion of nuclear spin isomers of polyatomic molecules is a very challenging problem only successful in a few cases. In the last years several theoretical models[3–8] have been proposed showing different behavior of the nuclear spin isomers after light excitation. Using model systems of reduced dimensionality, these previous works have shown that the differences on the excited state dynamics are due to the quantum interferences of the initial nuclear wave function built up for each nuclear spin isomer.

In this work we investigate whether these quantum interferences are still observable using systems of larger dimensionality. To achieve this we use MCTDH (multiconfigurational time-dependant hartree) and compare it to the semiclassical MCE (multiconfigurational Ehrenfest) method. Using these methods, we will for the first time be able to observe whether the different molecular behavior of nuclear spin isomers is still present when going beyond small model systems to a full dimensional treatment of molecules.

- [1] W. Heisenberg, *Z. Phys.* **41**, 239 (1927).
- [2] F. Hund, *Z. Phys.* **42**, 93 (1927)
- [3] T. Grohmann, M. Leibscher, *J. Chem. Phys.* **134**, 204316 (2011).
- [4] J. Floß, T. Grohmann, M. Leibscher, T. Seideman, *J. Chem. Phys.* **136**, 084309 (2012).
- [5] R. Obaid, D. Kinzel, M. Oppel, L. González, *J. Chem. Phys.* **141**, 164323 (2014).
- [6] R. Obaid, D. Kinzel, M. Oppel, L. González, *Theor Chem Acc* **134**, 46 (2015).
- [7] M. Waldl, M. Oppel, L. González, *J. Phys. Chem. A* **120**, 4907 (2016).
- [8] S. Gómez, M. Oppel, L. González, *Chem. Phys. Lett.* (in press) (2017).

## Theoretical Investigation of Silafulleranes with an Endohedral Guest

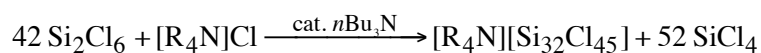
**Josef H. Wender, Martin Diefenbach, Max C. Holthausen**

*Institut für Anorganische und Analytische Chemie, Goethe-Universität,*

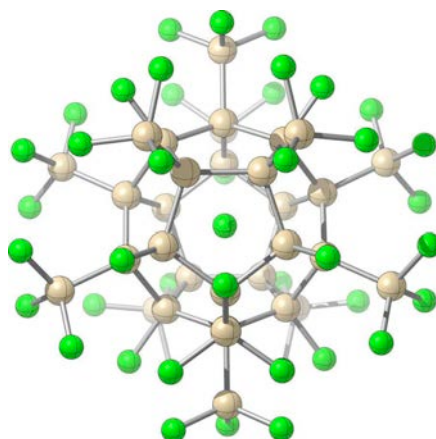
*Max-von-Laue-Str. 7, Frankfurt am Main, Germany*

*Email: wender@chemie.uni-frankfurt.de*

Recently, a remarkable dodecahedral [20]silafullerane with eight chloro and twelve trichlorosilyl substituents as well as one chloride ion as an endohedral guest has been synthesized.<sup>[1]</sup> This complex structure has selectively been formed from simple reactants via an apparent self-organization.



DFT calculations provide a rationale for this particular substitution pattern and also for the bonding between the bare cluster and its endohedral guest. Additionally, properties, *e.g.* <sup>29</sup>Si NMR shifts including spin-orbit coupling, are calculated. The twelve exohedral substituents exert a significant thermodynamic stabilization compared to a purely chlorine substituted homolog as does the incorporation of Cl<sup>−</sup> as endohedral guest.



[1] J. Tillmann, J. H. Wender, U. Bahr, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner *Angew. Chem. Int. Ed.* **54**, 5429–5433 (2015)

## First-order properties within MP2 using Cholesky decomposed density matrices and the resolution-of-the-identity approximation

**Sigurd Vogler<sup>1</sup>, Martin Ludwig<sup>1</sup>, Marina Maurer<sup>1</sup>, Christian Ochsenfeld<sup>1</sup>**

<sup>1</sup>*Chair of Theoretical Chemistry and Center for Integrated Protein Science Munich (CIPSM),  
Department of Chemistry, University of Munich (LMU), Butenandtstr. 7, 81377 Munich,  
Germany*

To obtain analytical first-order properties at the MP2-level such as nuclear gradients or hyperfine coupling constants with low computational cost, we recently introduced a new approach [1] based on the atomic orbital-based formulation by Schweizer *et al.* [2]. The first formulation, although linear scaling, entails large computational cost for small to medium-sized molecules as well as when moderate to large-sized basis sets are employed. Our ansatz therefore introduces both the Cholesky decomposition and the resolution-of-the-identity approximation, as was previously done for the atomic orbital-based MP2 energy computation [3]. This leads to a reduced computational cost and dependency on the basis set size when significant integral contributions are selected using our distance-including integral estimates (denoted as QQR). We present the reformulation of the method and results showing the accuracy and validity of the integral screening as well as the asymptotic scaling behavior and computational efficiency of our new approach.

- [1] S. Vogler, M. Ludwig, M. Maurer, C. Ochsenfeld, submitted.
- [2] S. Schweizer, B. Doser, C. Ochsenfeld, *J. Chem. Phys.* **128**, 154101 (2008).
- [3] S.A. Maurer, L. Clin, C. Ochsenfeld, *J. Chem. Phys.* **140**, 22412 (2014)

## **Towards a Roadmap of Chemical Space: Using Reaction Networks to Study Catalysis**

**Johannes T. Margraf, Karsten Reuter**

*Chair of Theoretical Chemistry, Technical University of Munich, Lichtenbergstr. 4, 85747 Garching, Germany*

The “chemical space” concept refers to the feature space of a given type of molecule, e.g. the set of all organic compounds up to a certain size, which adhere to simple design rules regarding chemical stability.[1] Researchers in this field have focused on finding structure-property relationships within chemical spaces, e.g. in order to estimate the pharmaceutical activity of unknown compounds.

We aim to devise a novel perspective of how chemical spaces can be explored, focusing on the chemical reactions that connect molecules. The space is thus transformed from a simple enumeration to a network of molecules and reactions.[2] The resulting reaction networks are immediately useful in chemical research, e.g., when considering the network of elementary steps leading from syngas ( $\text{H}_2+\text{CO}$ ) to more complex organic molecules like methanol.

The central challenge in using such networks to study reaction mechanisms is the sheer number of possible intermediates and reactions. To tackle this, we are devising a hierarchy of methods, which range from empirical machine-learning approaches that allow the quick estimation of the kinetics and thermodynamics of a large number of reactions, to first-principles electronic structure methods that can be used to accurately describe the most important reactions. Importantly, each rung of the hierarchy should provide an appropriate error bar along with the energetics. The question of how catalysts can be incorporated into such schemes, at different levels of complexity will also be addressed.

[1] L. Ruddigkeit, R. Van Deursen, L. C. Blum and J. L. Reymond, *J. Chem. Inf. Model.* **52**, 2864 (2012).

[2] J. T. Margraf, D. S. Ranasinghe and R. J. Bartlett, *Phys. Chem. Chem. Phys.* **19**, 9798 (2017).

## Increased accuracy and reduced computational cost within the resolution-of-the-identity random phase approximation

**Henry F. Schurkus, Christian Ochsenfeld**

*Chair of Theoretical Chemistry and Center for Integrated Protein Science Munich (CIPSM),  
Department of Chemistry, University of Munich (LMU), Butenandtstr. 7, D-81377 Munich,  
Germany*

We present a variety of new methods for increasing the efficiency of the direct random phase approximation for molecular systems. First, we introduce the concept of null space removal [1]. When a method is formulated with operators having non-trivial null space structure this would normally cause wasteful operations during evaluation. Null space removal allows to eliminate these superfluous operations. We apply this concept to the resolution-of-the-identity within RI-RPA achieving results which are effectively RI-error free but have only about 30% runtime overhead compared to traditional RI approaches. Furthermore, we extend our previous effective linear-scaling atomic orbital formulation [2] of the random phase approximation by introducing an attenuated Coulomb metric within the RI and Cholesky decomposition of the pseudo density matrices [3]. This allows us to reduce the scaling with basis set size by one order, while retaining the linear-scaling behavior with molecule size.

- [1] H. F. Schurkus, A. Luenser, and C. Ochsenfeld *J. Chem. Phys.* **146**, 211106 (2017).
- [2] H. F. Schurkus and C. Ochsenfeld, *J. Chem. Phys.* **144**, 031101 (2016).
- [3] A. Luenser, H. F. Schurkus, and C. Ochsenfeld, *J. Chem. Theory Comput.* **13**, 1647 (2017).

## A Local Coupled Cluster Investigation of Non-Heme Iron Complexes

Milica Feldt<sup>1</sup>, Ricardo A. Mata<sup>2</sup>, Jeremy Harvey<sup>1</sup>

<sup>1</sup>*Theoretical and Computational Chemistry Group, KU Leuven, Celestijnenlaan 200F box 2404, 3001 Leuven, Belgium*

<sup>2</sup>*Institut für Physikalische Chemie, Georg-August-Universität, 37077 Göttingen, Germany*

Heme and non-heme iron enzymes have attracted a lot of attention from both the biological and chemical community since many of them can monooxygenate different organic compounds with high efficiency and specificity [1]. These enzymes have the unique feature to catalyze the C-H activation with high regio- and stereoselectivity. The active species is usually an iron-oxo  $\text{Fe}^{\text{IV}}=\text{O}$  intermediate and the rate limiting step is the hydrogen atom transfer.

Furthermore, these reactions are an example of two-state reactivity reactions. Usually the ground state of non-heme iron-oxo species is the triplet state, but the quintet state is a low lying state. The transition state on the quintet surface has a lower barrier and thereby modulates the reaction.

Because of the high biological importance, these systems were investigated extensively both experimentally and theoretically. When it comes to the theory, due to their size they were mostly investigated using density functional theory (DFT) methods. Coupled cluster methods were applied only on the smallest model systems [2]. Unfortunately, accuracy of DFT methods is not always satisfactory. Therefore, we applied local coupled cluster methods to obtain better accuracy. Different local approaches of coupled cluster methods are available. Here we will test DLPNO-LCCSD(T) method as implemented in ORCA [3] as well as LCCSD(T0) from Molpro [4], including a new “hotspot” version in which the pair approximation was improved by treating more pairs at the coupled cluster level.

[1] M. Costas, M. P. Mehn, M. P. Jensen, L. Que, Jr., *Chem. Rev.* **104**, 939 (2004)

[2] H. Chen, W. Lai, S. Shaik, *J. Phys. Chem. Lett.* **1**, 1533 (2010)

[3] M. Saitow, U. Becker, C. Riplinger, E. F. Valeev, F. Neese, *J. Chem. Phys.* **146**, 164105 (2017)

[4] H.-J. Werner, M. Schütz, *J. Chem. Phys.* **135**, 144116 (2011)

## Origin of Regio- and Stereoselectivity in *Michael* Additions of Pyrrolidine Enamine Derivatives

**Tamara Husch<sup>1</sup>, Dieter Seebach<sup>2</sup>, Albert K. Beck<sup>2</sup>, Markus Reiher<sup>1</sup>**

<sup>1</sup>*Laboratorium für Physikalische Chemie, ETH Zürich, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland*

<sup>2</sup>*Laboratorium für Organische Chemie, ETH Zürich, Vladimir-Prelog-Weg 3, 8093 Zürich, Switzerland*

The origin of regio- and stereoselectivity in *Michael* additions catalyzed by pyrrolidine derivatives is often attributed to distinct conformational preferences of the enamine intermediates. We present an extensive conformational analysis of a diverse selection of enamines to provide a theoretical foundation for future mechanistic discussions. Our results are in agreement with the available experimental data, but illustrate that conformational preferences determined for one enamine are not readily transferable to other types of enamines. According to our analysis, the regio- and stereoselectivity in *Michael* additions cannot be explained by pronounced stability differences of the enamine conformers in general. Most prominently, *s-cis* and *s-trans* conformers are similarly stable for aldehyde- and ketone-derived enamines which is in contrast to previous hypotheses. We found that an appropriate conformational sampling is inevitable to arrive at meaningful conclusions in theoretical studies. The elucidation of the origin of regio- and stereoselectivity, therefore, requires further theoretical investigations of the elementary steps of the *Michael* additions.



## Two interacting molecules in a one-dimensional harmonic trap

**Anna Dawid<sup>1,2</sup>, Maciej Lewenstein<sup>2,3</sup>, Michał Tomza<sup>1,2</sup>**

<sup>1</sup>*Centre of New Technologies, University of Warsaw, Banacha 2C, 02-097 Warsaw, Poland*

<sup>2</sup>*ICFO - Institut de Ciències Fotòniques, The Barcelona Institute of Science and Technology,  
08860 Castelldefels, Spain*

<sup>3</sup>*ICREA - Institució Catalana de Recerca i Estudis Avançats, 08010 Barcelona, Spain*

We investigate the properties of two interacting polar molecules described as rigid quantum rotors effectively trapped in a one-dimensional harmonic potential. The molecules interact via a multichannel two-body contact potential incorporating the short-range anisotropy of intermolecular interactions including dipole-dipole interaction. The impact of external electric and magnetic fields resulting in Stark and Zeeman shifts of molecular rovibrational states is also included. Energy spectra and eigenstates are calculated by means of the exact diagonalization. The importance and interplay of the molecular rotational structure, anisotropic interactions, spin-rotation coupling, electric and magnetic fields, and harmonic trapping potential are examined in detail and compared to the system of two harmonically trapped distinguishable atoms.

## Formation of Deoxyribonucleotide in Prebiotic Conditions

**Danijela Barić<sup>1</sup>, Ivan Dragičević<sup>2</sup>, Borislav Kovačević<sup>1</sup>, Bernard T. Golding<sup>3</sup>,  
David M. Smith<sup>1</sup>**

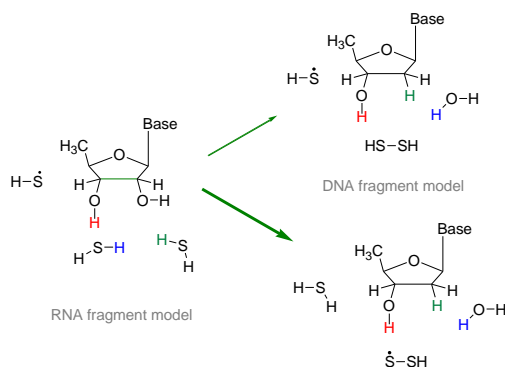
<sup>1</sup>*Division of Physical Chemistry, Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia*

<sup>2</sup>*Department of Chemistry, Faculty of Science and Education, University of Mostar, Matice hrvatske bb, 88000 Mostar, Bosnia and Herzegovina*

<sup>3</sup>*School of Chemistry, Newcastle University, Newcastle upon Tyne, UK, NE1 7RU, United Kingdom*

The occurrence of life on Earth was possible due to the existence of a "molecules of life": nucleic acids, amino acids and sugars. Prebiotic chemistry research has revealed persuasive pathways for the formation of the building blocks of RNA and proteins, but not DNA. The monomers of DNA, deoxyribonucleotides, nowadays are formed exclusively by enzymatically catalyzed reduction of ribonucleotides, involving radical enzymes ribonucleotide reductases.

This work computationally explores potential non-enzymatic paths of deoxyribonucleotide formation, inspired by the radical mechanisms of ribonucleotide reduction catalyzed by today's ribonucleotide reductase enzymes. Several computationally modeled mechanisms of ribonucleotide reduction in a putative  $\text{H}_2\text{S}/\text{HS}\cdot$  environment, without the presence of enzymes, will be presented.



## Chemically functionalized graphene derivatives for optoelectronic and chemical sensing applications

Lukas Eugen Marsoner Steinkasserer<sup>1</sup>, Beate Paulus<sup>1</sup>

<sup>1</sup>*Institut für Chemie und Biochemie, Freie Universität Berlin, Takustraße 3 14195 Berlin, Germany*

Using *first principles* methods implemented within the GPAW code we investigate the structural, electronic, and optical properties of chemically functionalized graphene derivatives. Our first project focuses on the investigation of the optical properties of partially brominated and chlorinated fluorographene derivatives. We find brominated and chlorinated fluorographene derivatives show stabilities close to those of graphane. A detailed investigation of the systems band structure further demonstrates significant 1D-localization of positively charged charge-carriers which might be exploited in order to boost quantum efficiency in photovoltaic applications. Lastly, using  $G_0W_0$  and BSE, we investigate the optical adsorption spectra of the investigated materials we show their first adsorption peak to lie close to the optimal peak position for photovoltaic applications.

Graphene pseudohalides are natural candidates for use in molecular sensing due to their greater chemical activity as compared to both graphene halides and pristine graphene. In this second part of our project, we employ vdW-DFT to study the structural and electronic properties of two selected graphene pseudohalides namely cyanographene and isocyanographene and investigate the potential use of the latter as a chemical sensor using electron transport calculations [2].

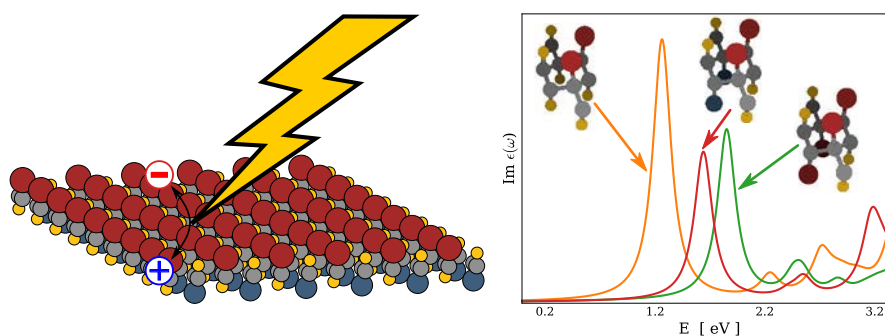


Figure 1: Calculated adsorption spectra for brominated and chlorinated fluorographene derivatives calculated at the BSE level.

- [1] L. E. Marsoner Steinkasserer, A. Zarantonello, and B. Paulus, *Phys. Chem. Chem. Phys.* **18**, 36 (2016).
- [2] L. E. Marsoner Steinkasserer and B. Paulus, *ArXiv*, **arXiv:1703.08582** (2017).

## **Fast prediction of the specific conductivity of electrolytes from the molecular structure of the solvent.**

**BOUTELOUP Rémi<sup>1</sup>, MATHIEU Didier<sup>1</sup>**

*<sup>1</sup>CEA Le Ripault, Monts 37260, France*

With the development of battery utilization in a lot of devices, the needs to improve their safety and performance are in expansion. For this purpose, new liquid electrolytes are investigated, which require new solvents and/or additives. In view of screening efficiently the chemical space for suitable candidate compounds, this work exposes a way to predict the specific conductivity of a nonaqueous electrolyte solution with a LiPF<sub>6</sub> salt.

The purpose of this method is to predict this property, quickly and simply, with only the 2D structure of each molecule of the solvent and their proportions as input parameters. To this aim, we have chosen the Casteel-Amis empirical equation [1] to represent the specific conductivity as a function of the salt concentration and the solvent composition.

The four parameters of this equation can be related to properties of the solvent, since in our case, the salt is always the same. The two properties that determine the specific conductivity are the ionic mobility and the ionic association. To connect them with solvent properties, we approximate that these two can be represented on the basis of the viscosity and the dielectric constant of the solvent, respectively. If we can predict them for each solvent, we can calculate the specific conductivity.

For the viscosity, we have developed an additive model, based only on the 2D structure of pure solvents. For the dielectric constant of pure compounds, we use the Fröhlich equation [2], that allows to calculate the dielectric constant from the molar volume, the refractive index and the parameter  $g\mu^2$  (with  $\mu$  the dipole moment) representing the orientation polarization of molecules. To this aim, we have developed additive models for these three properties.

[1] J. F. Casteel, E. S. Amis, *J. Chem. Eng. Data* **17**, 55-59 (1972).

[2] H. Fröhlich, *Theory of Dielectrics: Dielectric Constant and Dielectric Loss* (1949).

## Efficient Calculation of Electron-Phonon Coupling in Molecular Junctions

**Michael Deffner<sup>1</sup>, Martin Sebastian Zöllner<sup>1</sup>, Carmen Herrmann<sup>1</sup>**

<sup>1</sup>*Institute of Inorganic and Applied Chemistry, University of Hamburg, Martin-Luther-King Platz 6, 20146 Hamburg, Germany*

Electron transport through individual molecules is important for many biological processes and potential technological applications. Great experimental and theoretical progress in this field in recent years also provides insight into molecular junctions under unusual (nonequilibrium) conditions. Aside from elastic processes, inelastic ones such as the excitation of spin flips or vibrations can occur. The strength of the latter is dominated by the electron-phonon coupling and is experimentally studied within the framework of inelastic electron tunneling spectroscopy using break junctions or scanning tunneling setups [1].

The challenging aspect for theory is the sensitivity of the IET spectrum to minor changes of the molecule or the environment such as the junction geometry [2, 3]. Thus, efficient ways to study several junctions or structure–property relations are needed.

To provide an efficient framework for calculating IET spectra, we combine the mode-tracking algorithm (an iterative subspace approach for selectively calculating eigenvectors and -modes of the Hessian matrix) as implemented in MoViPaC [4, 5, 6] with our program package ARTAIOS [7, 8]. We show several results to validate the approach and demonstrate the capabilities of our mode-tracking approach.

- [1] M. A. Reed, *Materials Today* **2008**, 11, 4650.
- [2] M. Kula, J. Jiang, Y. Luo, *Nano Lett.* **2006**, 6, 1693-1698.
- [3] R. Frisenda, M. L. Perrin, H. S. J. van der Zant, *Beilstein Journal of Nanotechnology* **2015**, 6, 24772484.
- [4] T. Weymuth, M. P. Haag, K. Kiewisch, S. Lubner, S. Schenk, C. R. Jacob, C. Herrmann, J. Neugebauer, M. Reiher, *Journal of Computational Chemistry* **2012**, 33, 21862198.
- [5] M. Reiher, J. Neugebauer, *The Journal of Chemical Physics* **2003**, 118, 16341641.
- [6] C. Herrmann, J. Neugebauer, M. Reiher, *New Journal of Chemistry* **2007**, 31, 818.
- [7] C. Herrmann, G. C. Solomon, J. E. Subotnik, V. Mujica, M. A. Ratner, *The Journal of Chemical Physics* **2010**, 132, 024103.
- [8] C. Herrmann, L. Gross, T. Steenbock, M. Deffner, B. A. Voigt, G. C. Solomon, “ARTAIOS - a transport code for postprocessing quantum chemical electronic structure calculations, available from <https://www.chemie.uni-hamburg.de/ac/herrmann/software/index.html>”, 2016.

## Mechanism of methyl transfer between methylcobalamin and A-cluster in acetyl-Coenzyme A Synthase (ACS). DFT calculations.

Maria Jaworska<sup>1</sup>, Piotr Lodowski<sup>1</sup>, Pawel M. Kozlowski<sup>2,3</sup>

<sup>1</sup>*Department of Theoretical Chemistry, Institute of Chemistry, University of Silesia in Katowice, Szkolna 9, PL-40 006 Katowice, Poland*

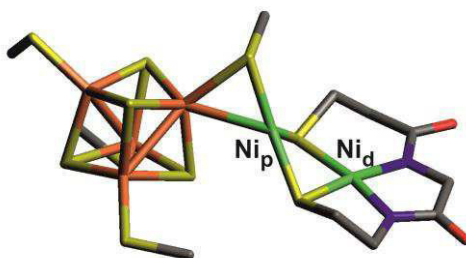
<sup>2</sup>*Department of Chemistry, University of Louisville, Louisville, Kentucky 40292, United States*

<sup>3</sup>*Visiting professor, Department of Food Sciences, Medical University of Gdansk, Al. Gen. J. Hallera 107, 80-416 Gdansk, Poland*

ACS enzyme catalyzes the formation of Acetyl-CoA from carbon monoxide, coenzyme A, and a methyl group provided by the corrinoid iron sulfur protein (CFeSP) according to reaction:



The active site of ACS consists of multinuclear metallic cluster (A-cluster) of  $\text{Fe}_4\text{S}_4\text{-Ni}_p\text{Ni}_d$  formula.



A-cluster

Several mechanisms were proposed for Acetyl-CoA formation differing in  $\text{Ni}_p$  oxidation state and the order of CO and  $\text{CH}_3$  addition.

DFT calculations were performed for the A-cluster model with the use of non-hybrid (GGA)BP86 exchange–correlation functional and TZVP basis set. The mechanism of methyl transfer from methylcobalamin to the A-cluster was proposed in which the reduction of  $\text{Ni}_p$  is coupled to protonation. Analysis of the electron density distribution on the A-cluster reveals that the role of the cubane  $[\text{Fe}_4\text{S}_4]$  consists of stabilization of the different oxidation states of the proximal nickel atom ( $\text{Ni}_p$ ), by acceptance of the excess electron density.

## Lattice energies of molecular solids from fragment and periodic approaches

Jaroslav Hofierka<sup>1</sup>, Jiri Klimes<sup>1</sup>

<sup>1</sup>*Department of Chemical Physics and Optics, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic*

Molecular solids represent important materials in nature, science, and industries. They often have a rich phase diagram, such as that of water ice, or exhibit polymorphism. The prediction of phase diagrams and polymorph stabilities from first principles is of significant current interest and relies on the ability to calculate lattice energies of solids with high accuracy. The density functional theory has become increasingly useful in the past decade for the description of molecular solids; however, state-of-the-art functionals with dispersion corrections struggle to describe molecular solids accurately [1]. Quantum Monte Carlo techniques are accurate enough but their computational cost limits their widespread use. Therefore, wavefunction, or post-Hartree-Fock (post-HF), methods are the natural choice as they can be systematically improved. Usually, the many-body (fragment) expansion is used to find the result as a sum of the contributions from dimers of molecules and corrections including the effects of trimers, tetramers, etc. However, the post-HF methods are becoming available in codes implementing periodic boundary conditions (PBC) and thus directly applicable to molecular solids. In principle, the fragment and periodic approaches should yield the same lattice energy, but published results vary considerably even for rather simple molecules [2]. In fact, there are several parameters that strongly affect results. Specifically, the fragment approach relies on fast convergence of the many-body expansion both with the number of molecules in a cluster and with the intermolecular distance. The PBC approach depends on the sampling of the Brillouin zone and the size of the cell used for the reference molecule. Also, an extrapolation to the complete-basis-set limit is often required to obtain comparable results. In our work, we want to establish if and how one can find identical results from both schemes. To this end, we calculated HF and MP2 lattice energies of solid methane, methanol, ammonia, and carbon dioxide. We found a very nice agreement for ammonia and carbon dioxide with the lattice energies differing by only about 0.1 kJ/mol or 0.3%. The agreement is worse for methane and methanol, where we found a difference of 2% and 1%, respectively. Both approaches have their strengths and weaknesses as well as different requirements in terms of compute cost and human time needed to obtain precise results. The fragment approach proved to be more efficient for smaller systems with dominating pairwise interactions, such as methane, due to a modest computational cost of pairwise interactions compared to larger clusters. On the other hand, the PBC approach performed well for systems with dominating dipolar interactions (methanol and ammonia). Finally, we also performed CCSD(T) many-body expansion calculations and compared them with previous results.

[1] J. Klimes, *J. Chem. Phys.* **145**, 094506 (2016).

[2] G. J. O. Beran, *Chem. Rev.* **116**, 5567–5613 (2016).

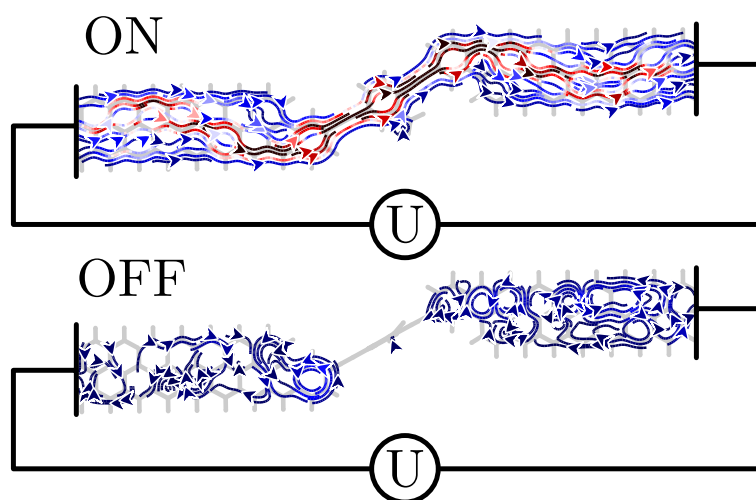
## Mechanistic Investigations of Electronic Current Dynamics Through a Single-Molecule-Graphene-Nanoribbon Junction

Vincent Pohl<sup>1</sup>, Jean Christophe Tremblay<sup>1</sup>

<sup>1</sup>*Institut für Chemie und Biochemie, Freie Universität Berlin, Takustraße 3, 14195 Berlin, Germany*

Recent quantum dynamical simulations have shown that the conductivity of nitro-substituted oligo-(phenylene ethynylene) attached to graphene nanoribbon leads can be switched in the spirit of a traditional field effect transistor.[1] Upon application of a static electric field, the central oligomer unit rotates and causes the interruption of the conjugated  $\pi$ -system along the nanoribbon direction, thereby drastically reducing the conductivity of the graphene wire.

In the present contribution, we investigate the time-dependent electron transport through this device for both of its logical states. First, we apply a localization scheme on the orthonormal set of molecular orbitals obtained from a standard density functional theory calculation to generate a localized basis for the different parts of the molecular junction. Using the driven Liouville-von-Neumann (DLvN) approach for time-dependent electronic transport calculations,[2] we simulate the electronic current dynamics for time-dependent potential biases. The transparent DLvN formalism allows us to directly access the density matrix, and thus, to reconstruct the time-dependent electronic current density (electronic flux density) unraveling unique mechanistic details of the electron transport.



[1] V. Pohl, J. C. Tremblay, *J. Phys. Chem. C* **120**, 28808 (2016).

[2] T. Zelovich, L. Kronik, O. Hod, *J. Chem. Theory Comput.* **10**, 2927 (2014).



## Testing semiempirical quantum mechanical methods on model systems relevant to computer-aided drug design

K. Kříž<sup>1,2</sup>, J. Řezáč<sup>1,3</sup>

<sup>1</sup>*Department of Computational Chemistry, Institute of Organic Chemistry and Biochemistry,  
Academy of Sciences of the Czech Republic, Flemingovo náměstí 542/2, 16610 Prague, Czech  
Republic*

<sup>2</sup>*Charles University of Prague in the Czech Republic, Faculty of Sciences*

<sup>3</sup>*jan.rezac@uochb.cas.cz*

The rapid development of information technology over the few past decades has opened many new frontiers of scientific research. One of them is computer-aided drug design which utilizes the tremendous computational power now available to estimate the binding properties of various pharmaceuticals to their target. One class of methods for such estimations are quantum mechanical methods based on solution of Schrödinger equation. While such methods are theoretically exact, for them still greater computational power is required to bear fruits in reasonable time when applied on larger systems. Semi-empirical quantum mechanical methods introducing empirical parameters in exchange for approximative approach offer a compromise between the time and accuracy [1]. Such methods are however often parametrized or tested on model systems that, although are basic and diverse, might not approximate protein-ligand interaction correctly regarding size and composition of the system. In this study, we compare the accuracy (in terms of interaction energy calculations) and speed of various quantum mechanical methods (DFT, HF-3c and semiempirical: PM7, XTB and semiempirical with corrections: DFTB, PM6 with D3H4 or D3H5). Interaction energies are calculated on complexes of a whole ligand and fragments of the protein, such as side chains. We have built 547 model complexes from 17 protein structures from the protein data bank-PDB. The same proteins with their ligands are currently being studied in our group by scoring, estimating their overall binding affinity. Because of the size of the systems, the point of reference for the accuracy of these calculations, the benchmark, is the DFT with B3LYP functional, def2-QZVP basis set and empirical dispersion correction D3 which is accurate while still reasonably fast. The speed has been calculated on artificial poly-alanine helices. We have found that among the semiempirical methods tested the PM6 with D3H4 [2, 3] corrections is the most accurate, followed by the DFTB D3H4 [4]. We also discuss various details in the setup of the D3H4 corrections. The PM6 was the fastest method (by far when the MOZYME linear scaling algorithm is applied).

- [1] M. Lepšík, J. Řezáč, M. Kolář, A. Pecina, P. Hobza, J. Fanfrlík, *ChemPlusChem* 78, 921 (2013).
- [2] J. Hostaš, J. Řezáč, P. Hobza, *Chem. Phys. Lett.* 568, 161 (2013).
- [3] J. Řezáč, P. Hobza, *J. Chem. Theory Comput.* 8, 141 (2012).
- [4] V. M. Miriyala, J. Řezáč, *J. Comput. Chem.* 38, 688 (2017).

## Modulation of a Weakly Coupled Peroxo-Dicopper(II) Complex by Interaction With Alkali Metal Ions.

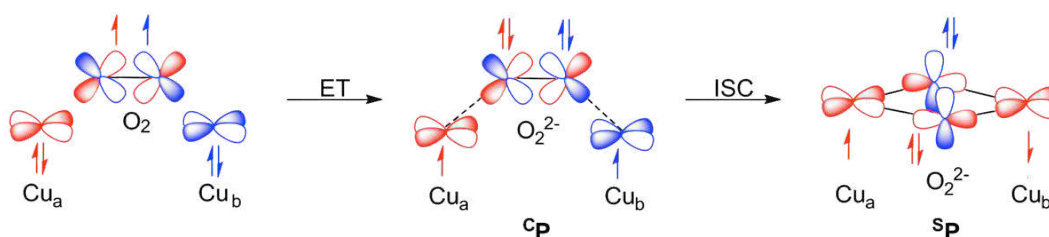
Lorenzo D'Amore<sup>1</sup>, Marcel Swart<sup>1,2</sup>, Alexander Brinkmeier<sup>3</sup>, Franc Meyer<sup>3</sup>

<sup>1</sup>*IQCC & Departament de Química, Universitat de Girona,  
c/Maria Aurèlia Capmany 6, 17003 Girona, Spain*

<sup>2</sup>*Institució Catalana de Recerca i Estudis Avançats (ICREA), Barcelona, Spain*

<sup>3</sup>*Institut für Anorganische Chemie, Georg-August-Universität Göttingen,  
Tammannstraße 4, 37077 Göttingen, Germany*

The dicopper center is the active site of many type III Cu proteins, which play an important role in the transport and activation of oxygen in many biological systems. Among all the different species that occur upon O<sub>2</sub> binding in these metalloproteins, the <sup>S</sup>P motif is the most commonly detectable one. Here we report the synthetic, fully characterized [1] Cu<sup>II</sup><sub>2</sub>(μ-η<sup>1</sup>:η<sup>1</sup>-O<sub>2</sub>) complex, featuring an unusual cis-peroxo binding (<sup>C</sup>P) and weak antiferromagnetic coupling, comparable with that of a theoretically predicted transition state for O<sub>2</sub> binding to T3Cu centers [2], thus supporting the biological relevance of this new compound. UV/vis spectroscopy and DFT computational studies allowed us to demonstrate how the electronic structure of the complex can be tuned by introducing different alkali metal ions (namely Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup>) which interact with the peroxo moiety. Furthermore, the binding of diverse alkali cations was also found to modulate the magnitude of the antiferromagnetic coupling, by modifying the extent of overlap in copper and oxygen centered orbitals through variations in (i) coordination environments of the Cu(II) ions and (ii) Cu-O-O-Cu torsion angle.



[1] K. E. Dalle, T. Gruene, S. Dechert, S. Demeshko, F. Meyer, *J. Am. Chem. Soc.* **136**, 7428 (2014).

[2] M. Metz, E. I. Solomon, *J. Am. Chem. Soc.* **123**, 4938 (2001).

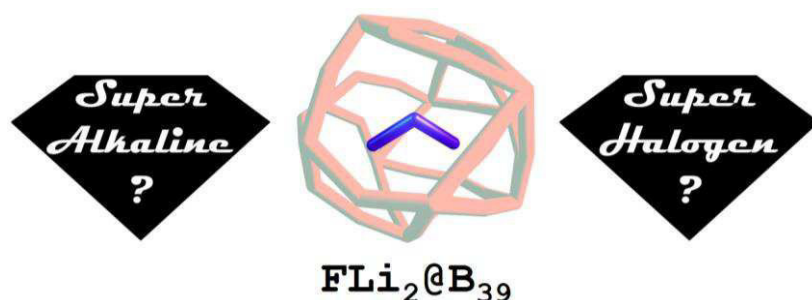
## The case of endohedral borospherene supersalt $\text{FLi}_2@\text{B}_{39}$ and its “super” properties.

Anton J. Stasyuk<sup>1</sup>, Miquel Sola<sup>1</sup>

<sup>1</sup> *Institute of Computational Chemistry and Catalysis (IQCC) of the University of Girona, C/ Maria Aurèlia Campany, 69, Girona, Spain.*

In the early 80s, Gutsev and Boldyrev demonstrated the existence of two classes of extraordinary molecular systems, the so-called superalkalis (SA) possessing lower ionization potentials (IPs) than those of alkali metals (5.39–3.89 eV), and superhalogens (SH) that demonstrate electron affinities (EAs) which may exceed the limit of chlorine (3.61 eV). One of most exciting of recent years in the chemistry of SH materials was connected with discovering of  $\text{B}_{39}^-$  nanocluster, produced via laser vaporization of a  $^{10}\text{B}$ -enriched boron target. Photoelectron spectroscopy for  $\text{B}_{39}^-$  cluster predict an adiabatic detachment energy of 3.84(5) eV that represents the EA of neutral  $\text{B}_{39}^0$ , which allowed attribution  $\text{B}_{39}^0$  species to the SH.<sup>[1]</sup>

We have designed and computationally studied behavior of unique endohedral borospherene based supersalt represented by superalkaline  $\text{FLi}_2$  species incorporated into superhalogen  $\text{B}_{39}$  cage at PBE0/6-311+G(2d) level. Singlet ground state and triplet excited state of  $\text{FLi}_2@\text{B}_{39}$  borospherene complex as well as its cationic and anionic doublet ground states have been investigated. All studied endohedral borospherenes, except complex formed by encapsulation of  $\text{FLi}_2^+$  into  $\text{B}_{39}$  in  $\text{FLi}_2@\text{B}_{39}^+$ , demonstrate thermodynamic stability caused most likely by electrostatic attraction and unpaired electron delocalization. Predicted ionization energies and electron affinities values demonstrate that  $\text{FLi}_2@\text{B}_{39}$  endohedral system loses both superalkaline and superhalogen properties inherent in individual subunits. Also we proved that easily available vertically estimated potentials could be successfully used (with the magnitude of the relative error at the level of few percent) for approximation of adiabatic values for endohedral borospherenes.



[1] Q. Chen *et al.*, *ACS Nano*, **9**, 754 (2015).

## Simulating Overtone Induced Chemistry with AIMD

Teemu Järvinen<sup>1</sup>, Jan Lundell<sup>1</sup>, Przemysław Dopieralski<sup>2</sup>

<sup>1</sup>*Department of Chemistry, University of Jyväskylä, P.O. Box 35, FI-40014 University of Jyväskylä, Finland*

<sup>2</sup>*Faculty of Chemistry, University of Wrocław, Poland*

The high overtone induced processes are initiated by promoting a molecule or a complex to chemically relevant energies in high vibrational excited states through the thermal excitation or direct absorption of visible (VIS) or near-infrared (NIR) radiation. Unlike the thermally induced processes, the reactions initiated by vibrational overtone-pumping of ground electronic state molecule through direct absorption of photon can be treated without the need to consider the collisional activation processes. In general, it is required that the energy is deposited into the initially excited vibrational state and subsequently transferred by intramolecular vibrational redistribution (IVR) to other modes of the molecule including the reaction coordinate. For example, it has been demonstrated that high overtone excitation of OH groups in carboxylic acids isolated in low temperature matrices leads to two different unimolecular processes: isomerization and/or decomposition of the molecules [1, 2, 3, 4]. Moreover, overtone pumping was used, for example, in the case of formic acid dimers to produce high-energy conformers within the hydrogen-bonded complexes [5, 6, 7]. Here we present an AIMD simulation study of formic acid and its water complex.

- [1] M. Pettersson, J. Lundell, L. Khriachtchev, M. Räsänen, *J.Am.Chem.Soc.* **119**, 11715 (1997).
- [2] A. Olbert-Majkut, J. Ahokas, J. Lundell, M. Pettersson, *Phys.Chem.Chem.Phys.* **12**, 7138 (2010).
- [3] A. Olbert-Majkut, J. Ahokas, J. Lundell, M. Pettersson, *J.Raman Spectrosc.* **42**, 1670 (2011).
- [4] A. Olbert-Majkut, J. Ahokas, M. Pettersson, J. Lundell, *J.Phys.Chem. A* **117**, 1492 (2013).
- [5] K. Marushkevich, L. Khriachtchev, J. Lundell, M. Räsänen, *J.Am.Chem.Soc.* **128**, 12060 (2006).
- [6] K. Marushkevich, L. Khriachtchev, J. Lundell, A. Domanskaya, M. Räsänen, *J.Phys.Chem.A* **114**, 3495 (2010).
- [7] K. Marushkevich, L. Khriachtchev, M. Räsänen, M. Melavuori, J. Lundell, *J.Phys.Chem.A* **116**, 2101 (2012).

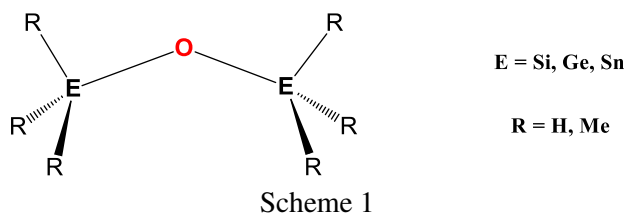
## New insights regarding chemical bonding within heavier analogues of ethers: siloxanes, germoxanes and stannoxanes

Ionut-Tudor Moraru, Gabriela Nemes

*Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, 11 Arany Janos Street, Cluj-Napoca, Romania*

Heavier analogues of the organic ethers, compounds containing E-O-E units (E = Si, Ge, Sn), are mainly used in the synthesis of new polymers. Therefore, the need of a full understanding of the chemical bonding within these precursors is required in order to gain accuracy in designing targeted materials. A large number of studies aimed to explain the nature of the Si-O bond, while for germoxanes and stannoxanes only few theoretical models are available. However, recent papers of Weinhold and West [1, 2] brought further clarification on the concept of vicinal hyperconjugative interactions, mainly used in explaining the structural features of siloxanes, in the last decades.

The aim of this work was to assess if the molecular structures of germoxanes and stannoxanes can be explained in terms of siloxane-like hyperconjugative interactions and in addition, to evaluate if  $p \rightarrow d$  back-bonding effects can also impact the structural behavior of these species. For these purposes, theoretical calculations were performed on the model compounds (Scheme 1), at several DFT levels of theory.



The adjacent hyperconjugative interactions were shown to dictate to a large extent the structural features of siloxanes, germoxanes and stannoxanes, according to NBO DEL optimizations. Moreover, the calculations revealed that  $p \rightarrow d$  back-bonding effects also influence the equilibrium geometry of these species, albeit to a lesser extent.[3] Similar results were additionally obtained for derivatives containing more than one E-O-E units.

[1] F. Weinhold, R. West, *Organometallics* **30**, 5815 (2011).

[2] F. Weinhold, R. West, *J. Am. Chem. Soc.* **135**, 5762 (2013).

[3] I.-T. Moraru, P. M. Petrar, G. Nemes, *J. Phys. Chem. A* **121**, 2515 (2017).

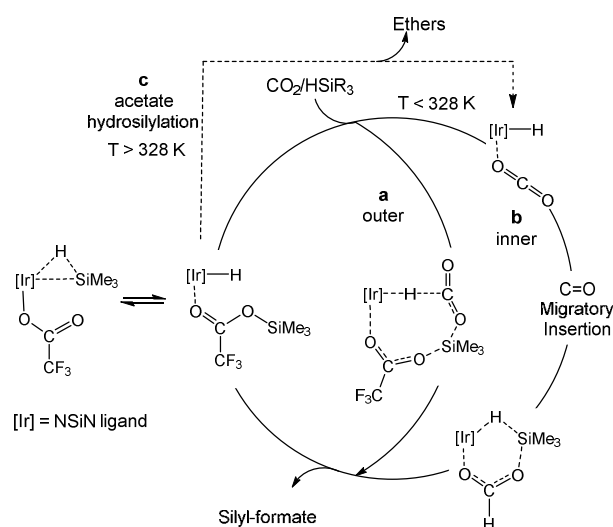
## A DFT Study on the Reduction of CO<sub>2</sub> to Silylformates Catalyzed by Ir-NSiN Species

Víctor Polo<sup>1</sup>

<sup>1</sup>*Departamento de Química Física and Instituto de Biocomputación y Física de los Sistemas Complejos (BIFI), Universidad de Zaragoza. Pl. S. Francisco S/N 50009 Zaragoza, Spain.*

Hydrosilylation of CO<sub>2</sub> to yield silylformates has emerged as a new methodology for the transformation of CO<sub>2</sub> into value-added chemicals. Using the appropriate catalyst, this reaction can be achieved under mild conditions and obtaining a good selectivity towards the silylformate product. In order to improve the efficiency of the catalyst, an understanding on all possible reaction pathways is necessary.

In this work, a detailed analysis on the reaction mechanism is provided using DFT calculations for two Ir-NSiN complexes bearing triflate[1] or trifluoroacetate[2] ligands which have been experimentally tested. Examination of possible pathways includes inner vs outer sphere mechanisms, metal-ligand cooperative bond activation. Electronic and steric effects on the key steps of the catalytic cycle are discussed.



[1] R. Lalrempuia, M. Iglesias, V. Polo, P. J. Sanz Miguel, F. J. Fernández-Alvarez, J. J. Pérez-Torrente, L. A. Oro, *Angew. Chem. Int. Ed.*, **51**, 12824 (2012).

[2] A. Julián, J. Guzmán, E. A. Jaseer, F. J. Fernández-Alvarez, R. Royo, V. Polo, P. García-Orduña, F. J. Lahoz, L. A. Oro, submitted.

## High-level theoretical rovibrational spectroscopy of HCN

**Benjamin Schröder<sup>1</sup>, Maximilian Rybarczyk<sup>1</sup>, Peter Sebald<sup>1</sup>**

<sup>1</sup>*Institut für Physikalische Chemie, Universität Göttingen, Tammannstraße 6, D-37077 Göttingen, Germany*

A near equilibrium potential energy surface (PES) and an electric dipole moment function (EDMF) for hydrogen cyanide (HCN,  $X^1\Sigma^+$ ) are employed in variational calculations for many rovibrational states and intensities of rovibrational transitions. The PES and EDMF are constructed in a high-level composite approach that combines explicitly correlated coupled cluster theory with corrections due to inner shell correlation, scalar relativistic effects and higher-order correlation up to pentuple excitations. Effects beyond the Born-Oppenheimer approximation are accounted for by inclusion of the diagonal Born-Oppenheimer correction in the PES. It will be shown that this level of *ab initio* calculations allows to reliably obtain an accurate molecular geometry, vibrational band origins to within  $1\text{ cm}^{-1}$  and rotational constants within 0.01 % of experiment [1]. The EDMF in combination with the calculated rovibrational wavefunctions is able to accurately reproduce the unusually low intensity of the CN stretching fundamental  $\nu_3$  around  $2096\text{ cm}^{-1}$  (cf. Figure 1) [2]. The overall performance shows that the applied approach provides close to perfect agreement with experiment without the need to empirically adjust the *ab initio* PES or EDMF.

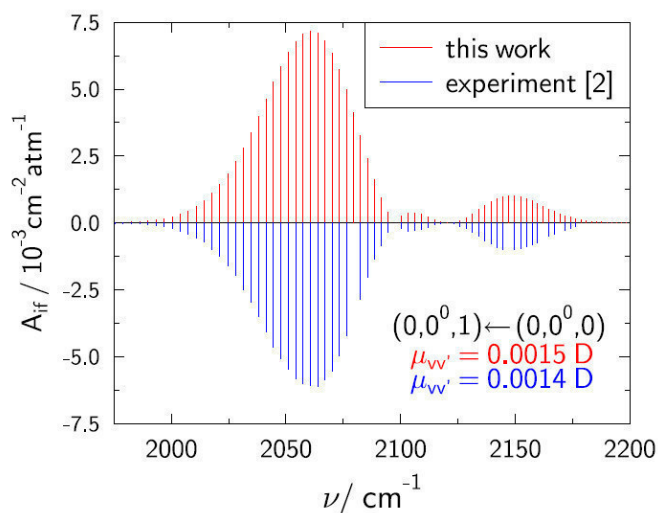


Figure 1 Comparison of calculated and experimental  $\nu_3$  line intensities

[1] G. C. Mellau, *J. Chem. Phys.* **134**, 234303 (2011).

[2] A. Maki *et al.*, *J. Mol. Spectrosc.* **174**, 365 (1995).

## What are the physical contents of HDvV and Hubbard Hamiltonian Parameters in the BS-DFT approach?

G. David<sup>1</sup>, N. Guihéry<sup>2</sup>, N. Ferré<sup>1</sup>

<sup>1</sup>Aix-Marseille Univ, CNRS, ICR, Marseille, France

<sup>2</sup>LCPQ, Université Paul Sabatier, 118 route de Narbonne, Toulouse, France

To evaluate the intensity of the magnetic couplings and to understand their underlying mechanisms, both experimentalists and theoreticians often use effective model Hamiltonians because they provide a description of the magnetic state manifold simpler than the one the full Hamiltonian does.[1] Even if the DFT Kohn-Sham approach has become the most standard method in quantum chemistry, it often fails to describe the magnetic systems because it cannot take into account the multi-configurational nature of the low spin states. Nevertheless, the most common method to estimate DFT-based magnetic exchange couplings is the Broken Symmetry approach (BS) combined with the spin-decontamination procedure.[1] In order to better understand the physics of the molecular systems featuring two magnetic centers, a decomposition method based on the Heisenberg-Dirac-van Vleck Hamiltonian (HDvV) was proposed to get the three main contributions to the magnetic exchange coupling  $J$  (Figure 1) : i) the direct exchange interaction  $J_0$  between the magnetic electrons, ii) the kinetic exchange interaction ( $\Delta J_{KE}$ ) allowing the delocalization of the magnetic orbitals and iii) the spin polarization ( $\Delta J_{SP}$ ) of the non-magnetic electrons.[2]

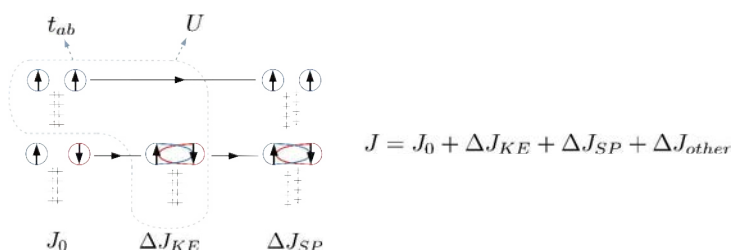


Figure 1: Schematic representation of the magnetic exchange coupling decomposition path and of the extraction of model Hamiltonian parameters[2]

In this communication, I present how HDvV and Hubbard Hamiltonian parameters can be extracted from the decomposition path. Owing to the well-known dependence of  $J$  to the exchange-correlation functional, the influence of the amount of Hartree-Fock exchange used in hybrid functionals on these parameters is highlighted.

[1] J.-P. Malrieu *et al*, *Chem. Rev.*, **114**, 429 (2014)

[2] E. Coulaud *et al.*, *J. Chem. Theory Comput.*, **9**, 3429 (2013).



**Predictive Multi-scale Modelling:  
from Atoms and Electrons to Drugs and Airplanes**

**Judith B. Rommel<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, University of Cambridge,  
Lensfield Road, Cambridge, United Kingdom*

Predictive multi-scale simulations are highly relevant to a wide range of industry sectors. Nano-scale engineering, advanced materials validation and design, nanotoxicity assessment, and computational drug design are all linked together by chemical simulations. They all require trust and reliability from the predicted outcomes. In many cases data from one scale are reused in models on another scale. The presentation will focus on the meaning of being predictive in chemical simulations and recent extensions [1] towards chemical engineering on the quantum level.

Secondly, an overview of multi-scale modelling strategies with roots in chemistry, physics, mathematics, and engineering will be discussed. Emphasis will lie on the most efficient and reliable techniques with respect to uncertainty and error quantification including communication across scales [2].

Further, we will highlight our latest advances in multi-scale simulations of chemical kinetics of self-assembling Glycine molecules on Cu{110} [3] and a coarse grained atomistic model [4]. The strategies and concepts presented are beneficial in industrial applications, e.g., in airplane design, nuclear reactor garbage storage, and drug development. They have the potential to grow scientific multi-scale modelling across business sectors while integrating the quantum scale to airplane design.

- [1] J. B. Rommel, *From Prescriptive to Predictive: Risk Assessment and Quality Control in Computational Chemistry*, submitted, 2017.
- [2] J. B. Rommel, *Reliable and Predictive Multi-scale and Multi-physics Simulations: from Atoms and Electrons to Drugs and Airplanes*, in preparation, 2017.
- [3] J. B. Rommel, D. J. Wales, *Kinetics of Molecular Diffusion and Self-Assembly: Glycine on Cu(110)*, to be submitted, 2017.
- [4] J. B. Rommel, *Density Embedding Methods: Quality Control and Efficiency for Large Metal Clusters*, in preparation, 2017.

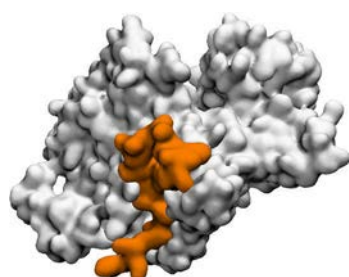
## Investigating complex formation of C99 with $\gamma$ -secretase, utilizing atomistic MM-MD simulations and free energy calculations.

Manuel Hitzenberger<sup>1</sup>, Martin Zacharias<sup>1</sup>

<sup>1</sup>Physics Department, Technical University Munich, James-Franck-Str. 1, 85748 Garching bei München, Germany

The intramembrane protein complex  $\gamma$ -secretase, consisting of four protein-subunits, functions as an aspartyl protease. It is best known for being part of the pathway processing the amyloid precursor protein (APP). Cleavage of APP's transmembrane domain C99 by  $\gamma$ -secretase, yields amino acid (AA) chains of different lengths: Among other peptides, two different forms of so called "Amyloid beta" (A $\beta$ ) fragments are produced: Shorter, 40 AA long peptides (A $\beta$ 40) and a 42 AA long variant, A $\beta$ 42. The A $\beta$ 42 fragments have been linked with familial Alzheimer's disease (FAD), as they are known to aggregate and form fibrillar structures. These structures are the primary component of amyloid plaques found in the brains of AD patients. Presenilin (PS) has been identified as the subunit responsible for the scission of C99, providing two catalytically active aspartate residues located deep within the hydrophobic region of the complex.

Due to their apparent importance in FAD research, the properties of  $\gamma$ -secretase, and especially PS have recently been under very thorough investigation. Special emphasis has been put on the recognition of C99 and its interactions with the protease complex.



*C99- $\gamma$ -secretase complex. C99 is depicted in orange and only trans-membrane regions are shown.*

Unfortunately, no structural data of the biologically active binding mode is available and therefore the mechanism of substrate recognition and the physico-chemical interactions mediating C99 cleavage are still not understood.

Molecular dynamics simulations are a capable tool for the investigation of structural and dynamical system properties that are currently inaccessible to experimental techniques, enabling predictions and working models that can be used to further investigate biologically relevant systems, such as the  $\gamma$ -secretase-C99 complex.

Starting from a recently published cryo-electron microscopy (cryo-EM) structure (PDB:5FN2) of  $\gamma$ -secretase we conducted atomistic, microsecond time scale molecular dynamics simulations of different C99-PS binding variants utilizing the AMBER14SB and Lipid14 force fields, respectively.

We investigated the three substrate entry sites that were most popular in the literature, but also sterically feasible and have identified at least one stable and reasonable binding mode, converging with existing mutational as well as structural data. Additionally, we calculated the potential of mean force of complex dissociation for every investigated and stable  $\gamma$ -secretase-C99 complex.

The model can be used as the basis for further experimental investigations of this biologically and medically highly relevant system.

## Quantum Chemical Calculation of Electron Ionization Mass Spectra for General Organic and Inorganic Molecules

Vilhálmur Ásgeirsson<sup>1</sup>, Christoph Alexander Bauer<sup>2</sup>, Stefan Grimme<sup>2</sup>

<sup>1</sup>*Faculty of Physical Sciences and Science Institute, University of Iceland, 107 Reykjavík, Iceland*

<sup>2</sup>*Mulliken Center for Theoretical Chemistry, Institute of Physical and Theoretical Chemistry, University of Bonn, Berlingstr. 4, 53115 Bonn, Germany.*

We present the computation of electron ionization (EI) mass spectra of organic, organometallic and inorganic molecules by our well established Quantum Chemistry Electron Ionization Mass Spectra (QCEIMS) approach[1] The efficient and robust GFN-xTB semi-empirical Hamiltonian[2] has been implemented in the `qceims` code, enabling its use as a standalone program. GFN-xTB has been parametrized for elements up to  $Z = 86$ . We show comparisons of experimental and computed mass spectra for (i) organic molecules that undergo rearrangement reactions (*e. g.*, the McLafferty rearrangement), (ii) organometallic compounds like ferrocene, and (iii) inorganic main group molecules.[3] GFN-xTB without any specific re-parametrization performs remarkably well for the computation of EI mass spectra and mostly outperforms other semiempirical methods. The efficiency of the GFN-xTB-QCEIMS combination and its accuracy allows a large-scale database validation of GFN-xTB computed mass spectra for structurally very different molecules which is planned in our laboratory as the next step.

[1] C. A. Bauer, S. Grimme, *J. Phys. Chem. A*, **120**, 3755–3766 (2016).

[2] S. Grimme, C. Bannwarth, P. Shushkov, *J. Chem. Theory Comput.* **13**, 1989-2009 (2017).

[3] V. Ásgeirsson, C. A. Bauer, S. Grimme, *Chem. Sci.* DOI: 10.1039/C7SC00601B (2017).

## Computational kinetics of industrially relevant carbonylation reactions from renewable resources

Emilija Kohls<sup>1</sup>, Matthias Stein<sup>1</sup>

<sup>1</sup>Max Planck Institute for Dynamics of Complex Technical Systems, Sandtorstr. 1, 39106 Magdeburg, Germany

In light of the depletion of petrochemicals, there is a need for alternative, sustainable feedstock for the chemical industry. The renewables of interest for industrial applications are primarily fats and oils that contain long carbon chains and C=C double bonds. Here, we study two homogeneously catalyzed, industrially relevant carbonylation reactions: hydroformylation and hydroesterification using 1-dodecene and methyl 10-undecenoate as long chain unsaturated model substrates (Figure 1).

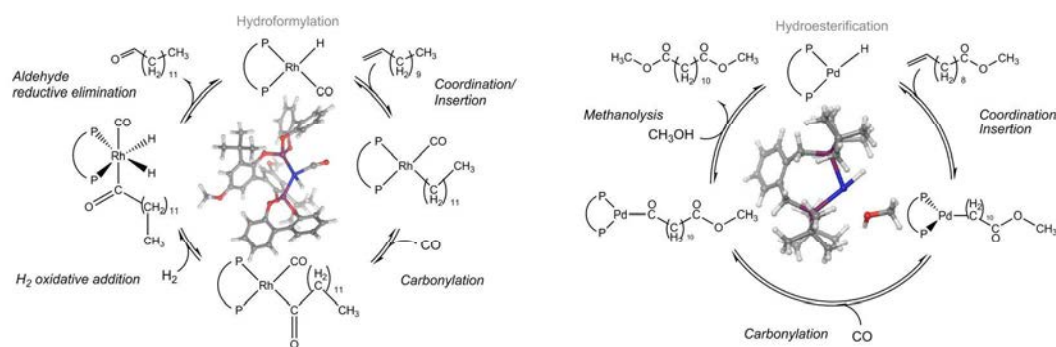


Figure 1. Schematic reaction cycles of hydroformylation (left) of 1-dodecene and hydroesterification (right) of methyl 10-undecenoate.

Detailed mechanistic pictures from DFT calculations required for the kinetic modeling of both of the processes are presented. Both catalytic cycles follow similar reaction pathways. The similarities and the differences of the two potential energy surfaces were compared. For the kinetic modeling, transition state theory and the energetic span model were used. The results were compared to experimental observations. The study elucidates the decisive steps for product selectivity and the calculated selectivities are in a very good agreement with experiment. Unreactive catalyst species and reasons for catalyst loss were identified.

## Quantum-Chemical Investigations on Photocatalytically Active Covalent Organic Frameworks

Gökçen Savasci<sup>1</sup>, Frederik Haase<sup>2</sup>, Tanmay Banerjee<sup>2</sup>, Kerstin Gottschling<sup>2</sup>,  
Bettina V. Lotsch<sup>2</sup>, Christian Ochsenfeld<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of Munich (LMU), 81377 Munich, Germany*

<sup>2</sup>*Max Planck Institute for Solid State Research, 70569 Stuttgart, Germany*

Covalent Organic Frameworks (COFs) are a novel class of crystalline organic materials with well-defined and predictable pore structures, assembled from molecular building blocks (see review [1]). Emerged from a successful result of reticular design, thoroughly selected organo-molecular building blocks are reacted in dynamic covalent reactions to form predesigned layered frameworks. These materials do not only have exceptional thermal stabilities, they also show permanent porosity with high specific surface areas. Their extraordinary and versatile properties have offered these materials superior potential in diverse applications, such as in gas storage, adsorption, catalysis and even for the use in biosensors [2], whereas recent applications investigate their utilization as drug delivery vessels [3]. A recently discovered azine-linked COF adds to the list of applications by showing promising photocatalytic activity [4], another one within a tunable framework for visible light-induced hydrogen generation [5].

In order to rationalize experimentally observed trends in photocatalytic activity, quantum-chemical calculations were performed. Model systems were selected as molecular clusters from building block units, to mimic the extent of the predesigned layered framework in small and systematic steps. We calculated band gaps and electronic excitations, as well as difference densities for the brightest excited states in order to compare the behavior of building blocks and more extended model systems for the investigated framework.

- [1] X. Feng, X. Ding, and D. Jiang, *Chem. Soc. Rev.* **41**, 6010 (2012).
- [2] P. Wang, Q. Wu, L. Han, S. Wang, S. Fang, Z. Zhang, and S. Sun, *RSC Adv.* **5**, 27290 (2015).
- [3] V. S. Vyas, M. Vishwakarma, I. Moudrakovski, F. Haase, G. Savasci, C. Ochsenfeld, J. P. Spatz and B. V. Lotsch, *Adv. Mater.* **28**, 8749 (2016).
- [4] L. Stegbauer, K. Schwinghammer, and B. V. Lotsch, *Chemical Science* **5**, 2789 (2014).
- [5] V. S. Vyas, F. Haase, L. Stegbauer, G. Savasci, C. Ochsenfeld, and B. V. Lotsch, *Nat. Commun.* **6**, 8508 (2015).

## Quantized Thermodynamic Properties from the Analysis of Smoothed Trajectories

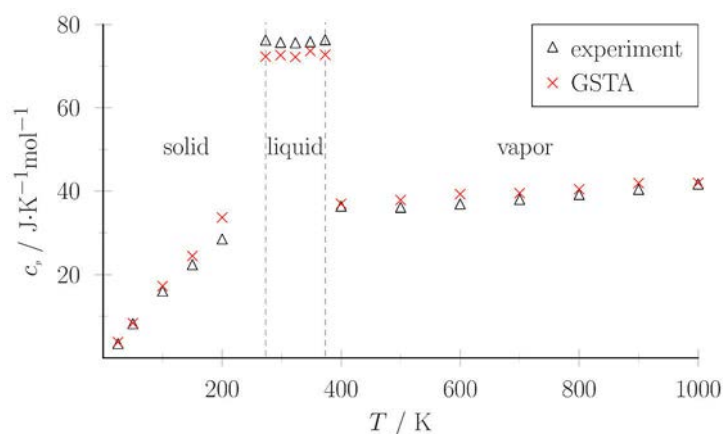
Dénes Berta<sup>1</sup>, Dávid Ferenc<sup>1</sup>, Imre Bakó<sup>1</sup>, Ádám Madarász<sup>1</sup>

<sup>1</sup>*Research Centre for Natural Sciences, Hungarian Academy of Sciences  
Magyar tudósok körútja 2., Budapest, Hungary, 1117*

Nuclear quantum effects (NQE) have significant contribution to thermodynamic quantities, and very expensive methods are necessary for their accurate calculations such as path-integral molecular dynamics (PIMD). Because of this, in most of the calculations NQEs are simply neglected or only taken into account within the quantum harmonic oscillator approximation.

Here we present a new method, Gaussian smoothed trajectory analysis (GSTA) to incorporate nuclear quantum effects from molecular dynamics simulations. To obtain quantum corrected data the time dependent variables of simulations such as coordinates, forces and velocities are smoothed with a Gaussian function. The proposed method gives the exact zero point energy for harmonic oscillator, and also leads to the correct heat capacities in the high temperature limit, even for anharmonic systems. One of the main advantage of GSTA is that the different motions do not need to be separated like rotation, translation, vibration etc. In other words, the exact partition functions do not need to be constructed.

The broad applicability is demonstrated on examples of harmonic oscillator and different states of water. Born-Oppenheimer Molecular Dynamics (BOMD) simulations have been performed for ideal gas at B3PW91/6-311g(d,p) level of theory up to the temperature of 5000 K. Classical molecular dynamics have been carried out with SPC/Fw water model for Ih ice, liquid water and vapor (Figure). Respect to the experimental heat capacity, GSTA outperforms previous calculations from the literature in a very wide temperature range at much smaller computational cost than PIMD.



Although we focus on heat capacity in this study, our method can be extended to determine nuclear quantum effect on other thermodynamic quantities such as entropy or free energies.

## State-average analytical gradients and multireference perturbation theory for density matrix renormalization group (DMRG)

Leon Freitag<sup>1</sup>, Yingjin Ma<sup>1, 2</sup>, Stefan Knecht<sup>1</sup>, Celestino Angeli<sup>3</sup>, Markus Reiher<sup>1</sup>

<sup>1</sup>*Laboratorium für Physikalische Chemie, ETH Zürich, Vladimir-Prelog-Weg 2, 8093 Zurich, Switzerland*

<sup>2</sup>*Department of High Performance Computing Technology and Application Development, Computer Network Information Center, Chinese Academy of Sciences, Beijing 100190, China*

<sup>3</sup>*Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Ferrara, Via Fossato di Mortara 17, 44121 Ferrara, Italy*

Density matrix renormalization group (DMRG)[1, 2] is now an established remedy for the exponential scaling problem of the multiconfigurational methods. Together with developments such as Cholesky decomposition of two-electron integrals (CD)[3], calculations of properties of increasingly larger systems featuring strong correlation, such as transition metal complexes, have become possible.

In this contribution, we present the formalism and implementation of analytical gradients for a state-average DMRG self-consistent field (DMRG-SCF) wavefunction, which may be employed in structure optimizations or ab-initio molecular dynamics simulations. We also present applications of the recently developed second-order n-electron valence state perturbation theory employing Cholesky decomposition and a DMRG reference wavefunction (CD-DMRG-NEVPT2)[4] on excited state, spin state and dissociation energies of a series of transition metal complexes.

- [1] K. H. Marti, M. Reiher, *Z. Phys. Chem.* **2010**, 224, 583–599.
- [2] G. K.-L. Chan, S. Sharma, *Annu. Rev. Phys. Chem.* **2011**, 62, 465–481.
- [3] F. Aquilante, L. Boman, J. Boström, H. Koch, R. Lindh, A. S. de Merás, T. B. Pedersen in *Linear-Scaling Techniques in Computational Chemistry and Physics* (Eds.: R. Zalesny, M. G. Papadopoulos, P. G. Mezey, J. Leszczynski), Springer Netherlands, **2011**, pp. 301–343.
- [4] L. Freitag, S. Knecht, C. Angeli, M. Reiher, *J. Chem. Theory Comput.* **2017**, 13, 451–459.

## Enantioselectivity and Computations: Random Phase Approximation for a Hydroboration Reaction

Paola Nava<sup>1</sup>

<sup>1</sup>*Aix Marseille Université, Centrale Marseille, CNRS, iSm2 UMR 7313, 13397 Marseille, France. e-mail: paola.nava@univ-amu.fr*

Recently, an asymmetric Rhodium-directed hydroboration reaction has been reported, which proceeds through the B-H bond activation of NHC-boranes (NHC=N-heterocyclic carbenes). [1] In order to get insights into the mechanism, theoretical calculations have been performed, on the pathways leading to either the *S* or the *R* product, the latest being the preferred one. These systems are quite challenging for computations, since differences in energies responsible for the enantioselectivity are usually small, close to the accuracy of standard levels of theory. Furthermore, non-covalent interactions are crucial, since the chirality transfer is a consequence of the constraints imposed by the bulky chiral ligands coordinated to the metal.

The RPA (Random Phase Approximation) method has been tested, since it improves upon standard DFT without the introduction of empirically parametrized terms for non-covalent interactions. [2] Some preliminary calculations, including CCSD(T), were performed on Wilkinson-like complexes to test the accuracy of the RPA (Random Phase Approximation) method for the hydride formation, which is a crucial step in the hydroboration mechanism. After some further tests on cationic systems, the RPA (Random Phase Approximation) method was employed to obtain accurate energies on systems of about 100 atoms.

Our calculations indicate that the preferred mechanism implies a [Rh]-H migratory insertion step and the enantioselectivity is the result of a subtle conjunction of thermodynamical and kinetic factors.

[1] M. Toure, O. Chuzel, J.-L. Parrain, *J. Am. Chem. Soc.*, **134**, 17892-17895 (2012).

[2] H. Eshuis, J. E. Bates, F. Furche, *Theor. Chem. Acc.*, **131**, 1084 (2012).



## Direct dynamic DFT study of possible reaction mechanism of low- $\kappa$ SiOCH films with nitrogen atoms

E.N. Voronina<sup>1,2</sup>, Yu.A. Mankelevich<sup>1</sup>, T.V. Rakhimova<sup>1</sup>

<sup>1</sup> Skobeltsyn Institute of Nuclear Physics, Lomonosov Moscow State University,  
119991, Moscow, Russia

<sup>2</sup> Faculty of Physics, Lomonosov Moscow State University, 119991, Moscow, Russia  
voroninaen@nsrd.sinp.msu.ru

Damage of porous organosilicate glass SiOCH-based films used as interlayer low- $\kappa$  dielectrics in modern ultra large scale integration devices is a serious problem for plasma processing technology. To reduce the damage of low- $\kappa$  films it is of importance to understand the detailed stages of the film etching by various radicals, including neutral F, O and N atoms [1]. Various working mixtures including nitrogen containing components ( $\text{NH}_3$ ,  $\text{N}_2$ ) are probed in order to reduce the damage of low- $\kappa$  films [2]. N atoms interactions with  $\text{CH}_x$  surface groups are also of importance for diamond chemical vapor deposition and doping [3].

Previously we have studied experimentally the damage of low- $\kappa$  films under neutral N atom impact and analyzed the obtained results via computer simulation with density functional theory (DFT) method [4]. Our DFT calculations showed that ground state atoms  $\text{N}(^4\text{S})$  do not react with  $\text{Si}-\text{CH}_3$  surface groups of OSG pristine films even at high translational energy. It means that reactive conversions are probably activated by excited nitrogen atoms, namely, by its insertion into C-H bonds resulting in the formation of metastable  $\text{Si}-\text{CH}_2\text{NH}$  groups. Incident N atoms can interact with these groups initiating a plenty of further reactions and surface groups.

In this work, we investigate possible reactions of the  $\text{Si}-\text{CH}_2\text{NH}$  groups with incident N atoms in the ground and excited states using direct dynamics simulation with DFT method implemented in VASP code. Our calculations were carried out for molecules of a medium size (~20 atoms) representing the essential bonding of the SiOCH films. The results obtained include the description of possible reactions, the potentials between interacting species and some statistical data.

This work is supported by the Russian Scientific Fund (RSF), Grant №16-12-10361.

- [1] M. R. Baklanov et al., *J. Appl. Phys.* **113**, 041101 (2013)
- [2] T. V. Rakhimova et al., *J. Phys. D: Appl. Phys.* **48**, 175203 and 175204 (2015).
- [3] M.W. Kelly et al., *J. Phys. Chem. A*, **121**, 2046 (2017).
- [4] E.N. Voronina et al., *Eur. Phys. J. D* **71**, 111 (2017).

## Recent Advances in Interactive Quantum Chemistry

Adrian H. Mühlbach<sup>1</sup>, Alain C. Vaucher<sup>1</sup>, Markus Reiher<sup>1</sup>

<sup>1</sup>Laboratory of Physical Chemistry, ETH Zürich, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland

Real-time quantum chemistry [1, 2, 3] has been introduced by our group as a new approach to computational studies in chemistry[4]. It is based on ultra-fast quantum chemical calculations and allows for an interactive exploration of chemical reactivity. An ongoing effort is made to improve the immersion [5] and broaden the scope of applications.

We present recent advances in the field of real-time quantum chemistry, especially concerning improvements with respect to self-consistent field (SCF) convergence [6, 7] and detection of possible charge- and spin-state changes during an exploration [8].

The inherently high computational cost of iterative SCF methods can be significantly reduced by providing a sufficiently good guess for the initial density matrix. We presented an extrapolation scheme that constructs such an initial density matrix guess, consequently reducing computational time drastically [6]. We also presented a fast and automated approach to detect and cure incorrect orbital convergence, which is especially suited for electronic structure calculations on sequences of molecular structures (as occurring in interactive explorations, ab initio molecular dynamics and structure optimizations) [7].

- [1] Marti, K. H.; Reiher, M., *J. Comput. Chem.*, **30**, 2010–2020, (2009).
- [2] Haag, M. P.; Reiher, M., *Int. J. Quantum Chem.*, **113**, 8–20, (2013).
- [3] Haag, M. P.; Reiher, M., *Faraday Discuss.*, **169**, 89–118, (2014).
- [4] Haag, M. P.; Vaucher, A. C.; Bosson, M.; Redon, S.; Reiher, M., *ChemPhysChem*, **15**, 3301–3319, (2014).
- [5] Vaucher, A. C.; Haag, M. P.; Reiher, M., *J. Comput. Chem.*, **37**, 805–812, (2016).
- [6] Mühlbach, A. H.; Vaucher, A. C.; Reiher, M., *J. Chem. Theory Comput.*, **12**, 1228–1235, (2016).
- [7] Vaucher, A. C.; Reiher, M., *J. Chem. Theory Comput.*, **13**, 1219–1228, (2017).
- [8] Vaucher, A. C.; Reiher, M., *J. Chem. Inf. Model.*, **56**, 1470–1478, (2016).

## Screening methods for linear-scaling short-range hybrid DFT calculations on CPU and GPU architectures

Matthias Beuerle<sup>1</sup>, Jörg Kussmann<sup>1</sup>, Christian Ochsenfeld<sup>1</sup>

<sup>1</sup>*Chair of Theoretical Chemistry, Department of Chemistry, University of Munich (LMU), Butenandtstrasse 7, D-81377 München, Germany and Center for Integrated Protein Science (CIPSM) at the Department of Chemistry, University of Munich (LMU), Butenandtstrasse 5-13, D-81377 München, Germany*

Hybrid density functionals, i.e., functionals that employ a fraction of exact exchange, are among the most successful functionals in density functional theory (DFT). While including exact exchange into DFT calculations enables more accurate results, it also increases the computational cost of the calculation. This is especially true for calculations in solids, where the exact exchange calculation might even lead to convergence problems. One approach to reduce the computational cost of hybrid DFT calculations and enable a more elaborate combination of exact exchange and density functional exchange are short-range hybrid functionals [1]. Short-range hybrid functionals use short-range exact exchange, introduced through the substitution of the Coulomb operator by an short-range Coulomb operator and resort to a DFT description in the long-range regime. The first and probably most popular short-range hybrid functional is the HSE functional [1–3].

For conventional exchange matrix calculations methods exist to reduce the computational cost of the calculation to linear scaling [4, 5] with respect to the number of basis functions. For short-range hybrid calculations those methods, however, do not include the additional decay introduced by the short-range Coulomb operator. Therefore we presented screening schemes that allow for efficient, linear-scaling short-range exchange calculations employing Gaussian basis sets for both CPU and GPU architectures [6]. The introduction of our screening methods allows for speedups of up to a factor 7.8 as compared to the underlying linear-scaling algorithm, while numerical control over the accuracy is retained.

- [1] Heyd, Scuseria, Ernzerhof, *J. Chem. Phys.* **118**, 8207 (2003)
- [2] Heyd, Scuseria, Ernzerhof, *J. Chem. Phys.* **124**, 219906 (2006)
- [3] Krukau, Vydrov, Izmaylov, Scuseria, *J. Chem. Phys.* **125**, 224106 (2006)
- [4] Ochsenfeld, White, Head-Gordon, *J. Chem. Phys.* **109**, 1663 (1998)
- [5] Kussmann, Ochsenfeld, *J. Chem. Phys.* **138**, 134114, (2013)
- [6] Beuerle, Kussmann, Ochsenfeld, *J. Chem. Phys.* **146**, 144108 (2017)

## Multiscale modeling of interfaces in photovoltaic devices

**Mattias L. N. Palsgaard<sup>1,2</sup>, Andrea Crovetto<sup>2</sup>, Tue Gunst<sup>2</sup>, Troels Markussen<sup>1</sup>,  
Ulrik G. Vej-Hansen<sup>1</sup>, Jess Wellendorff<sup>1</sup>, Ole Hansen<sup>2</sup>, Mads Brandbyge<sup>2</sup>, Kurt  
Stokbro<sup>1</sup>**

<sup>1</sup>*QuantumWise A/S, Fruebjergvej 3, DK-2100 Copenhagen, Denmark*

<sup>2</sup>*DTU Nanotech, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark*

$\text{Cu}_2\text{ZnSnS}_4$  (CZTS) is a promising material for use in thin film photovoltaics. Since it has a direct band gap, devices based on CZTS should absorb light more effectively than conventional Silicon-based solar cell devices which suffer from the indirect band gap of Silicon. Moreover, CZTS is based purely on earth abundant elements making it very cost effective compared to already successful thin film solar cell technologies like CdTe. So far, CZTS devices have much lower open circuit voltages (OCV) than expected. Disadvantageous (cliff-like) band-alignment between CZTS and its CdS buffer-layer has been the most popular explanation for this, even though measurement on the band-alignment in a state-of-the-art CZTS device with over 7% efficiency show favorable (spike-like/flat) band-alignments.

In this talk, we present an alternative explanation for the OCV-deficit. Using a method [1] based on tools available in the Atomistix Tool Kit (ATK) software package, we have studied the electronic structure at the interface between CZTS and CdS in detail. Here, we have identified a shallow state localized at the interface. When included in device level simulations, such a state leads to significant deterioration of the OCV, and when this is taken into account, we can quantitatively reproduce measurements on state-of-the-art CZTS solar cells. This shows how parameters needed for device characterization can be extracted from atomistic device simulations and how the interplay between atomistic and device level simulations can be a powerful tool in characterizing the thin-film solarcell devices of the future.

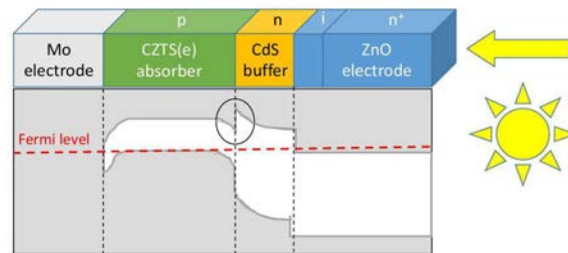


Figure 1: Sketch of photovoltaic device, including energy bands.

- [1] A. Crovetto, M. Palsgaard, T. Gunst, T. Markussen, K. Stokbro, M. Brandbyge and O. Hansen, *Appl. Phys. Lett.* **110**, 083903 (2017).

## Chemistry and physics at semi-infinite surfaces using the surface Green's function method

Søren Smidstrup<sup>1</sup>, Daniele Stradi<sup>1</sup>, Jess Wellendorff<sup>1</sup>, Petr Khomyakov<sup>1</sup>, Ulrik G. Vej-Hansen<sup>1</sup>, Maeng Eun Lee<sup>1</sup>, Hannes Jonsson<sup>2</sup>, Kurt Stokbro<sup>1</sup>

<sup>1</sup>QuantumWise A/S, Fruebjergvej 3, DK-2100 Copenhagen, Denmark

<sup>2</sup>Faculty of Physical Sciences, University of Iceland VR-III, 107 Reykjavík, Iceland

We present an efficient implementation of the Green's function method for density-functional simulations of a surface coupled to a bulk reservoir. This surface Green's function (SGF) method alleviates several fundamental issues with the commonly used slab approximation for surface calculations within the density functional theory formalism. The SGF method describes the surface as a truly semi-infinite system, in which the surface region is self-consistently coupled to the bulk reservoir. The method employs pseudopotentials and localized basis functions. We illustrate the versatility of the SGF method for a wide range of surface problems inherently problematic for the slab approximation, including metal work function calculations, band alignment in thin-film semiconductor structures, surface states of metals and topological insulators, and adsorbates interacting with surfaces in electrostatic fields. Comparisons with slab calculations and experimental data establish the efficiency and accuracy of the surface Green's function method.

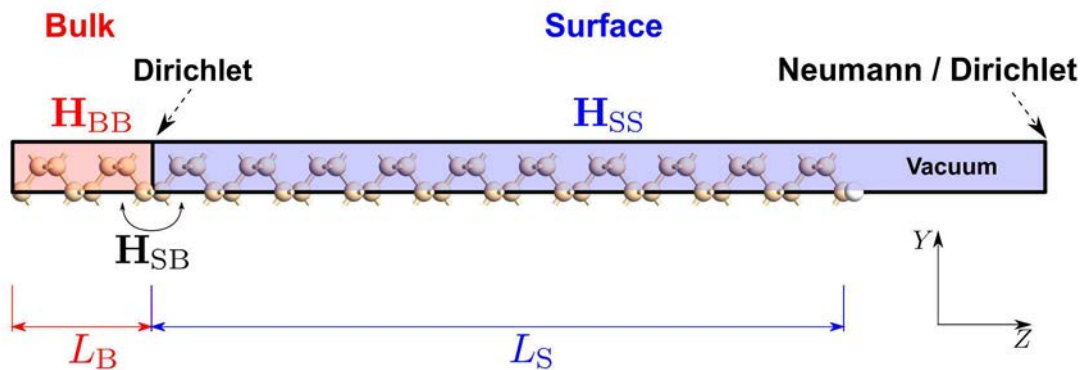


Figure 1: Illustration of a typical semi-infinite surface configuration. The Hamiltonians of the semi-infinite surface (HSS) and of the periodic bulk HBB, are coupled through the coupling terms HSB. A Dirichlet boundary condition is used at the boundary between the periodic bulk and the semi-infinite surface. In the vacuum region, a Neumann (Dirichlet) boundary condition is used for calculations without (with) an electric field.  $L_B$  and  $L_S$  are the lengths along the Z Cartesian direction of the periodic bulk and of the surface, respectively.

## A Genetic Algorithm for the 3D Structure Prediction of Peptides & Proteins

**Murat Kılıç, Marta A. S. Perez, Nicholas J. Browning, Ursula Rothlisberger**

*Laboratory of Computational Chemistry and Biochemistry (LCBC),  
Swiss Federal Institute of Technology Lausanne (EPFL), CH-1015 Lausanne, Switzerland*

The accurate prediction of the 3D structure of amino acid (AA) sequences is vital to the fast enumeration of protein libraries within the fields of bioinformatics and theoretical chemistry. We have already shown that Genetic Algorithms (GAs) can be utilized to explore training sets of small organic molecules for machine learning [1] and efficiently optimize functionality of biomimetic scaffolds [2]. We are now extending this technique to 3D structure prediction of AA sequences.

To facilitate this method, a fitness function, which characterizes structure stability must be designed. In this work, we explore different fitness functions and benchmark them against a database of 3D structures of peptides in gas-phase (at B3LYP//6-31G(d,p) level). We have benchmarked a variety of classical and ab initio methods as well as non-polarizable and polarizable force fields. We have additionally compared a variety of functional forms, which we discuss and validate in this work.

- [1] N.J. Browning, R. Ramakrishnan, O.A. von Lilienfeld, U. Rothlisberger, *J. Phys. Chem. Lett.*, **8**, 1351 (2017).
- [2] E. Brunk, M.A.S. Perez, P. Athri, U. Rothlisberger, *ChemPhysChem*, **17**, 3831 (2016).

## Radical N-heterocycle molecules: from excited states calculations to new molecular design

Arnaud Jaoul<sup>1</sup>, Grégory Nocton<sup>1</sup>, Carine Clavaguéra<sup>2</sup>

<sup>1</sup>Laboratoire de Chimie Moléculaire, Ecole Polytechnique, Université Paris-Saclay, Route de Saclay, 91128, Palaiseau, France

<sup>2</sup>Laboratoire de Chimie-Physique, Université Paris-Sud, Université Paris-Saclay, 91405 Orsay Cedex, France

N-heterocycles have found applications in multiple domains such as in medicinal chemistry, because they can act as powerful binding ligands. Recently, new molecules involving the formation of radical N-heterocycle ligands have been synthesized with transition metal<sup>[1]</sup> or lanthanide<sup>[2]</sup> ions. In these molecules, the heterocycle acts as an electron reservoir that could have impact during catalysis<sup>[3]</sup> or for magnetic<sup>[4]</sup> applications. As a result, fundamental understanding of the electronic structure of the radical N-heterocycles is of crucial importance.

Electronic absorption spectrum of phenanthroline radical has been evaluated using both *ab initio* and TDDFT methods. The poor comparison between the experimental and the mono-determinant theoretical spectra has been related to the inner electronic structure of phenanthroline radical that presents a multi-reference ground state involving two  $\pi^*$  orbitals. This property was further used to design new molecules that could have significant influence in the field of magnetism and catalysis by combining an organometallic specie, a lanthanide molecule and a radical N-heterocycle ligand<sup>[5]</sup>.

The electronic absorption spectra of phenanthroline radical will be detailed at the TDDFT, CC2, EOM-CCSD, CASSCF and CASPT2 level of theory. The electronic structure of the compound will then be linked to lanthanide derivatives containing a radical phenanthroline ligand. Finally, the design of molecules active in catalysis and in magnetism will be detailed.

[1] T. R. Dugan, E. Bill, K. C. MacLeod, G. J. Christian, R. E. Cowley, W. W. Brennessel, S. Ye, F. Neese, P. L. Holland, *J. Am. Chem. Soc.*, **134**, 20352–20364 (2012).

[2] G. Nocton, W. W. Lukens, C. H. Booth, S. S. Rozenel, S. A. Medling, L. Maron, R. A. Andersen, *J. Am. Chem. Soc.*, **136**, 8626–8641 (2014).

[3] P. J. Chirik, K. Wieghardt, *Science*, **327**, 794–795 (2010).

[4] C. A. Gould, L. E. Darago, M. I. Gonzalez, S. Demir, J. R. Long, *Angew. Chem. Int. Ed. Engl.*, **2017**, in press

[5] V. Goudy, A. Jaoul, M. Cordier, C. Clavaguéra, G. Nocton, *J. Am. Chem. Soc.*, **2017**, submitted

## Searching the growth mechanism of molybdenum disulfide: Atomic layer deposition under an electric field

Fabian Pieck<sup>1</sup>, Ralf Tonner<sup>1</sup>

<sup>1</sup>*Fachbereich Chemie and Material Sciences Center, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, 35032 Marburg, Germany*

The two-dimensional material molybdenum disulfide is of particular interest for microelectronic and optoelectronic devices because of its direct band gap in the range of visible light. [1]

A key step for the large-scale usage is a controlled synthesis route. The method of atomic layer deposition enables the synthesis of a few monolayers, but the growth mechanism is still unknown. A suitable starting point is the idea that the physical adsorption of the precursors is strengthened by an electric field, which is originated from charged impurities. [2] In addition the growth could be initiated by known defect sites.[3]

We use periodic density functional theory to identify the structures and reaction paths of the precursors molybdenum(V)chloride and hydrogen sulfide on a monolayer of molybdenum disulfide. By means of a homogenous external electric field we are able to estimate the influence of a charged impurity on the structures and reactions (Fig. 1.). These findings yield insights into the growth mechanism and allow to predict the plausibility of the field controlled growth versus the defect controlled growth.

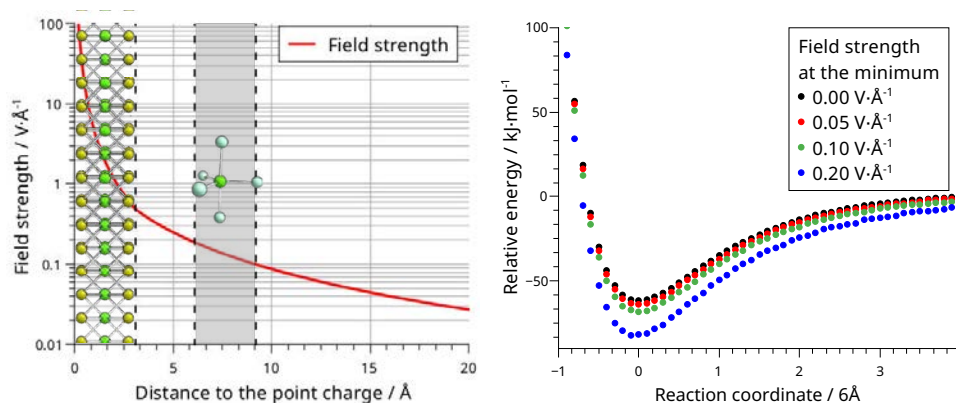


Figure 1: Field strength of a point charge ( $q = 1e$ ) screened by a MoS<sub>2</sub> monolayer ( $\epsilon_r = 3.09$ ) (left). Influence of a homogenous electric field on the adsorption potential. Field strength decreases as a function of the reaction coordinate (right).

[1] D. Jariwala et. al., *ACS Nano* **8**, 1102 (2014).

[2] Y. Kim et. al., *Sci. Rep.* **6**, 18754 (2016).

[3] W. Zhou et. al., *Nano Lett.* **13**, 2615 (2013).

This work was supported by the German Science Foundation (DFG) within the framework of the GRK 1782.



## Spin-dependent effects in electronic devices

**Martin Sebastian Zöllner<sup>1,\*</sup>, Mohammad Mehdi Ramin Moayed<sup>2</sup>, Thomas Bielewicz<sup>2</sup>, Christian Klinke<sup>2</sup>, Carmen Herrmann<sup>1</sup>**

<sup>1</sup>*Institute of Inorganic and Applied Chemistry, University of Hamburg, Martin-Luther-King Platz 6, 20146 Hamburg, Germany*

<sup>2</sup>*Institute of Physical Chemistry, University of Hamburg, Grindelallee 117, 20146 Hamburg, Germany*

\**martin.zoellner@chemie.uni-hamburg.de*

The first-principles based description of spin-dependent properties in molecular junctions and solid-state electronic devices (e.g. 2D nanosheets) is a very useful tool for the interpretation of experimental results and for the prediction of possible applications in the field of spintronics and spin-orbitronics [1, 2]. For molecular systems, magnetoresistance [3] and the chiral-induced spin selectivity effect [4], and for solid-state materials the Rashba spin-orbit coupling [2] can be mentioned as examples for interesting spin-dependent effects.

We are interested in a density-functional theory based description of spin-dependent properties of such systems. Among other things, we use our post-processing code ARTAIOS [5] to analyze the conductance of molecular junctions in the coherent tunneling regime.

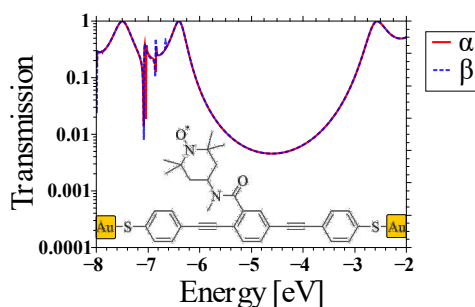


Figure 1: Transmission function for alpha and beta electrons of an organic radical [3].

- [1] A. R. Rocha, V. M. García-Suárez, S. W. Bailey, C. J. Lambert, J. Ferrer, S. Sanvito, *Nat. Mater.* **4**, 335 (2005).
- [2] M. M. Ramin Moayed, T. Bielewicz, M. S. Zöllner, C. Herrmann, C. Klinke, *Nature Commun.* **8**, 15721 (2017).
- [3] R. Hayakawa, M. A. Karimi, J. Wolf, T. Huhn, M. S. Zöllner, C. Herrmann, E. Scheer, *Nano Lett.* **16**, 4960 (2016).
- [4] R. Naaman, D. H. Waldeck, *Annu. Rev. Phys. Chem.* **66**, 263 (2015).
- [5] M. Deffner, L. Groß, T. Steenbock, B. A. Voigt, G. C. Solomon, C. Herrmann, ARTAIOS - a transport code for postprocessing quantum chemical electronic structure calculations, available from <https://www.chemie.uni-hamburg.de/ac/herrmann/software/index.html>.

**Explicitly dipole-polarizable, coarse-grained force fields from first principles.****Frank Uhlig<sup>1</sup>, Johannes Zeman<sup>1</sup>, Jens Smiatek<sup>1</sup>, Christian Holm<sup>1</sup>**<sup>1</sup>*Institute for Computational Physics, University of Stuttgart, Allmandring 3, 70569 Stuttgart, Germany*

Advances in computational power and algorithms have led to an expansion of research using molecular dynamics simulations. In particular, force-field based molecular simulations with explicit treatment of electronic polarizability are now routinely applied in theoretical research. However, introducing dipole-polarizability still substantially increases the computational cost of simulations. For systems comprised of molecules with many polarizable atoms, the inclusion of explicit dipole-polarizability can become a real bottleneck. Typical examples of such systems are ionic liquids, that are comprised of large bulky ions. For these ionic liquids, we hence adopt a coarse-graining scheme. This scheme is illustrated in the figure below for the 1-butyl-3-methyl-imidazolium cation.

We develop a scheme to generate parameters for polarizable force fields based on simple, physical principles. Based on the quantum-mechanical volume of atoms in molecules, we derive parameters of the dispersion interaction, and dipole-polarizability on an equal footing. Starting from a first-principles, atomistic representation, this scheme allows us to generate, in principle arbitrarily, coarse-grained representations. The resulting force-field, together with an appropriate point-charge distribution, accurately reproduces quantum-mechanical interactions.

We examine the validity and applicability of our new force-field at the example of 1-ethyl-/butyl-/hexyl-3-methyl-imidazolium hexafluorophosphate/tetrafluoroborate ionic liquids. Simulations with these novel force fields reproduce both experimental observables, as well as electronic properties extracted from density functional based molecular dynamics. Hence, we can generate accurate force fields that, due to their coarse-grained nature, allow for accurate simulations of large systems on long timescales.

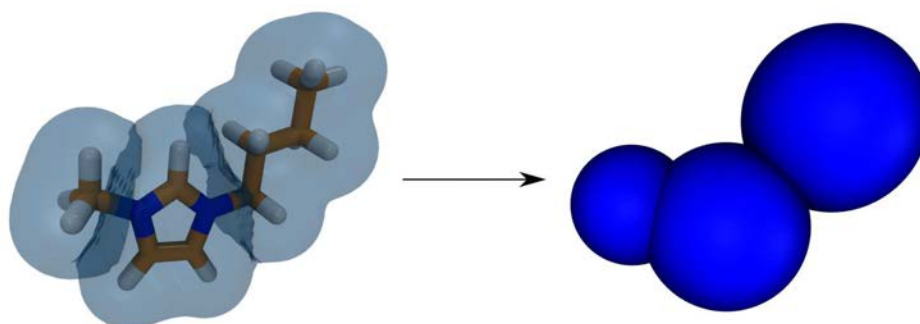


Figure 1: Illustration of the coarse-graining scheme at the example of the 1-butyl-3-methyl-imidazolium cation. Left side, atomistic representation with partitioned electron density shown as blue isosurfaces. Right side, coarse-grained representation.

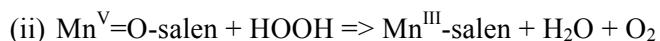
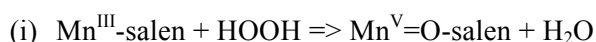
## CATALASE ACTIVITY OF MANGANESE(III) COMPLEXES

A.Romero Rivera<sup>1</sup>, M. Swart<sup>1,2</sup>

1. Institut de Química Computacional i Catàlisi, University of Girona, Spain.

2. ICREA, Barcelona, Spain

The study of oxidative stress and the close relationship this has with ageing means there is much interest in the effects of antioxidant complexes, which often contain manganese. Although experimental data in biological studies have shown very positive effects in prolonging the lifespan of mice,<sup>[1]</sup> there is much uncertainty about what is the origin of these effects and how they could be improved. Interestingly, very few chemical investigations have been performed on this subject,<sup>[2,3]</sup> and even less using computational chemistry. Therefore, we studied the mechanism of a catalase reaction of manganese-salen complex that proved beneficial at the biological level, using advanced methods of computational chemistry.<sup>[4]</sup> The catalase mechanism contains two phases, a first one in which a Mn<sup>III</sup>-salen complex captures an oxygen from a hydrogen-peroxide into water and oxygen:



Besides a detailed description of all the different reaction pathways present in the mechanism and the important role of the spin state,<sup>[5]</sup> we have found new results and concept that open the possibility of improving the efficiency and feasibility of the antioxidant complex. This is especially relevant for the initial part of the mechanism. Where the manganese complex has to capture the hydrogen-peroxide in order to activate it. Two important aspects for the description of the reaction mechanism is the ability of the computational methods to correctly describe the spin-state and the weak interactions, for which S12g performs excellently.<sup>[4]</sup>

[1] S. Doctrow, *Science* **289**, 1567 (2000).

[2] Y. G. Abashkin, *J. Phys. Chem. B* **108**, 2708 (2004).

[3] D. G. Nocera, *Inorg. Chem.* **45**, 7572 (2006).

[4] M. Swart, *Chem. Phys. Lett.* **580**, 166 (2013).

[5] A. Romero-Rivera, M. Swart, *in preparation* (2015).

## An Automated Approach for Structural Characterization of Complex Organic Compounds by Collisional Cross Section Computation

Sarah Moe<sup>1</sup>, Zhanfei Liu<sup>2</sup>, Alessandro Cembran<sup>1</sup>

<sup>1</sup>*Department of Chemistry and Biochemistry, University of Minnesota Duluth, 1049*

*University Dr., Duluth, USA*

<sup>2</sup>*Department of Marine Science, The University of Texas at Austin, 750 Channel View Dr.,  
Port Aransas, USA*

Ion mobility-mass spectrometry is a powerful experimental technique that allows for the separation of compounds based on their collisional cross section (CCS). We present a platform that allows to test a large number of compounds against experimentally derived CCS values, with the aim to deconvolute structural characterization by using computational methods. Our platform was first tested against a series of tetra-alkylammonium compounds with differing alkyl chain lengths, serving as a standard with which to compare theoretical and experimental values. Theoretical values were obtained using the MOBCAL software program, which is widely used to calculate collisional cross sections of organic compounds [1]. Energy minimized structures were generated at the molecular mechanical level, and CCS values calculated using MOBCAL were in excellent agreement with experimental values. Furthermore, we calculated CCS values for a set of singly-charged cationic compounds that were isolated from marine samples, including solanocapsine, leucyl-leucyl-norleucine, leucyl-leucine, and N(alpha)-t-butoxycarbonyl-L-leucine. A large ensemble of coordinate sets pertaining to each structure was generated using AM1 semi-empirical methods and simulated annealing implemented in CHARMM. The possibility of multiple protonation sites necessitated structure optimization with quantum mechanical calculations. Lowest energy conformations were obtained from each structural ensemble at the M06-2X/6-311++G(d,p) level. Our approach allows for the assignment of protonation sites by sampling ion positions, and it provides a means for structural analysis of versatile sets of organic compounds.

[1] M. Mesleh, J. Shvartsburg, G. Schatz, M. Jarrold, *J. Phys. Chem.* **100**, 16082 (1996).

[2] I. Campuzano, M. Bush, C. Robinson, C. Beaumont, K. Richardson, H. Kim, H. I. Kim, *Anal. Chem.* **84**, 1026 (2011).

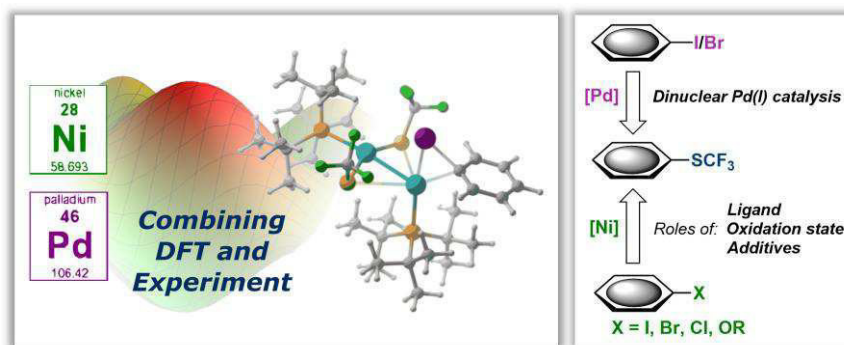
## Uncovering Mechanistic Details in Organometallic Catalysis – A Combination of Computation and Experiment

Indrek Kalvet, Franziska Schoenebeck

*Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany*

Reaching new levels of efficiency, reactivity and sustainability in chemical synthesis via the development of new catalytic systems is a subject of continuous efforts. Strong fundamental understanding of the processes involved is oftentimes crucial for making any further advances. Multiple possible reaction pathways, numerous potential active species and the difficulties in controlling the selectivities and reactivities are some of the challenges that burden homogenous transition metal catalysis. Fundamental studies, combining computations and experiments are a promising approach in overcoming these hurdles. In this regard, this poster will feature the uncovering of mechanistic insights in Pd- and Ni-catalysis from a computational perspective.

Included are our studies on the novel concept of direct dinuclear Pd(I) catalysis and its applications in the halogen exchange and trifluoromethylthiolation reactions.[1,2] In the context of Ni-catalysis, mechanistic studies have played a crucial role in the development of new methods for the trifluoromethylthiolation of aryl chlorides and C-O electrophiles.[3,4] Furthermore, pathways leading to catalyst deactivation, and the roles of oxidation states of Ni, and the ligands have been thoroughly examined.[5]



- [1] I. Kalvet, K. J. Bonney, F. Schoenebeck, *J. Org. Chem.* **79**, 12041 (2014).
- [2] G. Yin, I. Kalvet, F. Schoenebeck, *Angew. Chemie Int. Ed.* **54**, 6809 (2015).
- [3] G. Yin, I. Kalvet, U. Englert, F. Schoenebeck, *J. Am. Chem. Soc.* **137**, 4164 (2015).
- [4] A. B. Dürr, G. Yin, I. Kalvet, F. Napoly, F. Schoenebeck, *Chem. Sci.* **7**, 1076 (2016).
- [5] I. Kalvet, Q. Guo, G. J. Tizzard, F. Schoenebeck, *ACS Catal.* **7**, 2126 (2017).

## Calculation of the excited state properties of molecular photocatalysts based on Ruthenium and Osmium

Miłosz Martynow<sup>1</sup>, Julien Guthmuller<sup>1</sup>

<sup>1</sup>*Department of Theoretical Physics and Quantum Information  
Faculty of Applied Physics and Mathematics  
Gdańsk University of Technology  
st. Gabriela Narutowicza 11/12, 80-233 Gdańsk, Poland*

One of the promising approaches in energy production is looking for molecules which can be used as photocatalysts, generating molecular hydrogen from the solar radiation. Hydrogen obtained in this way can be stored and employed as fuel. A detailed understanding of the excited state properties is required to optimize the electron transfer and the efficiency of hydrogen production. In this contribution, the properties of the singlet and triplet excited states are investigated for a series of molecular photocatalysts [1]-[3] (Figure 1). The energy, oscillator strength, orbital character and geometry of the states are calculated at the DFT/TDDFT level with B3LYP including the effects of the solvent with the PCM. The differences between the systems are analyzed in order to predict how the changes in the excited state properties impact the electron transfer processes.

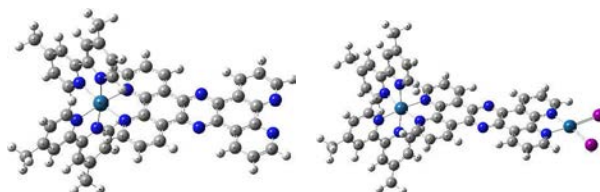


Figure 1: Example of investigated compounds. Geometry of  $(tbbpy)_2Os^{2+}(tpphz)$  (left) and  $(tbbpy)_2Os^{2+}(tpphz)PtI_2$  (right) molecules.

### Acknowledgements

The authors are grateful to the Narodowe Centrum Nauki (Project No. 2014/14/M/ST4/00083) for financial support. The calculations have been performed at the Wrocław Center for Networking and Supercomputing (grant no. 384) and at the Academic Computer Center TASK in Gdańsk.

- [1] J. Habermehl, D. Sorsche, P. Murszat, and S. Rau, *Eur. J. Inorg. Chem* **21**, 3423 (2016).
- [2] . Guthmuller, L. González, *Phys. Chem. Chem. Phys* **12**, 14812 (2010)
- [3] M. G. Pfeffer et al., *Angew. Chem. Int. Ed.* **54**, 6627 (2015).

## Core-level spectroscopy with the *GW* approximation

Dorothea Golze<sup>1</sup>, Patrick Rinke<sup>1</sup>

<sup>1</sup>*COMP/Department of Applied Physics, Aalto University, P.O. Box 11100, Aalto FI-00076, Finland*

Techniques such as X-ray photoelectron spectroscopy (XPS) can access the inner shells of the atoms and provide insight into the electronic structure of molecules and materials. Accurate simulation tools to reproduce XP spectra are important to support the interpretation of experimental spectra, in particular for complex molecules with unknown structure. Even though computationally efficient, density functional theory based approaches suffer from certain shortcomings and are often not accurate or consistent enough to resolve the spectrum.

Green's function theory in the *GW* approximation has become the method of choice for addition and removal energies of valence electrons in solids[1] and is now increasingly being applied to molecules and clusters[2]. However, *GW* core-level spectroscopy has thus far not received any attention. In this work, we present a method to extract core-level energies from all-electron *GW* calculations. In low-scaling, state-of-the-art *GW* implementations[3, 4, 5], the self-energy is typically computed in the imaginary frequency domain followed by an analytic continuation to the real frequency axis. However, the analytic continuation becomes highly inaccurate for frequencies far away from the fermi level and is not suitable for the computation of core excitations. Thus, we propose to evaluate the self-energy on the real-frequency axis using the contour deformation (CD) technique in combination with a resolution-of-the-identity approximation for the screened Coulomb interaction. We implemented this method in the FHI-aims program package[6]. We demonstrate that the CD technique yields the same valence excitations as the analytic continuation with the Pade approximation. For the core states, our method reproduces the features of the self-energy very well compared to the real-frequency implementation in Turbomole[7]. We also present benchmark studies of XPS data for small gas-phase molecules.

- [1] P. Rinke *et al.*, *New J. Phys.* **7**, 126 (2005).
- [2] M. J. van Setten *et al.*, *J. Chem. Theory Comput.* **11**, 5665 (2015).
- [3] X. Ren *et al.*, *New J. Phys.* **14**, 053020 (2012).
- [4] J. Wilhelm, M. Del Ben, J. Hutter, *J. Chem. Theory Comput.* **12**, 3623 (2016).
- [5] P. Liu, M. Kaltak, J. Klimes, G. Kresse *Phys. Rev. B* **94**, 165109 (2016)
- [6] V. Blum *et al.* *Comput. Phys. Commun.* **180**, 2175 (2009)
- [7] M. J. van Setten, F. Weigend, F. Evers *J. Chem. Theory Comput.* **9**, 232 (2012).

## Photophysical and photochemical properties of nitrobenzene from a static and dynamics perspective

Angelo Giussani,<sup>1</sup> Graham A. Worth<sup>1</sup>

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK.

Nitrobenzene is the smallest nitroaromatic compound, is a common environmental pollutant normally produced in urban atmospheres during incomplete combustion,[1] and is an ingredient in energetic materials.[2] Its photophysics is characterized by three lifetimes (100 fs, 6 ps, and 480 ps)[3] and by a particularly high value of the triplet quantum yield, greater than 0.8.[4] Under UV radiation the system can photoreact leading to the formation of different photoproducts, as NO<sub>2</sub>, NO and O.[5] In our group a static description of the system's photoresponse has been performed, obtained through CASPT2//CASSCF computations in the framework of the so-called "photochemical reaction path approach".[6] A dynamics study of the evolution of nitrobenzene after light absorption has then been performed, using the direct dynamics variational multi-configurational Gaussian (DD-vMCG) method, which is a full quantum dynamics methodology, allowing the resolution of the time-dependent nuclear Schrödinger equation variationally.[7] The latter study will allow extracting the timescales of the characterized processes, so rationalizing the reported experimental lifetimes, and evaluating the efficiency of the various decay paths obtained in the static study. In the present contribution the derived static description of nitrobenzene's photophysics and photochemistry is presented, together with the dynamics results obtained up to date.

[1] R. Atkinson, E. C. Tuazon, T. J. Wallington, S. M. Aschmann, J. Arey, A. M. Winer, J. N. Pitts, *Environ. Sci. Technol.* **21**, 64 (1987).

[2] T. B. Brill, K. James, *J. Chem. Rev.* **93**, 2667 (1993).

[3] M. Takezaki, N. Hirota, M. Terazima, *J. Chem Phys.* **108**, 4685 (1998).

[4] M. Takezaki, N. Hirota, M. Terazima, *J. Phys. Chem. A* **101**, 3443 (1997).

[5] D. B. Galloway, J. A. Bartz, L. G. Huey, F. F. Crim, *J. Chem. Phys.* **98**, 2107 (1993).

[6] A. Giussani, G. A. Worth *J. Chem Theory Comput.* DOI: 10.1021/acs.jctc.6b01149 (2017)

[7] G. W. Richings, I. Polyak, K. E. Spinlove, G. A. Worth, I. Burghardt, B. Lasorne, *Int. Rev. Phys. Chem.* **34**, 269 (2015).



## Reparameterization of PM6 Parameters for Manganese and Applications to Binuclear Manganese Complexes

**Toru Saito, Yu Takano**

*Department of Biomedical Information Sciences, Graduate School of Information Sciences,  
Hiroshima City University*

For closed-shell systems, semiempirical molecular orbital (SE-MO) methods have time-tested reliability and are now routinely used for many applications [1]. It is not true for open-shell species. Detailed verifications of their electronic and geometric structures have not seemed to be examined at the SE-MO levels. Previously, we re-optimized PM6 [2] (called rPM6) mainly focusing on the parameters for the basic elements (H, C, N, O, P, and S) [3, 4] by means of our own training set and part of GMTKN30 database [5]. The spin-unrestricted rPM6 (UrPM6) calculation showed significant improvement in computing open-shell species. While the original UPM6 is susceptible to the spin polarization (spin contamination) effect and thus overestimates the singlet-triplet energy gaps, UrPM6 provides the values similar to UDFT results. In the present study, we present a reparameterized set of parameters for manganese to compute magnetic interactions in binuclear manganese complexes. Several results of preliminary calculations will be presented.

- [1] W. Thiel, *WIREs: Comput. Mol. Sci.* **4**, 145 (2014).
- [2] J. J. P. Stewart, *J. Mol. Model.* **13**, 1173 (2007).
- [3] T. Saito, Y. Kitagawa, Y. Takano, *J. Phys. Chem. A* **120**, 8750 (2016).
- [4] T. Saito, Y. Kitagawa, T. Kawakami, S. Yamanaka, M. Okumura, Y. Takano, *Polyhedron*, *in press*.
- [5] L. Goerigk, S. Grimme, *J. Chem. Theory Comput.* **7**, 291 (2011)

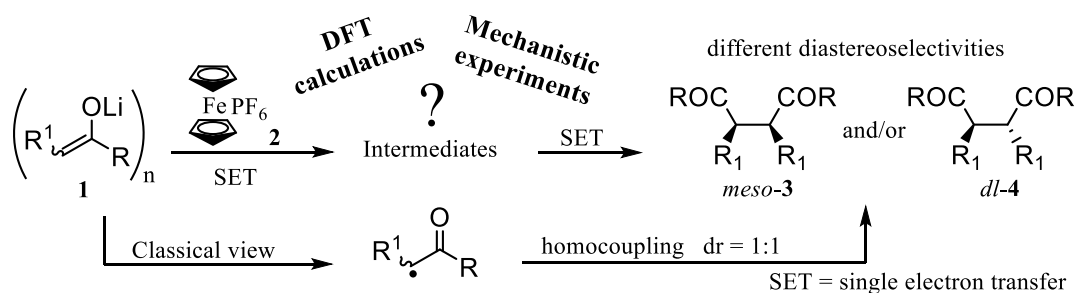
## Mechanism of Oxidative Enolate Dimerizations Elucidated through Computational and Experimental Investigations

Emanuela Jahn,<sup>1</sup> Prokopis C. Andrikopoulos,<sup>1</sup> Lubomír Rulíšek,<sup>1</sup>

Ullrich Jahn<sup>1</sup>

<sup>1</sup>*Institute of Organic Chemistry and Biochemistry of the Czech Academy of Science  
Flemingovo náměstí 542/2, 166 10 Praha 6, Czech Republic*

Oxidative dimerizations of enolates induced by metal salts offer a short access to 1,4-dicarbonyl compounds and were employed in the total syntheses of natural products [1]. The lack of selectivity, unless the enolates were auxiliary bound, led to the assumption that the mechanism was merely free radical homocoupling (Scheme). However, the fact that oxidation of enolate aggregate **1** by ferrocenium hexafluorophosphate **2** afforded dimers *meso*-**3** and *dl*-**4** with different selectivities points to a more complex mechanism.



Density functional theory calculations elucidated different pathways depending on the structure of aggregate **1** [2]. Initial electron transfer from **1** leads to an aggregated  $\alpha$ -carbonyl radical, which implies that the dimerization is an intramolecular reaction. The intermediate structures were optimized in gas phase and in implicit THF solution. The transition states were located and their nature confirmed by IRC calculations. The DFT calculations correctly predicted the dimer *meso*-**3** to be the major product in THF.

Mechanistic experiments prove the role of aggregation and the correlation of the diastereoselectivity with enolate geometry. They generally support the computational results.

[1] a) F. Guo, M. D. Clift, R. J. Thomson, *Eur. J. Org. Chem.* 4881, (2012). b) C. S. Yeung, V. M. Dong, *Chem. Rev.* **111**, 1215, (2011).

[2] a) H. J. Reich, *Chem. Rev.* **113**, 7130, (2013). b) A. Harrison-Marchand, F. Mongin, *Chem. Rev.* **113**, 7470, (2013).

## Quantum Mechanical Scoring of Protein-Ligand Binding Enhanced with Explicit-Solvent Effects

**Cemal Köprülüoğlu<sup>1,2</sup>, Martin Lepšík<sup>1</sup>, Jindřich Fanfrlík<sup>1</sup>, Susanta Haldar<sup>1</sup>,  
Haresh Ajani<sup>1,2</sup>, Pavel Hobza<sup>1,2</sup>**

<sup>1</sup> *Department of Computational Chemistry, Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, v.v.i., Flemingovo nám. 2, 166 10 Prague 6, Czech Republic*

<sup>2</sup> *Department of Physical Chemistry, Palacký University, 77146 Olomouc, Czech Republic*

Drug-target binding is determined mostly by noncovalent interactions including hydrogen bonding with bridging water molecules. A reliable quantitative description from the physical principles ultimately requires the use of quantum mechanical (QM) methods.<sup>[1]</sup> Coupled with an implicit solvent method, the energetics of protein-ligand interactions can be captured and native ligand poses identified.<sup>[2]</sup> However, the contributions of the bridging water molecules to the binding affinity can only be described when explicit water dynamics is included.

Here, we present the combined use of explicit-solvent molecular dynamics (MD) with semi empirical QM (SQM) based scoring featuring PM6-D3H4X/COSMO method.<sup>[3]</sup> We show that the affinities of 21 novel pyrazolo[1,5-a]pyrimidine cyclin-dependent kinase 2 (CDK2) inhibitors could only be satisfactorily interpreted when the implicit solvent treatment was enhanced by including explicitly six water molecules in the active site. Their entropies as calculated by explicit-solvent MD tool WaterMap, Schrodinger, LLC, were added to the SQM/COSMO score. A more refined view of the interplay between the dynamics of the protein, ligand and solvent was obtained from 80 ns explicit-solvent MD. The findings presented here stress the importance of including explicit waters and protein, ligand and solvent dynamics for a reliable explanation of drug-target affinities.

- [1] K. Raha, M. B. Peters, B. Wang, N. Yu, A. M. Wollacott, L. M. Westerhoff, K. M. Merz, *Drug Discov Today*. **12**, 725 (2007).
- [2] A. Pecina, R. Meier, J. Fanfrlík, M. Lepšík, J. Rezac, P. Hobza, C. Baldauf, *Chem. Commun.* **52**, 3312 (2016).
- [3] M. Hylsová, B. Carbain, J. Fanfrlík, L. Musilová, S. Haldar, C. Köprülüoğlu, P. S. Brahmakshatriya, R. Jorda, V. Kryštof, P. Hobza, A. Echalié, K. Paruch, M. Lepšík *Eur. J. Med. Chem.* **126**, 1118 (2017).

## A theoretical study on catalytic activity of h-BN monolayer by doping C atoms

Min Gao<sup>1,2</sup>, Ben Wang<sup>3</sup>, Maki Nakahara<sup>3</sup>, Masashi Adachi<sup>3</sup>, Andrey Lyalin<sup>4</sup>, Tetsuya Taketsugu<sup>1,2,4</sup>

<sup>1</sup>*Faculty of Science, Hokkaido University, Kita 10 Nishi 8, Kita-ku, Sapporo, Japan.*

<sup>2</sup>*ESICB, Kyoto University, Goryo-Ohara 1-30, Nishikyo-ku, Kyoto, Japan*

<sup>3</sup>*Graduate School of Chemical Sciences and Engineering, Hokkaido University, Kita 10 Nishi 8, Kita-ku, Sapporo, Japan.*

<sup>4</sup>*GREEN, National Institute for Materials Science, Namiki 1-1, Tsukuba, Japan.*

The catalytic reactions with molecular oxygen have attracted lots of interests due to its various crucial industrial chemical processes, such as selective oxidation and epoxidation, exhaust gas emission control for automotive applications, oxygen reduction reaction in fuel cells, and so on. Extensive efforts are devoted to the development of effective catalytic materials for oxygen activation. Currently, most of the industrially used catalysts are based on precious transition metals (Pt, Pd, Ru, etc.). Therefore, the development of effective, cheap and environment friendly catalysts based on the nonprecious abundant elements is an emerging task for commercial market. Recently, we have demonstrated theoretically [1] and proved experimentally that even inert and catalytically inactive materials, h-BN can be functionalized to become active catalysts at nanoscale [2]. Our findings open new and yet unexplored routes to design effective catalyst based on materials that have never been considered for catalytic applications.

In the present work, we performed a systematic theoretical investigation of the catalytic activity of the C doped h-BN monolayer toward a reaction with molecular oxygen adsorption. It is demonstrated that C doping into B position on the h-BN monolayer produces n-type semiconductor material with noticeable catalytic activity in the large area extended far away from the C impurity. The oxygen reduction reaction [3] and oxidation reactions of CO and C<sub>2</sub>H<sub>4</sub> are also considered. The details of the reactions will be shown in the presentation.

[1] A. Lyalin, M. Gao, T. Taketsugu. *Chem. Rec.* **16**, 2324-2337(2016).

[2] K. Uosaki, G. Elumalai, H. Noguchi, T. Masuda, A. Lyalin, A. Nakayama, T. Taketsugu, *J. Am. Chem. Soc.* **136**, 6542-6545(2014).

[3] M. Gao, M. Adachi, A. Lyalin, T. Taketsugu, *J. Phys. Chem. C* **120**, 15993-16001(2016)

## Dynamics of chloroethylene resonant anions surveyed by bound state and scattering calculations

F. Kossoski<sup>1,2</sup>, M. Barbatti<sup>1</sup>, M. T. do N. Varella<sup>3</sup>, M. A. P. Lima<sup>2</sup>

<sup>1</sup>*Aix Marseille Univ, CNRS, ICR, Marseille, France, fabris@if.usp.br*

<sup>2</sup>*Instituto de Física “Gleb Wataghin”, Universidade Estadual de Campinas, 13083-859  
Campinas, Brazil*

<sup>3</sup>*Instituto de Física, Universidade de São Paulo, 05314-970 São Paulo, Brazil*

When chloroethylene interacts with a free low-energy electron ( $<10$  eV), the formed compound may dissociate into the chloride anion and the corresponding neutral radical [1]. The current understanding on dissociative electron attachment (DEA) to chloroethylene is still at a qualitative level, given the absence of theoretical attempts to describe it. That is even more surprising when one realizes the relevance of electron-induced cleavages of halogen containing species in biological, environmental and plasma environments (see Refs. [2, 3] and references within). Here we report theoretical results on the electronic spectra and dynamics of chloroethylene anion. We described the electronic problem with bound state (multireferential configuration interaction) and electron scattering calculations (Schwinger multichannel method with pseudopotentials [4]). Still counting on both methodologies, potential energy surfaces for the anion states were built. Finally, we have performed quantum wavepacket and fewest-switches semi-classical propagations, while incorporating a model to describe the possibility of autodetachment in the later. We found that chloroethylene presents a lower-lying  $\pi^*$  shape resonance and a higher-lying  $\sigma^*$  resonance, this one dissociative along the C–Cl bond. DEA should initiate from electron capture into the  $\pi^*$  orbital, which acquires a  $\sigma^*$  character upon out-of-plane deformations, and then induces the bond stretching and the elimination of the chloride anion. On the other hand, direct formation of the  $\sigma^*$  resonance is ineffective for DEA, due to the smaller vertical autodetachment lifetime of this state. The present results provide a detailed picture on how DEA to chloroethylene takes place, and also allow for the computation of theoretical DEA cross sections. By comparing results obtained with different approaches, one can assess open theoretical and methodological questions regarding the dynamics of autodetaching resonances. The authors acknowledge financial support from São Paulo Research Foundation (FAPESP).

[1] J. K. Olthoff, J. A. Tossell, J. H. Moore, *J. Chem. Phys.* **83**, 5627 (1985).

[2] F. Kossoski, M. H. F. Bettega, M. T. do N. Varella, *J. Chem. Phys.* **140**, 24317 (2014).

[3] F. Kossoski, M. T. do N. Varella, *J. Chem. Phys.* **145**, 44310 (2016).

[4] K. Takatsuka and V. McKoy, *Phys. Rev. A* **24**, 2473 (1981).

## Conformational Entropy of Claisen Rearrangement

### Calculated by Rate Constant Matrix Contraction Method

Yosuke Sumiya<sup>1</sup>, Satoshi Maeda<sup>2</sup>

<sup>1</sup>*Chemical Sciences and Engineering, Hokkaido University, N13-W8, Kita-ku, Sapporo, Japan*

<sup>2</sup>*Department of Chemistry, Hokkaido University, N10-W8, Kita-ku, Sapporo, Japan*

Recently, reaction path networks has been made automatically with quantum chemical calculations. The artificial force induced reaction (AFIR) method can construct reaction path networks efficiently<sup>1</sup>. However, it is difficult to perform a simulation covering experimental timescales  $10^3$ – $10^5$  s on complex networks. In the networks, elementary steps that occur in short timescales  $\sim 10^{-12}$  s exist. That is, a small step-size ( $\ll \sim 10^{-12}$  s) must be used in the time evolution. This problem is called stiff problem.

In this study, we developed a new approach which solves the stiff problem and is applicable to complex networks<sup>2</sup>. This method (rate constant matrix contraction, RCMC) contracts fast elementary steps recursively. The RCMC was applied to the Claisen rearrangement reaction of  $\text{CH}_2\text{CHOCH}_2\text{CHCH}_2$ . The reaction network consists of 23 equilibrium structures (EQs) and 62 transition states (TSs) (Fig. 1). The reaction network includes many ultrafast steps corresponding to conformational rearrangements. To achieve chemical accuracy, the reaction network was made at CCSD(T)-F12a/jul-cc-pVTZ//M062X/6-311+G(2d, p) computational level.

By applying the RCMC, we got overall rate constants taking account of conformational changes. The overall rate constants obtained by the following three ways are compared: (1) the experimental value,  $2.875 \times 10^{-3} \text{ s}^{-1}$ , (2) the value estimated by the RCMC,  $1.794 \times 10^{-3} \text{ s}^{-1}$ , and (3) the value obtained by a simple method only considering the rate-determining step,  $1.486 \times 10^{-2} \text{ s}^{-1}$ . With regard to the activation free energy, the RCMC reproduced the experimental value with an error of 1.8 kJ/mol.

The difference between the activation free energies of (2) and (3) was 8.2 kJ/mol, which was attributed to the conformational entropy. It was found that the conformational entropy made a substantial contribution to the overall rate constant even in the Claisen rearrangement of small chain molecules.

[1] S. Maeda, et al. *J. Comput. Chem.* **35**, 166 (2014). [2] Y. Sumiya, et al., *J. Phys. Chem. A* **119**, 11641 (2015).

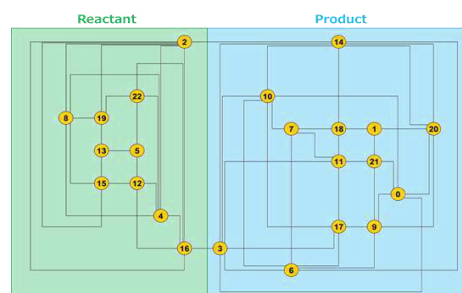


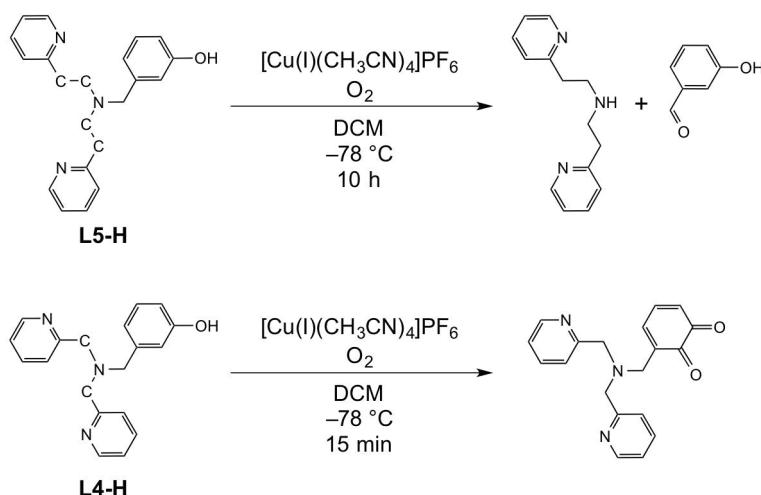
Fig. 1 The reaction network of Claisen rearrangement. Node and edge correspond to EQ and reaction path.

# A Mechanistic Investigation of the Biomimetic Ligand Hydroxylation in Coppy-Oxygen Complexes

J. Peschina<sup>1</sup>, M. C. Holthausen<sup>1</sup>

<sup>1</sup>*Institut für Anorganische und Analytische Chemie, Goethe-Universität, Max-von-Laue-Str. 7, 60438 Frankfurt/Main, Germany*

The enzymatic copper mediated hydroxylation inspired the development of various biomimetic tyrosinase models. Recently, Tuczek and coworkers synthesized the copper oxygen complexes **L5-H**<sup>[1]</sup> and **L4-H**<sup>[2]</sup>. Remarkably, only minor differences in steric demand, i.e. the number of linking carbon atoms in the supporting ligand, lead to markedly different reactivity: N-dealkylation (**L5-H**) and aromatic hydroxylation (**L4-H**) (Figure 1).



**Figure 1:** Investigated hydroxylation of **L5-H** (top) and **L4-H** (bottom) in presence of copper(I)-ions and dioxygen.

Here we report a detailed DFT study of Tuczek's copper mediated hydroxylation. Our results allow for a rationalization of the reactivity differences of the two copper-complexes and are in line with the experimental findings. Complementary TD-DFT studies provide further insights into the bis( $\mu$ -oxo) dicopper(III)  $\mu$ - $\eta^2$ : $\eta^2$ -peroxo dicopper(II) equilibrium, which determines the selectivity due to strongly directional interactions of the frontier orbitals.

[1] Rolff M., Hamann J. N., Tuczek F., *Angew. Chem. Int. Ed.*, **2011**, 50, 6924.

[2] Hamann J. N., Rolff M., Tuczek F., *Dalton Trans.*, **2015**, 44, 3251.

## Rotational tunneling of coupled methyl quantum rotors in $\gamma$ -picoline crystal within a pair-coupled model

Somayeh Khazaei and Daniel Sebastiani

*Institute of Chemistry, Martin-Luther-University Halle-Wittenberg, Von-Danckelmann-Platz 4, 06120 Halle (Saale), Germany*

At low temperature, methyl groups represent quantum rotors with quantized rotational states. The lowest excitation energy between the ground and first excited state, known as the tunnel splitting, is important in the context of hyperpolarization techniques in NMR spectroscopy[1, 2, 3, 4]. Complementarily, the extreme sensitivity of tunnel splitting on the potential energy surface (PES) gives rise to a unique probe of the interatomic interactions that are at the origin of the energy landscape.

Here, we present explicit calculations of the tunnel splitting from condensed-phase DFT energy profiles. The focus is on the effect of chemical environment (supramolecular packing) on the tunnel splitting. In particular, we study the influence of coupled motion of methyl rotors on the tunneling spectrum within a pair-coupled model. The quantum rotational energy levels are obtained by numerical solution of the corresponding two-dimensional time-independent Schrödinger equation. It turns out that the tunnel splitting caused by the coupling is maximized for the coupled rotors in which their total hindering potential is relatively shallow. Such a low hindered methyl rotational potential is predicted for  $\gamma$ -picoline at low temperature, where the shortest intermolecular distances of  $\approx 3.46$  Å are between face-to-face methyl groups. In this regard, given the recent success in computing methyl rotational PES using first-principles calculations[5], we compute two dimensional rotational energy profile of a pair of methyl rotors in  $\gamma$ -picoline crystal. The calculated energy levels agree very well with the measured multiplet structure of rotational-tunneling peaks. Moreover, the calculated density distribution of the three methyl protons resembles the experimental nuclear densities obtained from the Fourier difference analysis.

- [1] M. Icker, S. Berger, *J. Magn. Reson.* **219**, 1-3 (2012).
- [2] M. Icker, P. Fricke, T. Grell, J. Hollenbach, H. Auer and S. Berger, *Magn. Reson. Chem.* **51**, 815-820 (2013).
- [3] B. Meier, J.-N. Dumez, G. Stevanato, J. T. Hill-Cousins, S. S. Roy, P. Hakansson, S. Mamone, R. C. D. Brown, G. Pileio, and M. H. Levitt, *J. Am. Chem. Soc.* **135**, 18746 (2013).
- [4] J.-N. Dumez, P. Hakansson, S. Mamone, B. Meier, G. Stevanato, J. T. Hill-Cousins, S. S. Roy, R. C. D. Brown, G. Pileio and M. H. Levitt, *J. Chem. Phys.* **142**, 044506 (2015).
- [5] S. Khazaei, and D. Sebastiani, *J. Chem. Phys.* **145**, 234506 (2016).



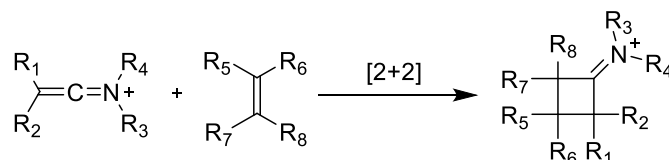
## The effect of substituents on the reactivity of keteniminium salts – a DFT study

**Gamze Tanriver,<sup>1</sup> Amandine Kolleth,<sup>2</sup> Alexandre Lumbroso,<sup>2</sup> Sarah Sulzer,<sup>2</sup> Alain De Mesmaeker,<sup>2</sup> and Saron Catak\*<sup>1</sup>**

<sup>1</sup>Department of Chemistry, Bogazici University, 34342 Bebek, Istanbul, TURKEY

<sup>2</sup>Syngenta Crop Protection AG, Crop Protection Research, Research Chemistry, Schaffhauserstrasse 101, CH-4332, Switzerland

Keteniminium chemistry is of recent interest due to its higher electrophilicity, reactivity and regioselectivity compared to ketenes.<sup>1</sup> The [2+2] cycloaddition reactions of keteniminium salts with alkenes have been by far the most studied; intermolecular as well as intramolecular reactions have been reported (Scheme 1).<sup>2</sup> Due to the limited general methods to attain substituted aminocyclobutanes/aminocyclobutenes, a straightforward general access from the corresponding iminium salts has gained considerable attention. An efficient new method for the synthesis of aminocyclobutanes via the [2+2] cycloaddition between various keteniminium salts and alkenes, followed by a reduction step<sup>3</sup> or by a nucleophilic addition<sup>4</sup> has been recently reported. These studies show that differing substituents play a significant role on the stability and reactivity of keteniminium salts. Herein, we outline a DFT study performed to investigate substituent effects on intermolecular [2+2] cycloaddition reactions and quantify the difference in both reactivity and stability of the keteniminium salts involved. In this context, various substituents were examined to gain insight on the influence of substituents and the results were compared with experimental data.



**Scheme 1.** Schematic representation of the [2+2] cycloaddition reaction of keteniminium salts and alkenes

[1] C. Madelaine, V. Valerio, N. Maulide, *Chem. Asian J.* **6** (9) (2011).

[2] a) B. Falmagne, J. Escudero, S. Taleb-Sahaoui, L. Ghosez, *Angew. Chem. Int. Ed. Engl.* **20** (1981). b) C. Houge, A. M. Frisque-Hesbain, A. Mockel, and L. Ghosez *J. Am. Chem. Soc.* **104** (1982). c) B. B. Snider, *Chem. Rev.* **88** (1988).

[3] A. Kolleth, A. Lumbroso, G. Tanriver, S. Catak, S. Sulzer-Mossé, A. De Mesmaeker, *Tetrahedron Lett.* **57** (2016).

[4] A. Kolleth, A. Lumbroso, G. Tanriver, S. Catak, S. Sulzer-Mossé, A. De Mesmaeker, *Tetrahedron Lett.* **57** (2016).

## **The generalized Bethe-Goldstone equation revisited: An incremental route towards the full configuration interaction limit**

**Janus Juul Eriksen<sup>1</sup>, Filippo Lipparini<sup>1</sup>, Jürgen Gauss<sup>1</sup>**

<sup>1</sup>*Institut für Physikalische Chemie, Johannes Gutenberg-Universität Mainz, Mainz, D-55128, Germany*

The full configuration interaction (FCI) model represents the exact solution to the electronic Schrödinger equation within a given fixed-sized one-electron basis set. However, its practical realization is generally impeded by the so-called curse of dimensionality, which is in general twofold; within a basis set of a certain quality, the scaling of the FCI model is exponential with respect to the number of electrons, and even for a fixed system size, the computational requirements grow exponentially with respect to the number of molecular orbitals. Here, it is demonstrated how FCI results in extended basis sets may be obtained to within sub-kJ/mol accuracy by decomposing the energy in terms of Bethe-Goldstone many-body expansions in the orbitals of the molecular system at hand. This extension of the FCI application range lends itself to two unique features of the current approach, namely that the total energy calculation can be performed entirely within considerably reduced orbital subspaces and may be so by means of embarrassingly parallel programming. Facilitated by a rigorous and methodical screening procedure and further aided by the use of virtual natural orbitals, all-electron numerical results are reported for H<sub>2</sub>O in core-valence basis sets ranging from double- to quadruple- $\zeta$  quality.

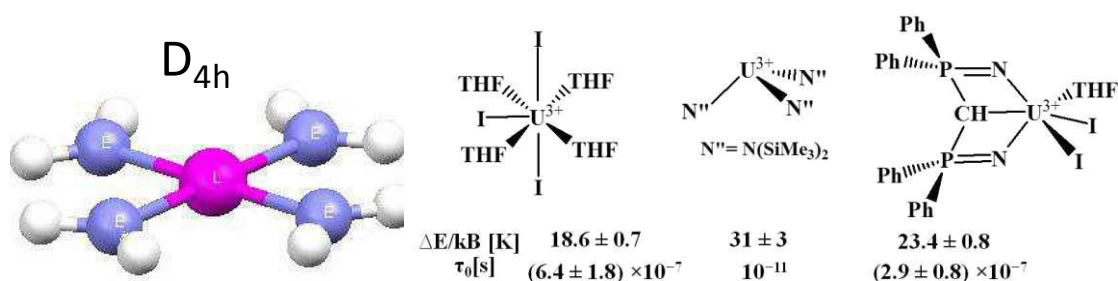
## Envisioning CO<sub>2</sub>-HCHO conversion, C-H activation catalysts and anisotropy in Actinide Molecular Nanomagnets : Theoretical Exploration

Tulika Gupta and Prof. Peter Comba

*Institute of Inorganic Chemistry, Heidelberg University, Germany*

*tulika.gupta@aci.uni-heidelberg.de*

Recent discovery of Molecular Nanomagnets (MnMs) by capture and fixation of CO<sub>2</sub> unravelled novel avenues in the enticing chemistry-physics-biology interphase. My preliminary focus remains efficient and selective conversion of CO<sub>2</sub> to HCHO. In compliance with earlier reported data [1], I am attempting optimization of this transformation in terms of selectivity, efficiency, catalyst stability, ligand variation on Ru<sup>II</sup> based catalyst harnessing DFT approach. I am also keen to estimate catalytic cycle for recently reported conversion of CO<sub>2</sub> to DMM (dimethoxy methane) using similar methodology after benchmarking [2]. Additionally, I intend to compute the structural, electronic and spectroscopic characteristics of C-H bond activation by unique Cu<sup>II</sup>-alkylperoxide complex. Despite significant utility of actinides, in the filed of MNMs they are at the nascent stage unlike lanthanides. In this relevance, I aim to understand apt metal coordination number, ligand field in dictating magnetic anisotropy behaviour in actinide based magnets sudyng U<sup>III/IV/V</sup>-N/O models [3].



- [1] S. Wesselbaum, V Moha, M. Meuresch, S. Broinski, K. M. Thenert, J. Kothe, T. V. Stein, U. Englert, M. Hölscher, J. Klankermayer and W. Leitner, *Chem. Sci.* **6**, 693 (2015).  
 [2] K. Thenert, K. Beydoun, J. Wiesenthal, W. Leitner and J. Klankmayer, *Angew. Chem. Int. Ed.* **55**, 12266 (2016). [3] J. D. Rinehart, K. R. Meihaus, J. R. Long, *J. Am. Chem. Soc.* **132**, 7572 (2010).

## General fit-basis functions and specialized coordinates in an adaptive density-guided approach to potential energy surfaces

Emil Lund Klinting<sup>1</sup>, Bo Thomsen<sup>2</sup>, Ian Heide Godtlielsen<sup>1</sup>, Ove Christiansen<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Aarhus University, Langelandsgade 140, Aarhus C, Denmark*

<sup>2</sup>*Theoretical Molecular Science Laboratory, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan*

The overall shape of a molecular energy surface can be very different for different molecules and different vibrational coordinates. This means that the fit-basis functions used to generate an analytic representation of a potential will be met with different requirements. It is therefore worthwhile to employ different types of fit-basis functions to provide more adequate fits. This becomes even more pronounced in an iterative  $n$ -mode expansion scheme such as the adaptive density-guided approach (ADGA) [1], where it is essential to capture the underlying physics quickly or risk introducing unnecessary single point calculations when constructing the molecular potential. We therefore present a uniform framework that can handle general fit-basis functions of any type which are specified on input [2]. This framework is implemented to suit the black-box nature of the ADGA in order to avoid arbitrary choices of non-linear parameters that are often contained in more specialized fit-basis functions.

We have tested different fit-basis functions including Morse and double-well shapes, which are clearly superior to the standard polynomial type fit-basis functions to represent these kinds of potentials. This results in a decreased number of single point calculations required during the potential construction. Especially the Morse-like fit-basis functions are of interest, when combined with rectilinear hybrid optimized and localized coordinates (HOLCs) [3], which can be generated as orthogonal transformations of the more standard normal coordinates (NCs). The HOLCs have a greater degree of locality compared to the NCs, which means that more one-mode potentials will have a Morse-like shape, resulting in a large decrease in the number of single point calculations required to construct a potential.

Curvilinear coordinates, of which the polyspherical coordinates [4] are a special class, can in this perspective provide even better conditions for the use of general fit-basis functions.

- [1] M. Sparta and D. Toffoli and O. Christiansen, *Theor. Chem. Acc.* **123** 413-429 (2009).
- [2] E. L. Klinting, B. Thomsen, I. H. Godtlielsen and O. Christiansen, *In Preparation*.
- [3] E. L. Klinting, C. König and O. Christiansen, *J. Phys. Chem. A* **119**, 11007-11021 (2015).
- [4] M. Ndong, L. Joubert-Doriol, H.-D. Meyer, A. Nauts, F. Gatti, and D. Lauvergnat, *J. Chem. Phys.* **136**, 034107 (2012).

## The Effect of Ions on the Clustering of Organic Acids and Sulfuric Acid

**Nanna Myllys<sup>1</sup>, Tinja Olenius<sup>2</sup>, Jonas Elm<sup>1</sup>, Theo Kurtén<sup>3</sup>, Hanna Vehkamäki<sup>1</sup>, and Ilona Riipinen<sup>2</sup>,**

<sup>1</sup>*Department of Physics, University of Helsinki, Finland*

<sup>2</sup>*Department of Environmental Science and Analytical Chemistry, Stockholm University, Sweden*

<sup>3</sup>*Department of Chemistry, University of Helsinki, Finland*

Atmospheric new-particle formation is believed to involve sulfuric acid coupled with a stabilizing component such as ions, bases, or oxidized organic compounds. We have previously studied the cluster formation between sulfuric acid and pinic acid or MBTCA, and found a favorable interaction between them. However, by cluster kinetics calculations we showed that the growth of the clusters is essentially limited by a weak binding of the largest clusters, suggesting that pinic acid and MBTCA cannot contribute the cluster growth when clustering occurs via neutral pathways [1]. Here we have investigated the ability of bisulfate anion, ammonium cation, and ammonia to enhance the formation and growth of sulfuric acid and pinic acid or MBTCA clusters.

Cluster structures have sampled using semi-empirical technique. Geometries are optimized and frequencies are calculated using three density functionals M06-2X, PW91, and  $\omega$ B97X-D with the 6-31++G\*\* basis set. Electronic energy corrections were performed using DLPNO-CCSD(T)/def2-QZVPP level of theory. Obtained Gibbs free energies are subsequently used to further investigate cluster kinetics.

The interaction with ions and sulfuric acid or carboxylic acid group is strong, and thereby small two-component ionic clusters are found to be very stable against evaporation. The presence of bisulfate stimulates the cluster formation by addition of sulfuric acid, whereas the presence of ammonium favors the addition of organic acids. Bisulfate and ammonium enhance the first steps of cluster formation; however, at atmospheric conditions cluster growth is limited due to the weak interaction of the larger three-component clusters which results in fast evaporation. [2]. Therefore, it is unlikely that organic acids and sulfuric acid, even together with bisulfate, ammonia, or ammonium can drive new-particle formation via clustering mechanisms, suggesting that perhaps chemical reactions are needed to explain observed atmospheric new-particle formation events in the presence of oxidized organic compounds.

[1] J. Elm, N. Myllys, T. Olenius, R. Halonen, T. Kurtén, H. Vehkamäki, *Phys. Chem. Chem. Phys.* **19**, 4877 (2017).

[2] N. Myllys, T. Olenius, T. Kurtén, H. Vehkamäki, I. Riipinen, J. Elm, *J. Phys. Chem. A*, accepted (2017).

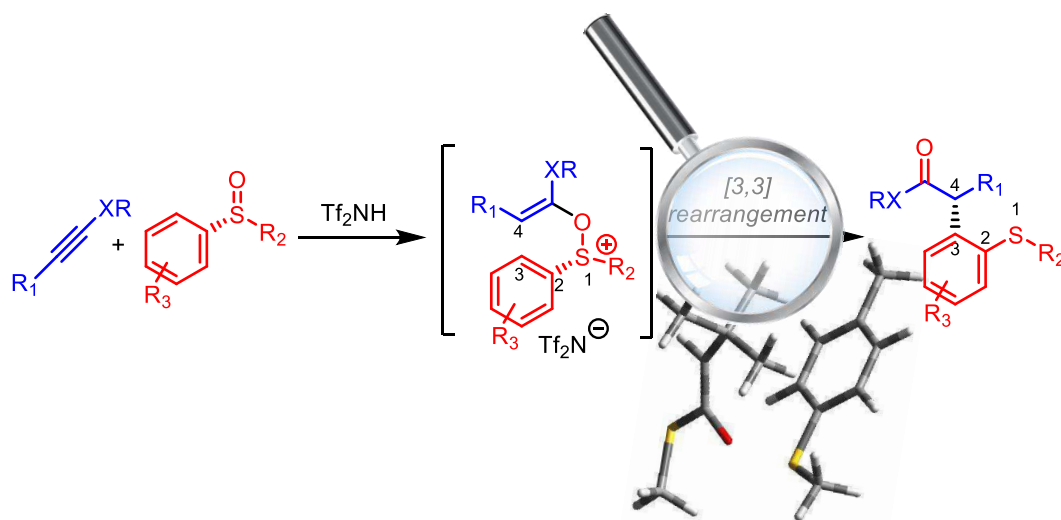
## Sulfoxide as a Chirality Information “Storage Device” to Perform Enantioselective Arylation: How Does It Work?

**Boris Maryasin<sup>1,2</sup>, Dainis Kaldre<sup>2</sup>, Daniel Kaiser<sup>2</sup>, Oliver Gajsek<sup>2</sup>, Nuno Maulide<sup>2</sup>, and Leticia González<sup>1</sup>**

<sup>1</sup>*Institute of Theoretical Chemistry, University of Vienna, Währinger Strasse 17, 1090 Vienna (Austria), leticia.gonzalez@univie.ac.at*

<sup>2</sup>*Institute of Organic Chemistry, University of Vienna, Währinger Strasse 38, 1090 Vienna (Austria), nuno.maulide@univie.ac.at*

The first example of a general 1,4-chirality transfer from sulfur to carbon via [3,3]-sigmatropic rearrangement is reported and thoroughly explored by modern theoretical methods in the present study [1]. The calculations suggest an elegant model, which does not only describe and explain the experimentally observed selectivity but also shows a way to improve the enantioselectivity via the strengthening of the important intramolecular interactions within the transition states. The suggested theoretical approach can be applied to design new enantio- and regioselective arylation reactions with the use of chiral sulfoxides as unique chirality storage systems.



[1] D. Kaldre, B. Maryasin, D. Kaiser, O. Gajsek, L. González, and N. Maulide, *Angew. Chem. Int. Ed.* **56**, 2212-2215 (2017).

## Efficient calculation of NMR shieldings including environmental effects

**Kevin Reiter<sup>1</sup>, Florian Weigend<sup>1,2</sup>**

<sup>1</sup>*Institute of Nanotechnology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz  
Platz 1, 76334 Eggenstein-Leopoldshafen, Germany*

<sup>2</sup>*Institute of Physical Chemistry, Karlsruhe Institute of Technology, Fritz-Haber-Weg 2,  
76131 Karlsruhe, Germany*

In calculations of chemical shieldings for a large systems the Coulomb part can easily become the time-dominating step. In order to reduce the computational effort, we implemented the resolution of the identity approximation for coulomb integrals (RI-J) [1] in TURBOMOLE's NMR module including the multipole-accelerated scheme (MARI-J) [2] adapted for chemical shieldings. Here, the coulomb interaction is divided into a near-field (evaluated via RI-J) and a far-field contribution, for which a multipole expansion is used. Further, to treat environmental effects, we implemented the conductor like screening model (COSMO) analogously to the related polarizable continuum model [3].

Efficiency is demonstrated for a negatively charged DNA segment with more than 1000 atoms (10220 basis functions). With MARI-J the effort for Coulomb part reduces by a factor of ca. 100, introduced errors are very small compared to changes when using a different basis or method.

- [1] O. Vahtras, J. Almlöf, M. W. Feyereisen, *Chem. Phys. Lett.* **213**, 514 (1993)
- [2] M. Sierka, A. Hogekamp, R. Ahlrichs, *J. Chem. Phys.* **118**, 9136 (2003)
- [3] R. Cammi, B. Mennucci, J. Tomasi, *J. Chem. Phys.* **110**, 7627 (1999)

**Automated workflows for molecular simulation and force field calibration****Koen M. Visscher<sup>1</sup>, Marc van Dijk<sup>1</sup>, Daan P. Geerke<sup>1</sup>**<sup>1</sup>*AIMMS Division of Molecular and Computational Toxicology, Faculty of Sciences, Vrije Universiteit Amsterdam, the Netherlands*

In this work we design, implement and integrate a generic eScience workflow for efficient and accurate force field calibration, building further on our current efforts to develop a heterogeneous workflow for molecular simulation. A workflow for the calibration of polarizable biomolecular force fields is presented, where a QM/MM approach [1] is used to develop transferable condensed-phase electrostatic parameters for a set of 70 small molecule side-chain analogs. Here we show that the transferability of force field parameters can be improved by a systematic approach to the calibration effort [2].

[1] C. R. Vosmeer, A. S. Rustenburg, J. E. Rice, H. W. Horn, W. C. Swope, D. P. Geerke, *J. Chem. Theory Comput.* **8**, 3839 (2012)

[2] K. M. Visscher, C. R. Vosmeer, R. A. Luijck, D. P. Geerke, *J. Comput. Chem.* **38**, 508 (2017).



## Theoretical investigations of biomimetic iron(IV)-oxo complexes

**Dieter Faltermeier, Peter Comba**

*Heidelberg University, Institute for Inorganic Chemistry, INF 270,*

*Interdisciplinary Center for Scientific Computing (IWR), INF 205,*

*69120 Heidelberg, Germany*

Mononuclear non-heme iron compounds play an important role in nature. They occur in many organisms and are indispensable. The chemical versatility of these enzymes is remarkable. Some examples of reactions with non-heme iron compounds include hydroxylation, halogenation and epoxidation. To understand enzymatic non-heme iron reactions, the study of biomimetic iron-oxo complexes is important.<sup>[1-6]</sup> Suitable biomimetic ligands for iron-oxo complexes are e.g. bispidines<sup>[7]</sup> or TMC ligands<sup>[8]</sup>. Due to the energetically close spin states ( $S=1$  and  $S=2$ ), it is very difficult to describe iron-oxo complexes without further theoretical investigations.<sup>[7]</sup> To attain a more accurate understanding of the chemical behavior of iron(IV)-oxo complexes, we use a broad variety of methods such as CASSCF (complete active space self-consistent field), CASPT2 (complete active space perturbation theory), NEVPT2 (n-electron valence state perturbation theory) and DFT (density functional theory).

- [1] W. Nam, *Acc. Chem. Res.*, **48**, 2415-2423 (2015).
- [2] W. Nam, Y.-M. Lee, S. Fukuzumi, *Acc. Chem. Res.*, **47**, 1146-1154 (2014).
- [3] E. I. Solomon, T. C. Brunold, M. I. Davis, J. N. Kemsley, S.-K. Lee, N. Lehnert, F. Neese, A. J. Skulan, Y.-S. Yang, J. Zhou, *Chem. Rev.*, **100**, 235-350 (2000).
- [4] M. M. Abu-Omar, A. Loaiza, N. Hontzeas, *Chem. Rev.*, **105**, 2227-2252 (2005).
- [5] C. Krebs, D. G. Fujimori, C. T. Walsh, J. M. Jr. Bollinger, *Acc. Chem. Res.*, **40**, 484-492 (2007).
- [6] C. A. Grapperhaus, B. Mienert, E. Bill, T. Weyhermüller, K. Wieghardt, *Inorg. Chem.*, **39**, 5306-5317 (2000).
- [7] P. Comba, S. Fukuzumi, C. Koke, B. Martin, A.-M. Löhre, J. Straub, *Angew. Chem. Int. Ed.*, **55**, 11129-11133 (2016).
- [8] J.-U. Rohde, J.-H. In, M. H. Lim, W. W. Brennessel, M. R. Bukowski, A. Stubna, E. Münck, W. Nam, L. Que Jr., *Science*, **299**, 1037-1039 (2003).

## A Sequential-QM/MM study of the electronic spectra of photochromic switches

**Marcelo Hidalgo Cardenuto<sup>1</sup>, Sylvio Canuto<sup>1</sup>**

*<sup>1</sup>Institute of Physics, University of São Paulo, São Paulo, Brazil*

In this work we present a theoretical study of a photochromic molecular switch. The target molecule is composed by two units of the dihydroazulene (DHA)/Vinylheptafulvene (VHF) covalently linked by a benzene ring. We use a sequential Quantum Mechanics/Molecular Mechanics (S-QMMM) methodology to investigate the solvent effects on the electronic spectra of these molecules. Four isomers of this molecule are studied depending on the open/close forms of the DHA/VHF unit. Classical Monte Carlo simulations are performed to obtain the liquid structures of the solvent and then quantum mechanics calculations are used to obtain the electronic spectra at Density Functional Theory level. The solvent effect is considered both as an electrostatic embedding composed by the point charges of the solvent molecules (acetonitrile) as well as the closest explicit acetonitrile molecules. The shifts of the absorption band in relation to the isolated molecules are calculated and the inhomogeneous broadening are obtained in good agreement with the experiment

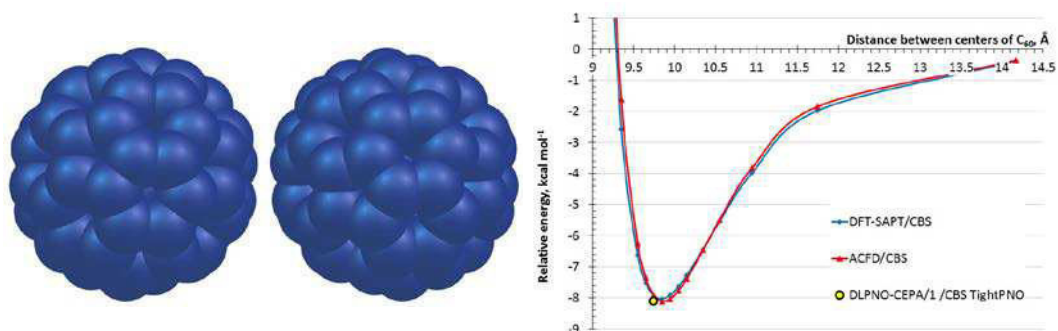
## Accurate Intermolecular Potential for the C<sub>60</sub> Dimer

D.I. Sharapa<sup>1</sup>, J. T. Margraf<sup>2</sup>, A. Hesselmann<sup>3</sup> and T. Clark<sup>1</sup>

<sup>1</sup>*Computer-Chemie-Centrum, Department Chemie und Pharmazie, Friedrich-Alexander-Universität Erlangen-Nürnberg, Nagelsbachstraße 25, 91052 Erlangen, Germany*

<sup>2</sup>*Quantum Theory Project, University of Florida, Gainesville, Florida 32611, United States*

<sup>3</sup>*Lehrstuhl für Physikalische und Theoretische Chemie, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany*



The self-assembly of molecular building blocks is a promising route to low-cost nanoelectronic devices. It would be very appealing to use computer-aided design to identify suitable molecules. However, molecular self-assembly is guided by weak interactions, such as dispersion, which have long been notoriously difficult to describe with quantum chemical methods. In recent years, several viable techniques have emerged, ranging from empirical dispersion corrections for DFT to fast perturbation and coupled-cluster theories. We test these methods for the dimer of the prototypical building block for nanoelectronics, C<sub>60</sub>-fullerene.

Benchmark quality data is obtained from DFT-based symmetry-adapted perturbation theory (SAPT), the adiabatic-connection fluctuation dissipation (ACFD) theorem using an adiabatic LDA kernel, and domain-based local pair natural orbital (DLPNO) coupled-pair and coupled cluster methods. These benchmarks are used to evaluate economical dispersion-corrected DFT methods, double-hybrid DFT functionals, and second-order Møller–Plesset theory. Furthermore, we provide analytical fits to the benchmark interaction curves, which can be used for a coarse-grain description of fullerene self-assembly. These analytical expressions differ significantly from those reported previously based on bulk data.[1]

[1] D.I. Sharapa, J. T. Margraf, A. Hesselmann and T. Clark, *JCTC*, **13**, 274-285, (2017).

## Theoretical Investigation of the Interaction of CO with Pd/MOR Catalyst

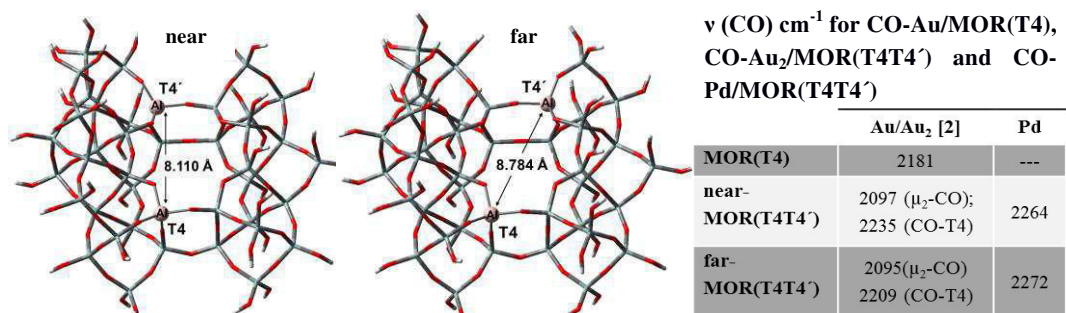
Aníbal Sierraalta<sup>1</sup>, Lenin Díaz<sup>2,3</sup>, Rafael Añez<sup>1</sup>, M. A. C. Nascimento<sup>3</sup>

<sup>1</sup>Laboratorio de Química-Física y Catálisis Computacional, Centro de Química, Instituto Venezolano de Investigaciones Científicas, Caracas

<sup>2</sup>Departamento de Física, Pontifícia Universidade Católica do Rio de Janeiro, RJ, Brazil

<sup>3</sup>Instituto de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil

ONIOM calculations have been carried out to determine geometries, adsorption energies and vibrational frequencies of CO on Pd mordenite catalysts (Pd/MOR) using DFT with the  $\omega$ B97X-D functional. In previous works we showed that the distribution of the acid sites influences both the NH<sub>3</sub> adsorption energy in MOR [1] and the CO adsorption in the Au/MOR system [2]. Here we examine the structure of Pd/MOR and CO-Pd/MOR systems considering the proximity of two crystallographic sites. The MOR unit cell contains four different tetrahedron (T) sites: T1, T2, T3, and T4. A model of MOR containing 264T sites was employed to perform a two-layer ONIOM calculations, with 223T in the low-level treated by the Universal Force Field (UFF) and 41T in the high-level treated with the  $\omega$ B97X-D functional. The MOR structures are created by replacing Si by Al at the positions T4 and T4', generating the near-MOR(T4T4') and the far-MOR(T4T4') structures.



The results show that the frequency of the CO adsorbed in Pd/MOR is little affected by the Al distance, contrary to the obtained with the Au/MOR system [2]. Comparison with experimental results [3] allow us to propose the most probable structures of CO-Pd to be present in the CO-Pd/MOR.

[1] L. Diaz, A. Sierraalta, M. A. C. Nascimento, R. Añez, *J. Phys. Chem. C* **117**, 5112 (2013).

[2] L. J. D. Soto, A. Sierraalta, R. Añez, M. A. C. Nascimento, *Appl. Catal. A* **526**, 53 (2016).

[3] A. N. Mendes, et al., *Appl. Catal. B* **195**, 121 (2016).

## Quantitative Prediction of Diastereoselective Radical Addition Reactions

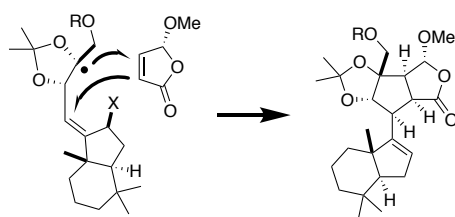
Mikko Muuronen<sup>1,2</sup>, Yuriy Slutskyy<sup>1</sup>, Daniel J. Tao<sup>1</sup>, Alexander Le<sup>1</sup>, Larry E. Overman<sup>1</sup>, Filipp Furche<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of California, Irvine, 1102 Natural Sciences II, Irvine, CA 92697-2025, USA*

<sup>2</sup>*Department of Chemistry, Technical University of Munich, Lichtenbergstr. 4, D-85747, Garching, Germany*

Bimolecular reactions where two fragments are united via  $sp^3$ - $sp^3$   $\sigma$ -sigma bond, forming two new stereocenters, present a fundamental challenge for organic chemistry [1]. Coupling of nucleophilic radicals, which are generated using modern photoredox catalysis, with electrophilic olefins has recently proved its unique potential for such fragment connections in the total synthesis of (-)-Chromodorolide B where three of the ten contiguous stereocenters were formed in a single radical cascade reaction [2]. The diastereoselectivity of the reaction was, however, low and the correct diastereomer was only obtained as a minor product.

Here, we present a multi-scale computational protocol, which has been successfully used to predict the diastereoselectivities of radical addition reactions at semiquantitative level [3]. The model is based on extensive conformational sampling at force field and DFT levels, and final energies are evaluated using resolution-of-identity random-phase approximation. Finally, the model was very recently used to predict the second generation radical cascade reaction in which two  $\sigma$ -sigma bonds and four stereocenters are formed in a single reaction. The prediction has been experimentally validated to yield a full stereocontrol of all formed centers.



- [1] K. W. Quasdorf, L. E. Overman, *Nature* **516**, 181 (2014).
- [2] D. J. Tao, Y. Slutskyy, L. E. Overman, *J. Am. Chem. Soc.* **138**, 2186 (2016).
- [3] D. J. Tao, M. Muuronen, Y. Slutskyy, A. Le, F. Furche, L. E. Overman, *Chem. Eur. J.* **22**, 8786 (2016).

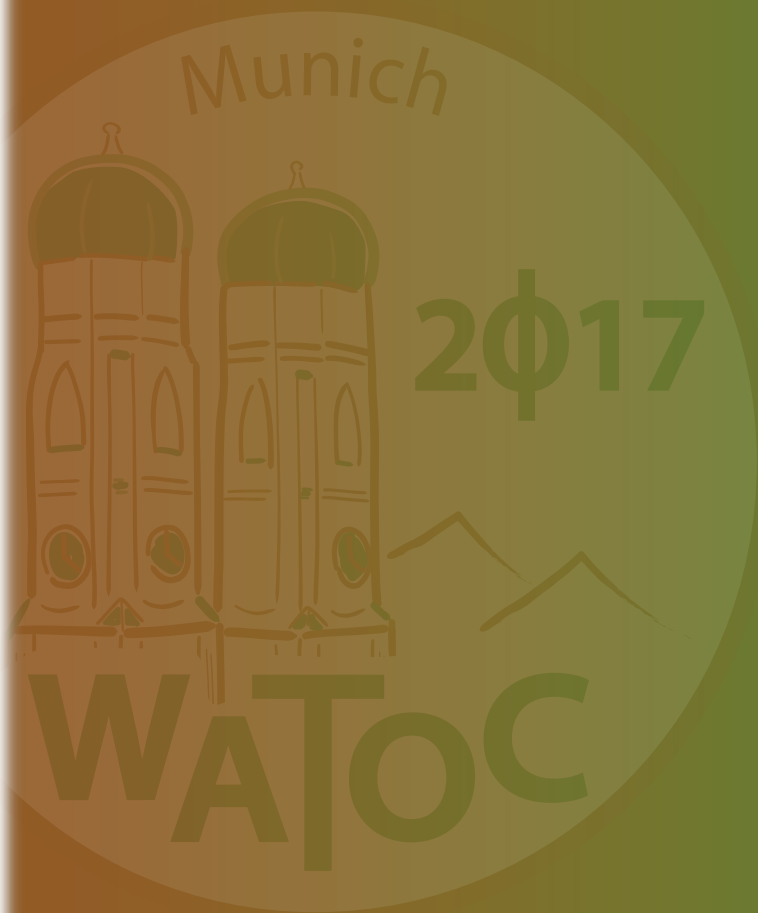
## **Fast Molecular Crystallization: Crystal Phase Transition Determines the Molecular Packing Kinetics.**

**Cheng Shang\*, Xiao-jie Zhang, Zhi-Pan Liu\***

Department of Chemistry, Fudan University, Shanghai 200433, China

\*cshang@fudan.edu.cn \*zpliu@fudan.edu.cn

Because of the weak intermolecular force and flexible molecular geometry, molecular crystals are renowned for their structure versatility (polymorphism) and great difficulty to control the crystal form during synthesis. Current theoretical approaches also fail generally in predicting molecular crystallization kinetics due to the complex potential energy surface (PES). Here we report the first global PES for molecular crystal obtained by novel stochastic surface walking global PES exploration in combination with solid reaction pathway sampling, which leads to resolving the crystallization ability of molecule quantitatively. Taking urea ( $\text{NH}_2\text{CONH}_2$ ) solid as an example, we demonstrate that the fast crystallization ability of urea can be attributed to the flat PES between major crystal forms that share the same hydrogen-bonding network pattern, where one crystal can transform to another facilely via solid-to-solid transition. Other crystal forms with distinct hydrogen-bonding network patterns can be excluded in crystallization for their poor thermodynamics stability and high barrier during solid-to-solid transition. A general theory for predicting molecular crystallization ability is proposed and illustrated by a simplified one-dimensional global PES.



# POSTER SESSION 3



## Theoretical study of a lipase-catalyzed reaction in organic solvent

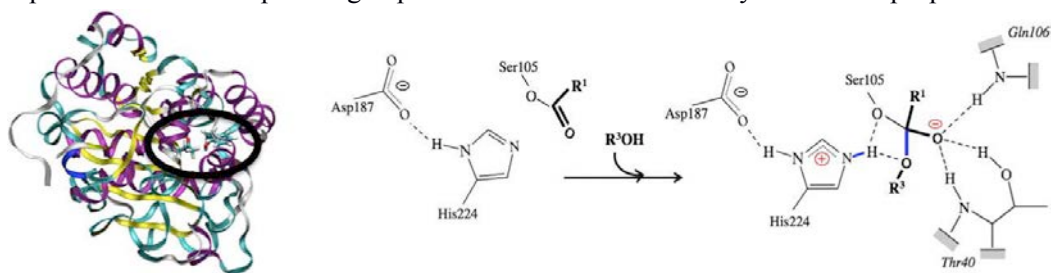
Zuzana Sochorová Vokáčová<sup>1</sup>, Damien Laage<sup>2</sup>, Eva Pluhařová<sup>1</sup>

<sup>1</sup>*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic,  
Dolejšková 2155/3, 18223 Prague 8 Czech Republic*

<sup>2</sup>*École Normale Supérieure – PSL Research University, Département de Chimie, Sorbonne  
Universités – UPMC Univ Paris 06, CNRS UMR 8640 PASTEUR, 24 rue Lhomond, 75005  
Paris, France*

Enzymes are extraordinary catalysts satisfying the needs of living organisms, but their efficiency and selectivity is also appealing for utilizing them in technological applications [1]. Perhaps surprisingly, a wide range of enzymes do not denature and moreover retain catalytic activity in organic solvents. This opens a path for carrying out new unnatural reactions. The change of reaction medium significantly alters enzyme activity, as well as chemo-, regio- and enantioselectivity. Solvent effects on enantioselectivity are complex; different types of enzymes exhibit qualitatively different behavior [2,3] and simple rules for rationalization are still missing.

Our aim is to systematically investigate enantioselectivity of a transesterification reaction catalyzed by *Candida antarctica* lipase B in acetonitrile, toluene and their mixtures of varying composition. First, we examine the detailed nature of the rate-limiting step using QM/MM calculations. Next, we sample the conformational space of the most important reaction intermediate for both enantiomers by classical molecular dynamics simulations and characterize the productive binding modes. The gained molecular level insight will help to understand the puzzling dependence of enantioselectivity on solvent properties.



**Figure 1** *Candida antarctica* lipase B with highlighted active site (left) with the scheme of the rate-limiting step of the transesterification reaction (right).

### References

- [1] A. M. Klibanov, *Nature* **409**, 241 (2001).
- [2] S. Tawaki, A. M. Klibanov, *J. Am. Chem. Soc.* **114**, 1882 (1992).
- [3] Y. Kitamoto, Y. Kuruma, K. Suzuki, T. Hattori, *J. Org. Chem.* **80**, 521 (2015).



## Temperature-dependent Triplet State Decay of Ir(ppz)<sub>2</sub>(F<sub>2</sub>ppy): Role of Metal Centered State

Xu Zhang<sup>1</sup>, Qian Peng<sup>2</sup>, Zhigang Shuai<sup>1,2</sup>

<sup>1</sup>Key Laboratory of Organic Optoelectronics and Molecular Engineering,

Department of Chemistry, Tsinghua University, Beijing 10084 P. R. China.

<sup>2</sup>Key Laboratory of Organic Solids, Beijing National Laboratory for Molecular Sciences,

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China.

**Abstract:** Cyclometalated iridium(III) complexes are widely used in the emissive layer of organic light-emitting diodes (OLEDs) due to their remarkable optical properties. Previous experiment investigations have shown that for the Ir(III) complexes, the temperature-dependent decay behavior demonstrated a competing mechanism between metal-ligand charge transfer (MLCT) state and metal centered (MC) state. However, there have been only a few theoretical studies on quantitatively description on the rate constant for various decay pathways. In this work, we have constructed a computation model to systematically investigate the decay mechanism of Ir(ppz)<sub>2</sub>(F<sub>2</sub>ppy). Both MLCT → S<sub>0</sub> transition and MLCT → MC transformation are considered in this model with decay rate constants calculated at the first-principles level. Two distinct optimized geometries are found on T<sub>1</sub> PES and then identified as MLCT or MC state based on spin density analysis. We found that the energy barrier of MLCT → MC transformation is low enough to overcome, and the rate constant of MLCT → MC transformation grows drastically as temperature increases, which indicates this pathway could be significant at high temperature. Strikingly, the calculated decay time vs. temperature shows a double-exponential form, which agrees with the experimental data. It is expected that the computation model in this work could be generalized to other Ir(III) complexes, as they have similar temperature-dependent decay behaviors.

[1] T. Sajoto, P. I. Djurovich, A. B. Tamayo, J. Oxgaard, W. A. Goddard III, M. E. Thompson, *J. Am. Chem. Soc.* **131**, 9813 (2009).

[2] Q. Peng, Y. Niu, Q. Shi, X. Gao, Z. Shuai, *J. Chem. Theory Comput.* **9**, 1132 (2013).

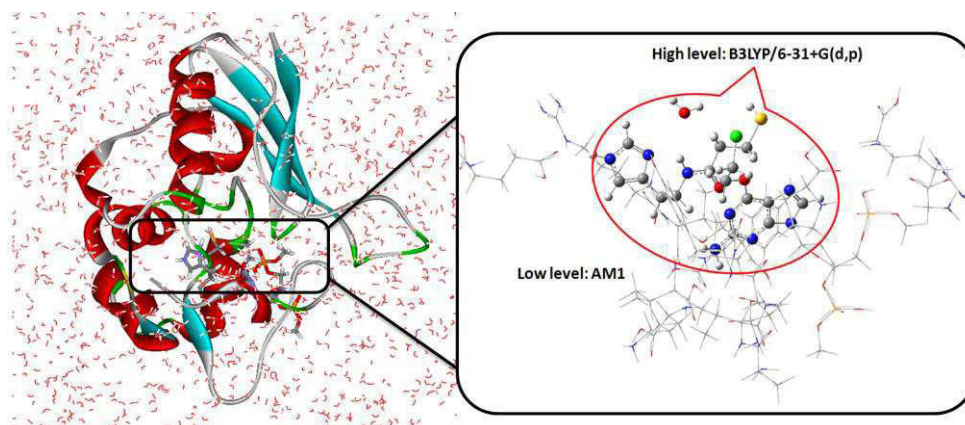
[3] D. Escudero, *Chem. Sci.* **7**, 1262 (2016).

## Mechanism of Drug Resistance of Chloroethylnitrosoureas Mediated by O<sup>6</sup>-Alkylguanine-DNA Alkyltransferase: An ONIOM Investigation

Lijiao Zhao, Ting Ren, Rugang Zhong

*Beijing Key Laboratory of Environmental & Viral Oncology, College of Life Science and Bioengineering, Beijing University of Technology, Beijing 100124, China*

**Abstract:** Chloroethylnitrosoureas (CENUs) are an important family of anticancer alkylating agents widely used in the clinical treatments of cancer. Experimental evidences indicated that CENUs induced formation of DNA alkylations, in which DNA interstrand crosslinks (ICLs) between G-C base pair was the most important lesion related to the anticancer effect of CENUs. However, O<sup>6</sup>-alkylguanine-DNA alkyltransferase (AGT) in tumor cells can repair DNA alkylation by removing the alkyl group on the O<sup>6</sup> position of guanine and consequently lead to drug resistance. In this study, the mechanisms of AGT-mediated repair of DNA ICLs were investigated using molecular docking, molecular dynamics (MD) simulation and ONIOM method. Moreover, the mechanism of DNA repair was compared with the mechanism of DNA ICLs formation to reveal the preference between drug resistance and anticancer effect of CENUs. Molecular docking and MD simulation were performed to obtain the stable conformations of the two complexes, AGT-O<sup>6</sup>-ClEtG and AGT-O<sup>6</sup>,N1-EtG. Then the active sites of these two stable conformations were picked out, and were employed as the computational models for the ONIOM computations at the B3LYP/6-31+G(d,p):AM1 theoretical level. This work will contribute to the further understanding of the mechanism of drug resistance of CENUs and will assist in the development of novel AGT inhibitors as adjuvant alkylating chemotherapies.



**Figure 1** AGT-O<sup>6</sup>-ClEtG complex obtained from MD simulation and the active site employed as the ONIOM computational model

## A wave function model for magnetic clusters

Tilman Bodenstein, Jeppe Olsen

*Department of Chemistry, Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark*

A compact wave function model for describing magnetic clusters comprising several open-shell metal ions (sites) is introduced. The approach is based on multireference ab initio wave function methods. A reduction of the parameter space dimensions is obtained by combining physically reasonable approximations with efficient numerical methods.

In particular, the interactions in magnetic clusters may be grouped such that, to zero order, the magnetic sites can be 'disentangled' by neglecting explicit inter-site couplings, i. e. charge-transfer configurations, leading to a direct product wave function

$$|\tilde{0}(\kappa, \mathbf{c})\rangle = \exp(-\hat{\kappa}) \prod_{K=1}^{\text{sites}} \sum_I c_{I_K} \mathcal{A}_{I_K} \mathcal{I} |\text{vac}\rangle \quad (1)$$

where the CI-basis is spanned by Slaterdeterminants, factorized into creation strings for inactive ( $\mathcal{I}$ ) and active ( $\mathcal{A}_{I_K}$ ) orbitals. The generator for infinitesimal orbital rotations is denoted  $\hat{\kappa}$ . Ansatz (1) yet contains inter-site interactions implicitly because of the spatial extent of the orbitals used to expand the electronic states.

Using non-orthogonal orbital expansions, the parameter space of such a MCSCF calculation can be further reduced [1, 2] while simultaneously improving the description of inter-site interactions compared to orthogonal (ground-manifold) MCSCF methods. [3, 4] Remaining contributions can be considered using techniques of internal contraction, e. g.

$$|\text{IC}\rangle = \sum_{[L,L']} C_{LL'} \mathcal{O}_L^{L'} |0\rangle \quad (2)$$

where  $|0\rangle$  represents the wave function (1) at the optimal expansion point. The brackets denote that the excitation strings  $\mathcal{O}_L^{L'}$  may be grouped and restricted to certain domains, e. g. adjacent sites  $L, L'$ , owing to the inherent strongly-correlated character of magnetic clusters. The present ansatz is compared to well-established multireference methods.

- [1] J. Olsen, *J. Chem. Phys.* **143**, 114102 (2015).
- [2] R. Broer, W. C. Nieuwpoort, *Theor. Chim. Acta* **73**, 405 (1988).
- [3] O. Kahn, *Molecular Magnetism*, Wiley-VCH, Weinheim (1993).
- [4] K. Fink, V. Staemmler, *Mol. Phys.* **111**, 2594 (2013).

## The impact of cholesterol flip-flop and concentration on the plasma membrane

Sebastian Thallmair<sup>1</sup>, Antara Mazumdar<sup>1</sup>, Elisabeth A. Ploetz<sup>2</sup>, Helgi I. Ingólfsson<sup>3</sup>, Siewert-Jan Marrink<sup>1</sup>

<sup>1</sup>*Faculty of Science and Engineering, University of Groningen, Nijenborgh 7, 9747 AG Groningen, The Netherlands*

<sup>2</sup>*John Hopkins University, Baltimore, Maryland, USA*

<sup>3</sup>*Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550, USA*

Cell membranes are highly complex systems consisting of various lipids and membrane proteins. They serve as the border of living cells, separating the cell interior from its environment. Typically, hundreds of different lipid types are present in a plasma membrane (PM). The detailed organization of cell membranes is therefore rather elusive. Cholesterol is known to stabilize liquid-ordered domains and flip-flops rapidly between both membrane leaflets. Recently, large-scale coarse-grained molecular dynamics (MD) simulations provided a near atomic view on the lipid organization of PMs [1]. The investigated PM model consists of 63 different lipid types (Fig. 1). The formation of transient domains with liquid-ordered character was observed. Here, we investigate the influence of cholesterol flip-flop as well as concentration on the PM properties. In doing so, we performed 50  $\mu$ s coarse grained MD simulations of membrane patches with a size of  $\sim 40 \times 40$  nm<sup>2</sup>. We compare simulations where the cholesterol flip-flop was suppressed with ones allowing cholesterol flip-flop. Besides the influence on global membrane properties like area per lipid, lipid tail order, and lateral density, our particular focus is on the inter-leaflet coupling. We find that correlations of the transient domains enriched with cholesterol occur on a hundreds of nanoseconds time scale and show a spatial extent of  $\sim 10$  nm.

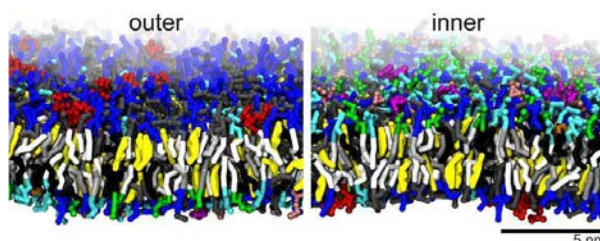


Figure 1: View on the outer and inner leaflet of the plasma membrane [1].

In addition, we varied the cholesterol concentration in our PM model from 0–50 mol-%. The cholesterol distribution between the leaflets shows an asymmetry which decreases as the cholesterol concentration increases. The global membrane properties reveal the effect of increasing lipid tail order with higher cholesterol concentration. Furthermore, we will discuss its effect on the inter-leaflet coupling in comparison with the other results.

[1] H. I. Ingólfsson, et al., *J. Am. Chem. Soc.* **136**, 14554 (2014).

**Thermodynamic aspects of the electrocatalysis of proton reduction by diiron benzenedithiolate carbonyl complex**

**Mihajlo Etinski<sup>1</sup>, Rakesh C. Puthenkalathil<sup>2</sup>, Bernd Ensing<sup>2</sup>**

<sup>1</sup> *Faculty of Physical Chemistry, University of Belgrade Studentski trg 12-16 11000 Belgrade, Serbia*

<sup>2</sup> *Van 't Hoff Institute for Molecular Sciences (HIMS), University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands*

The transformation of electric into chemical energy by electrochemical reduction of protons to molecular hydrogen has gained considerable attention as a promising process for the global aim to switch to a clean fuel economy. The design of reduction catalyst is a critical step for the development of suitable technology. Although noble metals are efficient catalysts for this reaction, cheaper catalysts based on abundant materials are desirable for broad application. Diiron benzenedithiolate (bdt) carbonyl complex is a biomimetic catalyst based on diiron-hydrogenases a class of enzymes responsible for H<sub>2</sub> production in microbes. It is a robust catalyst whose proton reduction mechanisms depend on proton donor strength [1,2]. Although many experimental and theoretical studies examined its properties, the catalytic mechanisms are still not completely understood. We have examined the catalytic pathways of proton reduction by Fe-bdt employing density functional theory and implicit solvent model. The computed free energies of singly, doubly and triply reduced and/or protonated Fe-bdt isomers were used to compute a thermodynamic map and Pourbaix diagram for the catalyst. Based on the relative energies of the isomers and their proton dissociation constants we propose electrochemical mechanisms for the proton reduction.

[1] J. F. Capon, F. Gloaguen, P. Schollhammer, J. Talarmin, *J. Electroanal. Chem.*, **595**, 47 (2006).

[2] G. A. N. Felton, A. K. Vannucci, J. Chen, L. T. Lockett, N. Okumura, B. J. Petro, U. I. Zakai, D. H. Evans, R. S. Glass, D. L. Lichtenberger, *J. Am. Chem. Soc.*, **129**, 12521 (2007).

## Accelerated Dynamics Simulations of Supramolecular Ruthenium-Based Water Oxidation Catalysis

Joachim O. Lindner<sup>1</sup>, Merle I. S. Röhr<sup>1</sup>, Roland Mitrić<sup>1</sup>

<sup>1</sup>*Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, 97074 Würzburg, Germany*

Water oxidation is a key step in the development of new sustainable methods towards artificial photosynthesis and solar fuels. A promising approach for efficient water splitting is the design of supramolecular Ru-based catalysts. [1] Only recently, a macrocyclic system containing three Ru(bda) units (bda = 2,2'-bipyridine-6,6'-dicarboxylate) has been synthesized that is able to compete with the best catalysts up to date in TOF and TON while mechanistically following a pathway characterized by the nucleophilic attack of a water molecule. [2]

QM/MM molecular dynamics simulations allowed us to observe the whole catalytic cycle of this supramolecular catalyst in solution. Furthermore, by comparison of systems with increasing ring sizes we could show that the high catalytic activity and characteristic absorption bands in the UV/Vis spectra are due to pronounced hydrogen bonding networks that are formed preferably in the macrocycle with intermediate size. [3] Cooperative effects lead to the stabilization of dissociated protons and thus facilitate proton-coupled electron transfer processes.

In order to gain a deeper understanding of the mechanistic details in these supramolecular systems, we apply the metadynamics approach to quantitatively identify the rate-determining steps of the catalytic cycle as well as possible changes in the reaction pathway affecting the enhanced water oxidation activity of the macrocycle.

- [1] V. Kunz, D. Schmidt, M. I. S. Röhr, R. Mitrić, F. Würthner, *Adv. Energy Mater.*, doi: 10.1002/aenm.201602939 (2017).
- [2] M. Schulze, V. Kunz, P. D. Frischmann, F. Würthner, *Nat. Chem.* **8**, 576–583 (2016).
- [3] V. Kunz, J. O. Lindner, M. Schulze, M. I. S. Röhr, D. Schmidt, R. Mitrić, F. Würthner, *Energy Environ. Sci.*, submitted.

## **Spontaneous insertion and interaction of non-structure 3 protease protein domain with PIP2-containing membrane**

**Huynh Minh Hung, Tran Dieu Hang and Minh Tho Nguyen**

*Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium*

**Abstract:** Hepatitis C virus (HCV), the leading cause of liver cirrhosis, viral hepatitis and hepatocellular carcinoma, affected more than 150 million people globally. The HCV non-structure 3 (NS3) protease protein domain plays a key role in HCV replication and pathogenesis; and is currently a primary target for HCV antiviral therapy. Through unbiased molecular dynamics simulations taking advantage of the novel highly mobile membrane mimetic model, we constructed the membrane-bound state of the protein domain at the atomic level. Our results indicated that protease domain of NS3 protein can spontaneously bind and penetrate to an endoplasmic reticulum complex membrane containing phosphatidylinositol 4,5-bisphosphate (PIP2). An amphipathic helix  $\alpha_0$  (amino acids 13-22) which deeply inserted into the membrane shows as the primary anchoring role to keep the protein on the membrane surface, which agrees well with previous experimental studies. Along with the role of helix  $\alpha_0$ , a loop S1 around residue T40 was found to deeply penetrate to the membrane while the small helix S2 and loop S3 bind but incompletely insert into the membrane. Proper orientation of the protein domain at membrane surface was also identified through measuring tilt angles of two specific vectors, in which residue R161 play a crucial role in its final orientation. Importantly, PIP2 molecules were found to bind to three main sites of the protease via electrostatic contacts and hydrogen bonds. Hydrophobic interactions between inserted parts of NS3pro with the membrane along with these PIP2-interactions have tendency to stabilize the NS3 - membrane complex.

- [1] J. L. Baylon, I. L. Lenov, S. G. Sligar and E. Tajkhorshid, J. Am. Chem. Soc. 135, 8542–8551 (2013).
- [2] H.M. Hung, T.D. Hang, M.T. Nguyen, Biochem. Biophys. Res. Commun. 478, 193–198 (2016).
- [3] D.I. Soumana, N. Kurt Yilmaz, A. Ali, K.L. Prachanronarong, C.A. Schiffer, J. Am. Chem. Soc. 138 (2016) 11850–11859.

## Theoretical insights of supramolecular assembly on 2D atomic crystals

Hongde Yu<sup>1</sup>, and Dong Wang\*<sup>1</sup>

<sup>1</sup>*MOE Key Laboratory of Organic OptoElectronics and Molecular Engineering,  
Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China*

A large variety of organic molecules are known to assemble on various 2D atomic crystals and form specific patterns, which have been investigated by STM since 1990s. Herein, using both DFT-D3 method and Grimme's D3 dispersion parameters, we explored the interplay of substrate-adsorbate and adsorbate-adsorbate interactions in the assembly of oleamide on hexagonal BN lattice. By calculating the translational and rotational potential energy surfaces of a single oleamide molecule adsorbed on monolayer BN, we corroborated that alkyl chains of oleamide molecules tend to align along a specific direction on BN, which is the zigzag lattice direction with the densest atomic density. More importantly, when oleamide molecules are adsorbed on the periodic lattice of BN substrate at the energetically most favorable positions, they will assemble into a one-dimensional nanoribbon along the zigzag crystal direction of BN. Our potential energy scans of a 2nd layer of oleamide adsorbed on the 1st molecular layer of nanoribbon showed that oleamide molecules in the 2nd layer prefer to align parallel to the underneath 1st layer ones and stack right on top of them. We concluded that substrate-adsorbate interactions serve as primary interactions, and adsorbate-adsorbate interactions as secondary ones in the assembly of oleamide on 2D atomic crystals. Our investigation highlights the feasibility of probing the crystallographic orientation of 2D atomic crystals with supramolecular assembly

### References

- [1] Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. J. Chem. Phys., 2010, **132**, 154104.



## Structural properties and THz spectroscopic fingerprints of microsolvated ion-water clusters

Prashant Kumar Gupta, János Daru, Dominik Marx

*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum*

Small ion-water clusters are excellent model systems to study microsolvation and its impact on spectroscopic properties. It is, however, unclear to what extent such small clusters are meaningful minimal models of the first solvation shell of ions in bulk solution, keeping in mind that it is well established from experiments that the effect of ions on the water structure is largely limited to their first solvation shells. In this study we have undertaken an extensive density functional-based *ab initio* molecular dynamics study of various equilibrium structures and the corresponding THz spectra of cationic and anionic solvation in small water clusters, namely  $X \bullet (H_2O)_n$  where  $X = Na^+$  and  $Cl^-$ ,  $n = 3-7$ . In this context, the issue of including or rather omitting empirical dispersion interaction corrections turns out to be intricate with reference to wavefunction-based benchmarks on structure and relative energetics. *Ab initio* molecular dynamics simulations are performed at several temperatures in order to probe the structural dynamics of distinct microsolvated clusters in direct comparison to the same ions at bulk solvation conditions. Finally, their THz spectra are computed and also decomposed in terms of well-defined intra- and inter-molecular contributions including solute-solvent couplings in order to compare those to what has been found in the bulk solvation limit.

## Density functional theory predictions of self-assembly on metal surfaces: Is it successful?

**James Hooper<sup>1</sup>, E. Zurek<sup>2</sup>, A. Enders<sup>3</sup>**

<sup>1</sup>*Department of Theoretical Chemistry, Jagiellonian University, R. Ingardena 3, Krakow, Poland*

<sup>2</sup>*Department of Chemistry, State University of New York at Buffalo, 14260, Buffalo, USA*

<sup>3</sup>*Physikalisches Institut, Universität Bayreuth, 95440 Bayreuth, Germany*

The ability to predict from computations alone whether or not small molecules will form interesting networks on a given substrate is a particularly challenging and enticing problem. One example, among many, is croconic acid (CA), a polar organic molecule which crystallizes with ferroelectric behavior in its bulk form.[1] Such a molecule may also be of interest when deposited on a surface to, for example, create a two-dimensional network with ferroelectric behavior.

In this work, we first explore experimentally-characterized hydrogen-bonded networks which assemble from CA when it is deposited on coinage metal substrates, ie. Cu, Ag, and Au.[2] The networks are influenced by the substrate onto which they are deposited and, as could be expected from the literature, can be predicted from first-principles with Density Functional Theory (DFT) energies with varying degrees of success. Building on this, DFT calculations are used here to explore how the dependence of the CA-inspired network architectures compare with, in particular, inter-molecular binding (ie. hydrogen-bonding), preferential binding sites, and electrostatic interactions between the adsorbate and substrate. From this, we show what is needed from computations, beyond energies, to simply predict the networks. Further, we comment on modelling the adsorption of a bis-BN cyclohexane precursor molecule ( $\text{B}_2\text{N}_2\text{C}_2\text{H}_{12}$ ) on reactive Rh(111) and Ir(111) substrates, and discuss its role in helping to fashion an elusive metastable graphene-like boron-carbon-nitrogen monolayer.[3]

[1] S. Horiuchi, R. Kumai, Y. Tokura, *Adv. Mater.* **11**, 123–456 (2011).

[2] J. Hooper, D. Kunkel, E. Zurek, A. Enders, *J. Phys. Chem. C*, **119**, 26429 (2015).

[3] S. Beniwal, J. Hooper, D. Miller, P. Costa, G. Chan, S. Y. Liu, P. A. Dowben, E. C. H. Sykes, E. Zurek, A. Enders, *ACS Nano*, **11**, 2486 (2017).

## **Energetics of proton coupled-electron transfer reactions in the NADH-binding site of respiratory complex I**

**Patricia Saura<sup>1</sup>, Ville R. I. Kaila<sup>1</sup>**

<sup>1</sup>*Department Chemie, Technische Universität München, Lichtenbergstr. 4, Garching, Germany.*

Complex I functions as a redox-driven proton pump in aerobic respiratory chains. It catalyzes the two electron transfer from NADH to quinone through a series of iron-sulfur (FeS) centers. The free energy released is employed to pump protons across the membrane domain, localized *ca.* 200 Å away from the quinone-binding site. The process is initiated by a hydride transfer from NADH to FMN, followed by the subsequent release of the oxidized NAD<sup>+</sup>. During this process, the two electrons are introduced into the FeS centers chain, followed by their sequential transfer to the quinone, which is reduced to quinol. Two of the FeS centers, N1a and N3, are located in the proximity of the NADH-binding site, but only N3 has been proposed to directly participate in the electron transfer to quinone, whereas the exact role of N1a is still unclear. To understand the molecular mechanism, energetics, and dynamics of this proton-coupled electron transfer (PCET) process linked to the NADH/FMN chemistries, we have employed here multi-scale quantum and classical molecular simulations. We have merged together different quantum mechanical subsystems including the initial electron donor, NADH/FMN, and acceptors, N1a/N3 in the calculations. We present energetics of likely PCET steps in these processes, and discuss their mechanistic implications for the function of complex I.

## Rational design of single molecule magnets

Asha Roberts, Peter Comba

*Institute of Inorganic Chemistry, Heidelberg University, INF 270,  
Interdisciplinary Center for Scientific Computing (IWR), INF 205,  
HGS MathComp Graduate School, INF 205,  
69120 Heidelberg, Germany*

Single molecule magnets (SMMs) are a class of compounds containing one or more magnetic centres (d- or f-block metals). In many cases the discovery of new SMMs is left to chance, with serendipitous assembly of metal clusters being a common synthetic approach. As a better understanding of the structural requirements of these complexes is obtained, a rational approach to their design is highly desirable and advantageous. While early SMMs were comprised primarily of transition metal ions, significant spin-orbit coupling and strong magnetic anisotropy of lanthanides makes them particularly suitable in this field. To date the best SMMs have been simple mononuclear lanthanide complexes.<sup>[1-2]</sup> Although ligand field effects for lanthanides are comparatively weak, they are a significant perturbation upon spin-orbit coupling, and are crucial in controlling SMM behaviour. This study presents investigations into geometrical influences on the electronic and magnetic properties of a series of mononuclear complexes with the aim of rationally designing complexes for application as SMMs. Structures are designed and optimised in Gaussian 09. Single point calculations to determine the magnetic properties are carried out using MOLCAS 8.0,<sup>[3]</sup> whereby spin-free CASSCF wave functions are first generated, spin-orbit coupling is introduced through RAS state interaction, and the relevant magnetic properties are calculated from the spin-orbit multiplets with the SINGLE\_ANISO module.

[1] J. Liu, Y. C. Chen, J. L. Liu, V. Vieru, L. Ungur, J. H. Jia, L. F Chibotaru, Y. Lan, W. Wernsdorfer, S. Gao, X. M. Chen, M. L. Tong, *J. Am. Chem. Soc.***138**, 16 (2016).

[2] C. R. Ganivet, B. Ballesteros, G. de la Torre, J. M. Clemente-Juan, E. Coronado, T. Torres, *Chemistry* **19**, 4, (2013).

[3] F. Aquilante, L. De Vico, N. Ferré, G. Ghigo, P. A. Malmqvist, P. Neogrády, T. B. Pedersen, M. Pitonak, M. Reiher, B. O. Roos, L. Serrano-Andrés, M. Urban, V. Veryazov, R. Lindh, *J. Comput. Chem.* **31**, (2010).

## Computational DFT-D3 and Amber FF Study of Z-DNA and its Sugar-Guanine Stacking Motif

Holger Kruse<sup>1</sup>, Klaudia Mráziková<sup>1</sup>, Jiri Šponer<sup>1</sup>

<sup>1</sup>*Institute of Biophysics of the CAS, Královopolská 135, 61265 Brno, Czech Republic*

The peculiar left-handed, zig-zag structure of Z-DNA features a highly rigid backbone skeleton and typically comprises alternating d(CG) dinucleotide sequences. Among the special structural features is the T-shaped stacking of a ribose sugar with a guanine nucleobase (cf. Fig. 1). Analysis of X-ray databases shows that this geometrical motif exhibits a surprisingly short oxygen-to-nucleobase distance ('oxygen- $\pi$  interaction') of about ca. 2.9 Å; much shorter than the typical nucleobase stacking distances of about 3.4 Å in helical structures.

To study the motif we mapped the PES of the sugar-nucleobase interaction with a model system at the B3LYP-D3(BJ)/def2-QZVP level of theory (cf. Fig. 1, 399 energy evaluations), and could support the correctness of bioinformatics studies, showing that the unexpected short distance in the X-ray structures is physically correct. As modern DNA force fields (FFs) are still deemed problematic for Z-DNA we repeated the scan using the non-bonded parameters of the Amber FF. While the Amber FF sufficiently reproduces the main features of the DFT-D3 surface, it has clear limitations with details. Geometry-adapted point charges are explored, but only offer a small improvement.

A COSMO-TPSS-D3(BJ)/def2-TZVP optimization of a high-resolution, 12-nt large X-ray structure validates the findings from the model and also shows the applicability of DFT-D3 for Z-DNA beyond toy systems.

Furthermore we discuss why the so-called oxygen- $\pi$  interaction is best understood as a mere geometrical descriptor instead of a 'new' interaction type using the accurate SAP2+3/jun-cc-pVTZ energy decomposition scheme.

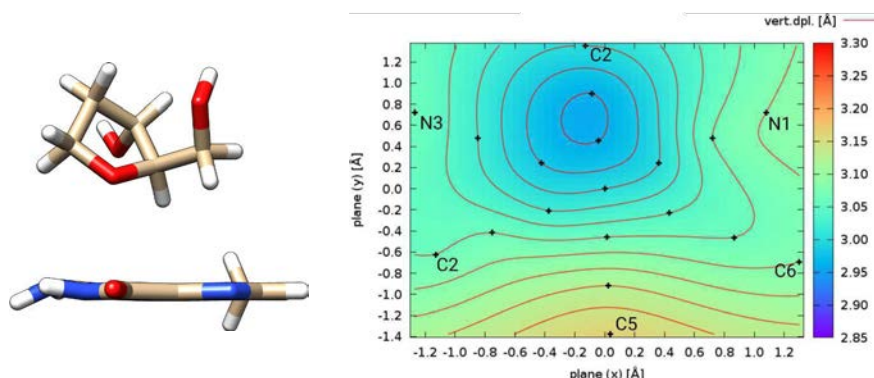


Figure 1: left: guanine-sugar model; right: lowest-energy distance surface of the guanine-sugar motif over the pyrimidine ring of guanine with atom labels.

H. Kruse, K. Mráziková, L. D'Ascenzo, P. Auffinger, J. Šponer *in preparation*

## **Linking Protein Motion and Function: Combining Markov State Modelling and Hybrid Quantum Mechanics/Molecular Mechanics**

**Eliot Boulanger<sup>1</sup>, Jeremy Harvey<sup>1</sup>**

*<sup>1</sup>Department of Chemistry, Quantum Chemistry and Physical Chemistry, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium*

Understanding the link between the molecular structure and the function of biomolecules is one of the key scientific challenges, and addressing this question requires drawing in techniques from biology, chemistry and physics. Furthermore, it has also been known for some time that protein structure is not fixed – proteins are intrinsically dynamical in the sense that they are constantly in motion, and it is also known that the structural changes can be linked to functional changes.

We aim at bridging those two aspects by the mean of computational methods. First, we run extensive molecular dynamics simulations on the protein and its surrounding to sample its conformational space. Out of the generated data we construct a Markov State Model (MSM)[1] which allows us to identify the different key conformers of the protein, get their relative free energies and the transition rates in between them. We then generate structures belonging to the different sampled conformations and use hybrid Quantum Mechanics/Molecular Mechanics (QM/MM)[2] to compute electronic properties proper to the function of the studied protein such as chemical reaction or electronic excitation. Combining both, we obtain a complete picture of the mode of action of the protein.

To exemplify our approach, we first focus on Myoglobin which has been extensively studied both computationally and experimentally. This protein has two well defined states (R and T) which are differently accessed depending on the binding of oxygen or carbon monoxide to the heme group.[3] We then apply our method to the P2Y<sub>12</sub> G-Protein-Coupled Receptor (GPCR) which is found in blood platelets and is a common target for antithrombic agent.[4] Drugs like Clopidogrel or Prasugrel bind covalently to the protein, inducing significant conformational changes to trigger a biological response. The covalent binding necessitates QM/MM to be studied and MSM is used to characterize the conformational changes.

[1] J. Chodera, F. Noé, *Curr. Opin. in Stuct. Bio.* **25**, 135 (2014).

[2] H. M. Senn, W. Thiel, *Angew. Chem. Int. Ed.* **48**, 1198 (2009).

[3] N. Strickland, A. J. Mulholland, J. N. Harvey, *Biophys. J.* **90**, L27 (2006).

[4] K. Zhang et al., *Nature* **509**, 115 (2014).

## FROM SURFACES TO NANOPARTICLES: AB-INITIO STUDY OF RUTHENIUM OXIDE AND ITS INTERACTION WITH WATER

**J.Heras-Domingo, X.Solans-Monfort, M. Sodupe**

*Dept. Química, Facultat de Ciències, Universitat Autònoma de Barcelona,*

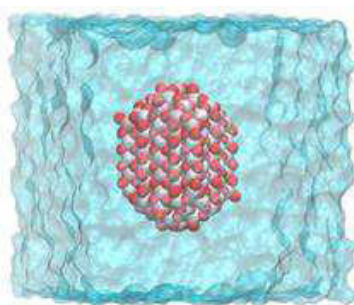
*08193 Bellaterra (Cerdanyola del Vallès), Spain*

*e-mail: [Javier.heras.domingo@uab.cat](mailto:Javier.heras.domingo@uab.cat)*

The formation of molecular oxygen from the oxidation of water is the most challenging step in water splitting process. To overcome this critical semi-reaction, heterogeneous catalyst or nanoparticles based on metal oxides have been used. In particular, ruthenium oxide based materials can be a good candidate, due to its unique redox surface chemistry and versatile behaviors in oxidative reactions.[1] RuO<sub>2</sub> is widely applied in chemistry due to its with many industrial applications such as electrochemical capacitors, sensor or catalyst due to its conductive behaviors and high thermal stability.

In this contribution, DFT calculations with periodic boundary conditions [2] have been carried out to analyze the electronic and adsorption properties of RuO<sub>2</sub> materials. In particular, the surface energy of the most relevant low-index crystallographic orientations has been determined. After that, water adsorptions onto these surfaces have been studied paying special attention in to the effect of water coverage. Moreover, computed surface energies have allowed us to determine the shape of nanoparticle different size through the Wulff construction [3] approach and analyze size-dependent properties and enhanced surface capabilities as compared with those of the bulk material.

Results show that water coverage and the surface morphology play an important role in the degree of water dissociation and that the formation of [H<sub>3</sub>O<sup>+</sup>]<sup>+</sup> units appears to be a driving force to allow the proton transfer process [4].



[1] H.Over *Chem. Rev.*, **2012**, 112 (6), 3356–3426

[2] G. Kresse, J. Fuhrmuller, *Phys. Rev. B*, **1993**

[3] G. Wulff, *Z. Kyrstal. Min.* **1901**, 34, 449

[4] R.Mu, D.C.Cantu, V-A.Glezakou, I.Lyubinetzky, *et al. J.Phys.Chem.C*, **2015**, 119, 23552-23558

## Unexpected contrast and “dark contours” in chiral STM markers

Sanz-Matias, Ana<sup>1</sup>, Harvey, Jeremy N.<sup>1</sup>

<sup>1</sup>Chemistry Department, KU Leuven, Celestijnenlaan 200F, Heverlee, Belgium

The design of chiral organic building blocks for two-dimensional self-assembled systems often involves using substituents to create stereogenic centers. Being able to visualize the stereogenic centers with Scanning Tunneling Microscopy (STM) is highly convenient for assessing their impact on self-assembly. Chiral substituents that serve as STM markers make it possible to identify the chiral components of the system and facilitate investigating kinetic and thermodynamic interfacial phenomena[1]. Despite the frequent use of methyl substituents as building block modifiers, there is little research on their STM marker characteristics: they are difficult to unambiguously detect in STM images, and when they have been detected[2, 3], image topography displays unexpected and stark contrast variations (i.e. “dark contours” and “bright features”).

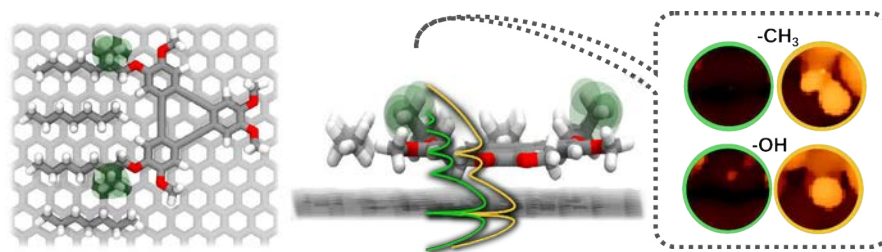


Figure 1: Chiral DBA on graphene with log(LDOS) curves as a function of  $z$  and STM simulated images.

We investigate computationally the STM marker characteristics of methylated, as well as hydroxylated, chiral derivatives of alkanes and dehydrobenzo[12]annulenes (DBAs) on graphitic surfaces (Fig. 1a). Self-interaction corrected density functional theory (DFT) calculations reveal a sharp change of the local density of states in the substituent regions in the energy range close to the Fermi level (Fig. 1b). As a result, the marker appearance depends heavily on the bias voltage used for image simulation (Fig. 1c), gradually ‘illuminating’ from a topographical depression to a protrusion. This appears to explain not only the unexpected “dark contours” observed in cDBAs experimental images, but also the general contrast variations. Furthermore, subtle differences in the voltage at which the contrast variation occurs for methyl and hydroxyl substituents may allow to distinguish between them, in a sort of traffic light effect.

- [1] C. L. Claypool et al, *Langmuir* **15**, 2817 (1999).
- [2] Y. Fang et al, *Nat. Chem.* **8**, 711 (2016).
- [3] S. de Feyter et al, *J. Phys. Chem. B* **101**, 5978 (1997).



# A quantum-chemical study of the DNA base-excision repair of 8-oxoguanine

Andrea Kreppel<sup>1</sup>, Christian Ochsenfeld<sup>1</sup>

<sup>1</sup>*Chair of Theoretical Chemistry, Department of Chemistry, Ludwig-Maximilians-University, Butenandtstr. 7, D-81377 Munich, Germany*

For the binding of the DNA lesion 8-oxoguanine (8OG) in the active site of the enzyme formamidopyrimidine DNA glycosylase (Fpg), two different binding modes have been proposed, one where the purine base adopts the *anti*-conformation and another with the base in *syn*-conformation (see Figure 1 a)). While it was found that both orientations of 8OG are stable within the active site [1, 2], it remained unclear whether the base can also be excised by Fpg in both orientations. Therefore we performed systematic QM/MM calculations. For *syn*-bound 8OG we recently found an excision mechanism with base specific protonation [3]. For another *anti*-bound DNA lesion we revealed an excision mechanism that is base independent [4]. In

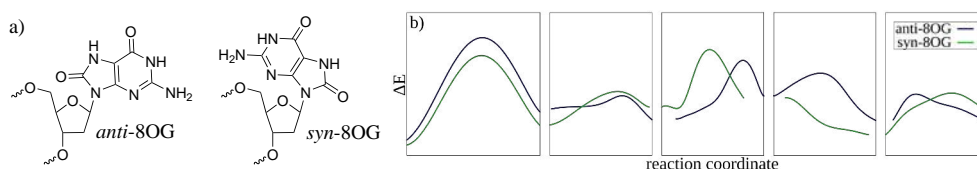


Figure 1: a) 8OG nucleotide in *anti*- and *syn*-conformation b) energy profile of the excision of 8OG by Fpg in both conformations.

our present work, we calculated the energy profile of the excision of 8OG in both orientations (Figure 1 b)) following the path of the base independent excision mechanism. Our calculations allow for comparing both energy profiles and indicate that 8OG can possibly be excised by Fpg in both conformations. Additionally, we show that *syn*-bound 8OG is not only excised by the base specific mechanism but also by the base independent mechanism. The findings of this work provide further evidence that the base excision mechanism is base independent and that no discrimination between DNA lesions occurs within the active site.

- [1] K. Song, V. Hornak, C. de Los Santos, A. P. Grollman, C. Simmerling, *Biochemistry* **45**, 10886 (2006).
- [2] R. A. Perlow-Poehnelt, D. O. Zharkov, A. P. Grollman, S. Broyde, *Biochemistry* **43**, 16092 (2004).
- [3] K. Sadeghian, D. Flaig, I. D. Blank, S. Schneider, R. Strasser, D. Stathis, M. Winnacker, T. Carell, C. Ochsenfeld, *Angew. Chem., Int. Ed.* **53**, 10044 (2014)
- [4] I. D. Blank, K. Sadeghian, C. Ochsenfeld, *Sci. Rep.* **5**, 10369 (2015)

## Quantum entanglement within the polarization propagator approach

**Leonardo A. Millán<sup>1</sup>, Claudia G. Giribet<sup>2</sup> and Gustavo A. Aucar<sup>1</sup>**

<sup>1</sup>*Physics Department, Natural and Exact Science Faculty, Northeastern University of Argentina and Institute of Modeling and Innovation on Technology (IMIT) CONICET-UNNE, Corrientes, Argentina*

<sup>2</sup>*Physics Department, Physics Institute of Buenos Aires, Natural and Exact Science Faculty, University of Buenos Aires and CONICET, Buenos Aires, Argentina*

For vicinal and indirect NMR J-couplings there is a well-known empirical rule, the Karplus rule, which states a functional dependence of such J-couplings with the dihedral angle between the coupled nuclei.

Recently we have found that the two-electron integrals that both, introduce the electron correlation at the RPA level of approach within the polarization propagator formalism and follow the Karplus rule, have a non-local behavior.[1] After this finding we started to think about whether the excitations that contain those orbitals are entangled. If indeed they are, we might suggest that quantum entanglement would be the phenomenon that can explain the Karplus rule.

Until now it was not possible to study the quantum entanglement applying polarization propagators. The reason is the fact that it is not an easy task to define a proper density function and then to calculate the entropy of the system using those propagators.

In this presentation we propose a partition function that is valid within the polarization propagator scheme.[2] From such a function we take an additional step forward and define a density function, which allow us to quantify the entanglement between molecular orbital excitations.[3]

We present preliminary results calculated with our novel scheme, where it is shown that the above mentioned excitations are actually entangled.

[1] G. A. Aucar, R. H. Romero, A. F. Maldonado, *Int. Rev. in Phys. Chem.* **29**, 1-64 (2010).

[2] G. A. Aucar, *Phys. Chem. Chem. Phys.* **16**, 4420-4438 (2014).

[3] K. Boguslawski, P. Tecmer, G. Barcza, O. Legeza, M. Reiher, *J. Chem. Theory Comput.* **9**, 2959-3973 (2013)

## **RmatReact: Developing Novel Theoretical Methodology to Investigate Ultra-cold Atom-Molecule Collisions over Deep Potential Wells**

**Laura K McKemmish<sup>1,2</sup>, Tom Rivlin<sup>1</sup>, Jonathan Tennyson<sup>1</sup>**

<sup>1</sup>*Department of Physics and Astronomy, University College London, London, UK*

<sup>2</sup>*School of Chemistry, University of New South Wales, Kensington, Sydney, Australia*

Cutting-edge experimental studies in the field of molecular science are pushing the limits of current theoretical frameworks, requiring the development of new quantum chemistry methodologies that are capable of describing systems in increased detail, particularly at high levels of internal energy up to and above dissociation.

One key area that would benefit from improved theoretical description is experimental ultracold chemistry studies, which aim to understand and ultimately control chemical processes at the quantum level, with reactants and products being fully specified in terms of quantum numbers. Adequately conceptualising such reactions presents the greatest challenge to chemical theory whilst accurate computation presents the greatest challenges to both electronic-structure theory and the quantum theory of nuclear motion, especially when the collisions occur over deep potential wells. We are working on developing a new methodology [?], RmatReact, to address these significant challenges by dividing a modelled molecular collision into two spatial regions: an inner-region solved once using an expensive, high accuracy calculation and a fast outer-region calculation performed for a fine grid of collision energies that provides process and reaction cross-sections. This technique has the potential to provide the theoretical framework to describe and motivate a whole generation of new experiments, addressing important and fundamental scientific problems associated with quasi-bound resonance states formed when two atomic or molecular systems collide at specific ultra-cold energies over deep wells.

[1] J. Tennyson, LK McKemmish, T Rivlin, Faraday Discussions, 195 (2016)

**From Sequence to Function, QM/MM and Virtual Screening  
identify enzyme function and substrate scope**

**Marco Bocola<sup>1,2</sup>, Gaurao V. Dhoke<sup>1</sup>, Mehdi D. Davari<sup>1</sup>**

<sup>1</sup>*Department/ Lehrstuhl für Biotechnologie, RWTH Aachen University,  
Worringer Weg 3, D-52074 Aachen, Germany*

<sup>2</sup>*ProteDes , Protein Engineering and Design  
Siemensstr. 6g, D-53757 Sankt Augustin, Germany*

Bioinformatic databases contain sequence data for millions of proteins and enzymes of unknown function. Enzymes identified from natural sources often have interesting biocatalytic properties. NADH-dependent ADH from *Candida parapsilosis* (cpADH5), is a candidate for the selective reduction of diketones to industrially important chiral hydroxy ketones. [1] The natural function and substrate scope of cpADH5 is not known.

Computation methods can help to solve the quest from sequence to enzyme function by virtual screening and QM/MM calculations to identify function and substrate scope.

To this end we have investigated the catalytic mechanism by QM/MM calculations [3], based on the X-ray crystal structure [2] of cpADH5 in the substrate free resting state. We have validated a mechanism based predictive molecular docking method for the ranking of Zn<sup>2+</sup>-dependent medium chain dehydrogenase substrates. [4,5]

The presented computational substrate screening strategy [6] combining virtual screening, pathway database search and QM/MM calculations for “in silico” substrate scope identification presents a promising technique for mechanism based enzyme annotation of (metallo)-enzymes of unknown function and set the stage for biocatalyst design.

- [1] A. Jakoblinnert et al. *ChemBioChem*, **13**, 803–809 (2012).
- [2] H. Man et al. *ChemCatChem*, **6**, 1103–1111 (2014).
- [3] G. V. Dhoke et al., *ACS Catalysis* **5**, 3207–3215 (2015).
- [4] G. V. Dhoke et al., *J. Comput. Aided Mol. Des.* **29(11)**, 1057–1069 (2015).
- [5] C. Loderer et al., *ChemBioChem* **16**, 1512–1519 (2015).
- [6] G. V. Dhoke et al., *J. Chem. Inf. Model.* **56 (7)**, pp 1313–1323 (2016).

## Probability current analysis and the charge transfer integral in organic semiconducting materials

**Sang-Yeon Hwang<sup>1</sup> and Woo Youn Kim<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, KAIST, 291, Daehak-ro, Yuseong-gu, Daejeon, Republic of Korea*

Being one of the essential parameters characterizing molecular charge transfer reactions, the electronic coupling element, called the charge transfer integral, has served as a central subject of investigation in the field. Accordingly, a profuse number of theories have been developed for computing the quantity, where a standard method uses the frontier orbitals of a transfer pair and evaluates the matrix element of the (Kohn-Sham-)Fock Hamiltonian. Alexei Stuchebrukhov's tunneling current theory also estimates the charge transfer integral, based on its distinctive feature of incorporating the charge carrier's probability current [1-2]. As the theory was mostly applied to protein systems to analyze charge transfer pathways, in this research we focused on the charge transfer integral itself and probed the method's applicability on small and medium sized organic systems. To make quantitative analysis possible, we used the molecule dimers in the works of Adam Kubas and co-workers [3-4]. We evaluated the transfer integrals by the tunneling current theory as well as the standard Fock matrix method, and the former showed smaller errors from those by high-level calculations. As we used the same frozen-core diabatic determinants for the both methods, we attribute the performance to the exact derivation (after the frozen transition-state assumption) of the transfer integral in the former theory. In addition, we computed the probability currents in the dimer conformers of an organic semiconductor molecule and visualized how structural changes affect the charge transfer tendency. Besides reliable estimation of transfer integrals, the probability current makes structure-based design of improved charge transfer materials more viable.

- [1] A. A. Stuchebrukhov, *J. Chem. Phys.* **104**, 8424 (1996).
- [2] A. A. Stuchebrukhov, *J. Chem. Phys.* **108**, 8499 (1998).
- [3] A. Kubas, F. Hoffmann, A. Heck, H. Oberhofer, M. Elstner, and J. Blumberger, *J. Chem. Phys.* **140**, 104105 (2014).
- [4] A. Kubas, F. Gajdos, A. Heck, H. Oberhofer, M. Elstner, and J. Blumberger, *Phys. Chem. Chem. Phys.* **17**, 14342 (2015).

## Pairwise specific reaction parameterization: a straightforward approach to improve semiempirical QM methods

Antoine Marion<sup>1</sup> and Iris Antes<sup>1</sup>

<sup>1</sup>Center for Integrated Protein Science Munich at the Department of Biosciences, Technische Universität München, Emil-Erlenmeyer-Forum 8, D-85354 Freising, Germany

Over the past decades, the interest in semiempirical quantum mechanical (SQM) methods has consistently increased together with the popularization of hybrid QM/MM approaches to model complex reactions within their corresponding environment. These approximate and parameterized QM Hamiltonians allow a quantum description of electronic structures for a computational cost that is compatible with extensive sampling techniques. Although very appealing and despite a constant improvement of the models, SQM approaches still suffer from several shortcomings that can result in quantitative or qualitative errors during the calculation of reaction energy profiles. This fact has led to the development of dedicated corrections focused either on the entire set of SQM parameters [1,2] or on specifically identified, faulty parts of the Hamiltonian [3,4]. Such approaches allow reaching qualitative and quantitative agreement between SQM methods and more accurate *ab initio* Hamiltonians. However, the development of such corrections is often tedious and requires a strong expertise in order to result in the optimization of an objective, consistent, and effective set of parameters.

We present a new and straightforward approach to improve SQM methods for a given reaction: Pairwise Specific Reaction Parameterization (PSRP). Unlike other strategies that optimize new parameters for all atoms in the molecular system [1-4], we introduce here the novel idea of a parameterization of only a few specific, targeted pairs, identified to be responsible for the inaccurate behavior of the original Hamiltonian, while all other atomic interactions remain unchanged. This crucial difference confers great advantages to the PSRP approach: i) the parameterization is straightforward and can be done on small isolated molecular models, and ii) the procedure is robust and does not introduce spurious artifacts for chemical groups that were not in the parameterization range since it is focused only on targeted parts of the system. Through our first applications we show that the PSRP strategy allows to successfully model reactions as complex and challenging as the catalytic activity of HCV-protease towards its natural substrate.

- [1] X. Wu, W. Thiel, S. Pezeshki, H. Lin, *J. Chem. Theory. Comput.* **9**, 2672 (2013).
- [2] S. Liang, A. E. Roitberg, *J. Chem. Theory. Comput.* **9**, 4470 (2013).
- [3] M. I. Bernal-Uruchurtu, M. F. Ruiz-lópez, *Chem. Phys. Lett.* **330**, 118 (2000).
- [4] A. Marion, G. Monard, M. F. Ruiz-lópez, F. Ingrosso *J. Chem. Phys.* **141**, 034106 (2014).

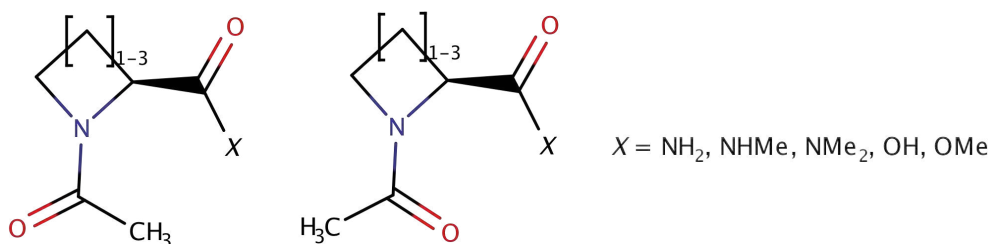
## Quantum-Chemical Calculations on the Influence of Molecular Dipole Moments on Conformational Equilibria.

Johannes C. B. Dietschreit<sup>1</sup>, Tobias Schnitzer<sup>2</sup>, Helma Wennemers<sup>2</sup>,  
Christian Ochsenfeld<sup>1</sup>

<sup>1</sup>Department of Chemistry, University of Munich (LMU), Butenandtstr. 7, 81377 Munich, Germany

<sup>2</sup>Laboratory of Organic Chemistry, D-CHAB, ETH Zürich, Vladimir Prelog Weg 3, CH-8093 Zürich, Switzerland.

The correlation between dipole moments and solvent polarity on the conformational equilibrium of proline-analogues is investigated using quantum-chemical calculations. The proline-analogues are capped amino acids with four, five, and six membered rings. The N-terminus is acetylated and the C-terminus carries one of five possible modifications (X=NH<sub>2</sub>, NHMe, NMe<sub>2</sub>, OH, OMe). The different C-terminal cappings lead to different dipole moments and thus different cis-trans equilibria for the N-terminal cap.



Our work is in line with an earlier study performed for prolines carrying different electron withdrawing groups on the ring [1]. In our present study, molecular geometries were obtained using the polarisable continuum model COSMO [2] at the PBEO-D3/def2-tzvp level [3-5]. The combined computational and experimental study indicates a connection between the solvent polarity and the molecular dipole. Their influence governs the conformational equilibrium measured in solution.

- [1] C. Siebler et al. *Chem. Sci.* **6**, 6725 (2015).
- [2] TURBOMOLE V7.02, 2015, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007, available from <http://www.turbomole.com>.
- [3] J.P. Perdew, M. Ernzerhof, K. Burke *J. Chem. Phys.* **105**, 9982 (1996).
- [4] S. Grimme, J. Antony, S. Ehrlich, and S. Krieg *J. Chem. Phys.* **132**, 154104 (2010).
- [5] F. Weigend, R. Ahlrichs *Phys. Chem. Chem. Phys.* **7**, 3297 (2005)

## Reduced scaling explicitly correlated coupled cluster methods for large molecular systems

Fabijan Pavošević<sup>1</sup>, Chong Peng<sup>1</sup>, Frank Neese<sup>2</sup>, Edward F. Valeev<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Virginia Tech, Blacksburg, Virginia, USA*

<sup>2</sup>*Max Planck Institute for Chemical Energy Conversion, Stiftstr. 34-36, 45470 Mülheim an der Ruhr, Germany*

In the first part of our talk, we will present a linear-scaling formulation and implementation of the coupled cluster singles doubles and perturbative triples method with perturbative treatment of explicit correlation. Our approach is based on the local domain pair natural orbital methodology using the SparseMap infrastructure developed by F. Neese and E. F. Valeev [1]. All post-mean-field steps in the DLPNO-CCSD(T)-F12 have computational cost that grows linearly with the system which is shown for *n*-alkane with up to 200 carbon atoms in the def2-TZVP basis set. The robustness of the DLPNO-CCSD(T)-F12 method was validated against the massively-parallel canonical CCSD(T)-F12 method in the MPQC4 package [2] for a 20-water cluster and applied to the L7 benchmark dataset for non-covalent interactions [3]. In the second part of our talk, we will present a massively-parallel implementation of the Laplace-transform perturbative triple correction (T) to the CCSD energy within density fitting framework [4]. We will validate precision of the method with respect to number of quadrature points on large molecular systems. Furthermore, we will compare the performance to a state of the art implementation in the NWChem quantum chemistry software [5] on a DNA base-pair, a system with more than one thousand basis functions.

- [1] P. Pinski, C. Riplinger, E. F. Valeev, F. Neese, *J. Chem. Phys.* **143**, 034108 (2015).
- [2] C. Peng, J. A. Calvin, F. Pavošević, J. Zhang, E. F. Valeev, *J. Phys. Chem. A* **120**, 10231 (2016).
- [3] F. Pavošević, C. Peng, P. Pinski, C. Riplinger, F. Neese, E. F. Valeev, *J. Chem. Phys.* **146**, 174108 (2017).
- [4] F. Pavošević, C. Peng, E. F. Valeev, *Manuscript in preparation*.
- [5] V. M. Anisimov, G. H. Bauer, K. Chadalavada, R. M. Olson, J. W. Glenski, W. T. C. Kramer, E. Aprà, K. J. Kowalski, *J. Chem. Theory Comput.* **10**, 4307 (2014).



## Efficient and Accurate Born-Oppenheimer Molecular Dynamics for Large Molecular Systems

Laurens D. M. Peters<sup>1, 2</sup>, Jörg Kussmann<sup>1, 2</sup>, Christian Ochsenfeld<sup>1, 2</sup>

<sup>1</sup>*Chair of Theoretical Chemistry, Department of Chemistry, University of Munich (LMU),  
Butenandtstr. 7, D-81377 München, Germany*

<sup>2</sup>*Center for Integrated Protein Science (CIPSM) at the Department of Chemistry, University of  
Munich (LMU), Butenandtstr. 5–13, D-81377 München, Germany*

Born-Oppenheimer molecular dynamics (BOMD) simulations have become a powerful tool for sampling potential energy surfaces, predicting experimental spectra, and calculating thermodynamic properties. These observables are usually obtained as means or integrals of properties, so that many time steps are necessary to yield accurate results. Consequently, a huge number of minimizations of the electronic wavefunction and determinations of the gradient of the electronic ground state are required. BOMD simulations are, therefore, computationally demanding especially when the system contains more than 100 atoms.

Here, we introduce a scheme that enables efficient and accurate BOMD simulations of large molecular systems [1]. It combines three recent developments from the fields of BOMD, electronic structure theory, and computer technology: (1) The corrected small basis set Hartree-Fock (HF-3c) method by Sure and Grimme [2], which yields accurate interaction energies and geometries (comparable to large basis set density functional theory calculations) at the cost of one Hartree-Fock calculation with a minimal basis set, (2) the extended Lagrangian BOMD (XL-BOMD) method by Niklasson *et al.* [3], which reduces the number of necessary self-consistent field cycles, and (3) efficient methods for calculating Coulomb and exchange terms on graphics processing units (GPUs) within our FermiONs++ program package [4, 5].

To explore the performance of our strong scaling implementation of the method we present timings and first illustrative applications by extracting high-quality vibrational spectra from simulated trajectories of several molecular systems containing up to 500 atoms. We conclude that the presented BOMD scheme may be used as a cost-efficient and reliable tool for computing vibrational spectra and thermodynamics of large molecular systems with more than 100 atoms and explicit solvent molecules.

- [1] L. D. M. Peters, J. Kussmann, C. Ochsenfeld, *to be published*.
- [2] R. Sure, S. Grimme, *J. Comput. Chem.* **34**, 1672 (2013).
- [3] A. M. N. Niklasson, P. Stenetag, A. Odell, N. Bock, M. Challacombe, C. J. Tymczak, E. Holmström, G. Zheng, V. Weber, *J. Chem. Phys.* **130**, 214109 (2009).
- [4] J. Kussmann, C. Ochsenfeld, *J. Chem. Phys.* **138**, 134114 (2013).
- [5] J. Kussmann, C. Ochsenfeld, *J. Chem. Theory Comput.* **11**, 918 (2015).

## Resonant inelastic X-ray scattering amplitudes and cross-sections in the ADC/ISR framework

Dirk R. Rehn<sup>1</sup>, Andreas Dreuw<sup>2</sup>, Patrick Norman<sup>1</sup>

<sup>1</sup>*Department of Theoretical Chemistry and Biology, School of Biotechnology, Royal Institute of Technology, 100 44 Stockholm, Sweden*

<sup>2</sup>*Interdisciplinary Center for Scientific Computing, University of Heidelberg, Im Neuenheimer Feld 205, 69120 Heidelberg, Germany*

With the development of 4th generation synchrotron radiation sources one has not only reached an unprecedented control of energy, momentum, and polarization of the source photons but also provided access to light of ultra-high brilliance. This combination has in turn led to a rapid recent development in experiments based on the resonant inelastic X-ray scattering (RIXS) phenomenon. The refinement of RIXS remains in the spotlight even though it has been an established method for decades.

*Ab initio* simulations of RIXS cross-sections based on the Kramers-Heisenberg-Dirac (KHD) formula offer valuable support for the interpretation and in-depths understanding of the complex experimental spectra. However, common approaches based on the KHD expression are usually limited to a qualitative description including only selected channels.

The algebraic diagrammatic construction [1] (ADC) scheme of the polarization propagator together with the so-called intermediate state representation (ISR), offers a convenient and straightforward way to evaluate the full electronic part of the RIXS scattering amplitudes. This is achieved by transforming the KHD formula into a closed-form matrix expression which can be solved using standard numerical techniques.

We present an implementation [2] which provides to our knowledge for the first time access to a quantitative theoretical description of RIXS amplitudes and transition strengths for medium-sized molecular systems. Based on the ADC/ISR approach our implementation facilitates the simulation of RIXS maps up to third order in perturbation theory.

[1] A. Dreuw and M. Wormit, *WIREs Comput. Mol. Sci.* **5**, 82, 2015

[2] D. R. Rehn, A. Dreuw and P. Norman, *J. Chem. Theory Comput.*, submitted

## Simulation of absorption and emission spectra of Laurdan in bilipid layer systems

**Mirza Wasif Baig,<sup>1</sup> Marek Pederzoli,<sup>1</sup> Lukasz Cwiklik<sup>1</sup> and Jiri Pittner<sup>1</sup>**

*<sup>1</sup>Department of Theoretical Chemistry, J Heyrovsky Institute of Physical Chemistry  
Dolejškova 2155/3, 182 23 Prague 8, Czech Republic*

**Abstract:** Fluorescence is a process following light absorption in which a molecule emits photons of longer wavelength than the photon absorbed during absorption. This shift toward lower energy results from vibrational relaxation of the molecule in the excited state. In condensed phases, in particular in water, polarity of solvent often has a very pronounced effect on emission wavelength because in the excited state the relaxation processes include both fluorophore and solvent relaxation. This solvatochromic effect is often utilized in fluorescence spectroscopy methods, for instance, in time resolved emission spectroscopy (TRES) where both the total energy shift and relaxation kinetics can be measured. In biological environments, such as lipid bilayers, the solvatochromic effects are typically used for probing system hydration and dynamics at the nanometer and nanosecond levels. To this end, environmental sensitive fluorescent probes are which significant solvatochromic shifts are used.

Laurdan (6-Dodecanoyl-2-Dimethylaminonaphthalene), is often employed to investigate lipid membrane hydration and mobility. Still, exact mechanism of Laurdan fluorescence in lipid bilayers is not fully understood. We investigate absorption and fluorescence spectra of Laurdan in two phospholipid bilayers, DOPC and DPPC, characterized by different hydration and rigidity. Classical molecular dynamics simulations are employed to sample conformations of Laurdan in both membranes. Empirical force field is used to describe both ground and excited state dye in MD simulations. For selected snapshots, excited state molecular dynamics simulations employing a quantum mechanical and molecular mechanical approach with time-dependent density functional theory (TD-DFT QM/MM MD) are performed. The resulting spectra are compared with experimental ones in different membrane environments.

**Reaching graphene-water systems:  
A new electronic-structure-based force field**

**Sergi Ruiz-Barragan<sup>1</sup>, Daniel Muñoz-Santiburcio<sup>1</sup>, Dominik Marx<sup>1</sup>**

<sup>1</sup>*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum*

Since its discovery, graphene is receiving an ever-increasing attention due its fascinating properties and applications [1, 2]. Although there are many experimental and theoretical studies about graphene in contact with water [2], the interaction between these two components is difficult to determine experimentally [3]. On the other hand, the computational determination of the water/graphene interaction energy is rather cumbersome because of its really weak character, taking into account that the most exact methods are not feasible for large systems. For this reason, the values in the literature are discordant [4], which makes it difficult to properly define a force field for the water/graphene interaction.

In this work, a new force field based on RPBE-D3 calculations is presented. RPBE-D3 is computationally affordable and its description of the water/graphene interaction is in agreement with previous CCSD(T) results [5]. We show how this force field can reproduce properly the features of water/graphene interface obtained at the *ab initio* level. This new force field can be used to estimate slowly-converging properties only reachable with simulation times in the order of nanoseconds, not accessible with *ab initio* MD.

- [1] A. Geim, K. Novoselov, *Nature Materials* **6**, 183 (2007).
- [2] A. Striolo, M. Angelos, J. Laurent, *Annu. Rev. Chem. Biomol. Eng.* **7**, 533 (2016).
- [3] F. Taherian, V. Marcon, N. van der Vegt, *Langmuir* **29**, 1457 (2013)
- [4] Y. Wu, N. Aluru, *J. Phys. Chem. B* **117**, 8802 (2013)
- [5] E. Voloshima, D. Usvyat, M. Schütz, Y. Dedkov, B. Paulus, *Phys. Chem. Chem. Phys.* **13**, 12041 (2011)

## Site-Occupation Embedding Theory using Bethe Ansatz Local Density Approximation

**B. Senjean<sup>1</sup>, N. Nakatani<sup>2</sup>, M. Tsuchiizu<sup>3</sup>, E. Fromager<sup>1</sup>**

<sup>1</sup>*Laboratoire de Chimie Quantique, Institut de Chimie, CNRS/Université de Strasbourg, Strasbourg, France*

<sup>2</sup>*Institute for Catalysis, Hokkaido University, N21 W10 Kita-ku, Sapporo, Hokkaido 001-0021, Japan*

<sup>3</sup>*Department of Physics, Nagoya University, Nagoya, Japan*

Modelling strongly correlated electronic systems is still challenging in both quantum chemistry and condensed matter physics. A system is said to be strongly correlated if its physical properties are governed by non-trivial electron-electron interactions. For instance, this is the case for transition metal oxides when the electrons are close to a metal-insulator transition. In this case, mean-field approaches such as the Hartree Fock give a wrong description of the properties of the system. To deal with such systems, we have to go beyond the mean-field approximation:

- On the one hand, the interaction can be computed thanks to an explicit treatment of the electronic wavefunction (Density Matrix Renormalization Group[1], post Hartree-Fock methods), which is computationally expensive.
- On the other hand, Kohn-Sham Density Functional Theory (KS-DFT)[2] is a computationally low cost method with a relatively good accuracy. However, standard approximations made for the density functionals often fail to describe strong correlation energies.

One strategy is to build a theory which makes the best compromise between computation time and accuracy. In this context, an embedding scheme in principle exact called Site-Occupation Embedding Theory (SOET)[3,4] treats the correlation explicitly on some sites (called impurities), while the rest of the system is noninteracting (called bath) and treated with a density functional. SOET is therefore a rigorous combination of wavefunction method (DMRG) and DFT. The Hubbard model (see Figure) will be our laboratory because of its simplicity as well as its physical richness. In this embedded context, approximate density functionals based on KS-DFT applied to model Hamiltonians[5] and on the standard Anderson impurity model[6] are studied.

[1] S.R. White, *Phys. Rev. Lett.* **69**, 2863 (1992)

[2] W. Kohn and L. Sham, *Phys. Rev.* **140**, A1133 (1965)

[3] E. Fromager, *Mol. Phys.* **113**, 419 (2015)

[4] B. Senjean, M. Tsuchiizu, V. Robert and E. Fromager, *Mol. Phys.* **115**, 48 (2017)

[5] N. Lima, M. Silva, L. Oliveira and K. Capelle, *Phys. Rev. Lett.* **90**, 146402 (2003)

[6] P.W. Anderson, *Phys. Rev.* **124**, 41 (1961) ; K. Yamada, *Progr. Theoret. Phys.* **53**, 970 (1975) ; J.P. Bergfield, Z.F. Liu, K. Burke and C.A. Stafford, *Phys. Rev. Lett.* **108**, 066801 (2012)

## Chemical dynamics simulations to study tandem mass spectrometry peptide fragmentation: polyproline series [pro<sub>n</sub>-H]<sup>-</sup> as example.

Ana Martin-Somer<sup>1,2</sup>, William. L. Hase<sup>3</sup>, and Riccardo Spezia<sup>2</sup>

<sup>1</sup>*Departamento de Química, Universidad Autónoma de Madrid, Madrid (Spain)*

<sup>2</sup>*CNRS, Université d'Evry, Evry (France)*

<sup>3</sup>*Texas Tech University, Lubbock, Texas (USA)*

Positive mode mass spectrometry (MS) is routinely used in fields like proteomics [1]. Negative mode, is however less popular, while being a rather good complement to the aforementioned positive mode. A number of questions can be put forward about the fragmentation chemistry involved in negative mode MS. Where does the peptide deprotonate in absence of acidic residues? After activation of peptide anions, are protons mobile in a similar fashion as in their protonated analogues? Does the size of the peptide-chain influence the fragmentation?

Polyprolines are good models to address these questions since they possess no amide or acidic protons. In this work we studied pro<sub>2</sub><sup>-</sup>, pro<sub>3</sub><sup>-</sup> and pro<sub>4</sub><sup>-</sup> fragmentation using direct dynamics simulations[2] (the potential energy surface is computed on-the-fly using PM3 semiempiric Hamiltonian). We performed two kinds of simulations: i) the molecule is internally excited, considering a uniform distribution of the energy within the molecule. ii) the anion is made to collide with Ar in such a way that the translational energy is transferred to the vibrational and rotational modes of the peptide.

Using this technique we could explain, at an atomic level, the unimolecular reactivity of [pro<sub>n</sub>-H]<sup>-</sup>, *i.e.*, the mechanisms leading to the different fragments (as for example the typical b<sub>2</sub><sup>-</sup> and y<sub>1</sub><sup>-</sup>). We also observed some differences between the two ways of activating the molecule. For internally excited trajectories unimolecular dissociation follows exponential decay while in collision activation the initial population decays in a non-exponential way [3]. Furthermore, the thermal simulations allowed us to compute the temperature dependent rate constants,  $k(T)$ , and the Arrhenius  $A$  and  $E_a$  parameters. To complete the information provided by trajectories we compared results with those obtained experimentally. To the best of our knowledge, this is the first time that dynamics simulations are applied to explain the fragmentation of negative peptide ions.

[1] A.Bensimon, A.J.R. Heck, and R.Aebersold, *Annu. Rev. Biochem.*, **81**, 379 (2012).

[2] S.Pratihar, X.Ma, Z.Homayoon, G.L.Barnes, W.L.Hase, *J. Am. Chem. Soc.* **139**, 3570 (2017).

[3] R.Spezia, A.Martin-Somer, V.Macaluso, Z.Homayoon, S.Pratihar and W.L.Hase, *Faraday Discuss.* **195**, 599 (2016).

## Oxidation of metallocenes as external stimuli to enhance the reactivity of catalytically active metal complexes

**Stephan Kohaut<sup>1</sup>, Alexander Feyrer<sup>2</sup>, Frank Breher<sup>2</sup>, Karin Fink<sup>1</sup>**

<sup>1</sup> *Institut für Nanotechnologie, Karlsruher Institut für Technologie (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

<sup>2</sup> *Institut für Anorganische Chemie, Karlsruher Institut für Technologie (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany*

Hydrosilylation is one of the key catalytic reactions in the synthesis of organosilicon compounds. Depending on the catalytically active metal center two possible reaction paths have been proposed [1]. In contrast to its heavier neighbor platinum it was concluded for rhodium that the hydrosilylation reaction proceeds through a modified Chalk-Harrod mechanism [2]. Recently it was shown that a redox-active, mesityl(Mes)-substituted phosphafferrocenophane (FcPMes) can influence the reactivity of a coordinated transition metal within the proposed modified Chalk-Harrod mechanism [3]. Oxidation of the metal center in the metallocene led to enhanced reactivity and selectivity towards the hydrosilylation of alkynes by a rhodium complex. Thereby it was observed from DFT based calculations, that the positive partial charge from the metallocene was partially shifted to the rhodium atom which led to a significantly lower barrier for the final reductive elimination step. In addition to the previous work we studied the influence of the oxidation of the metal center on the other steps of the catalytic process.

For a detailed understanding of the role of the metallocene unit on the reaction at the rhodium site, we investigated several model systems. The role of the iron center is analyzed by substitution with different 3d elements (Co, Zn) or by removing the metal center completely. This allows to differentiate between cooperative effects between the metal centers and the sterical effect due to the metallocene unit.

[1] A. K. Roy, *Adv. Organomet. Chem.* 2008, **55**, 1 (2008).

[2] S. Sakaki, M. Sumimoto, M. Fukuhara, M. Sugimoto, H. Fujimoto, S. Matsuzaki, *Organometallics* **21**, 3788 (2002).

[3] A. Feyrer, M. K. Armbruster, K. Fink, F. Breher, *Chem. Eur. J.* **23**, 7402 (2017).

We thank the DFG for funding within the collaborative research centre SFB/TRR 88 “Cooperative effects in homo- and heterometallic complexes (3MET)”, projects B1 and B4.

**Electronic structure and reactivity with alkenes of iron carbenes complexes:  
Towards iron-based olefin metathesis.**

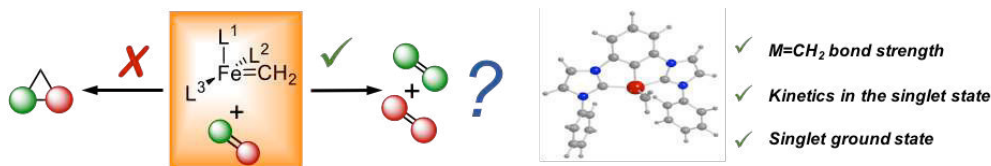
**Xavier Solans-Monfort,<sup>1</sup> Égil de Brito Sá,<sup>1,2</sup> Luis Rodríguez-Santiago,<sup>1</sup>  
Mariona Sodupe<sup>1</sup>**

<sup>1</sup> *Universitat Autònoma de Barcelona, Cerdanyola del Vallès, 080290, Barcelona-Espanya*

<sup>2</sup> *Universidade Federal do Piauí, Campus Ministro Reis Velloso, Parnaíba, 64202-020, Piauí-Brasil*

Olefin Metathesis (OM) is an efficient synthetic tool for carbon-carbon double bond formation. It requires the presence of a metal carbene  $[M]=CR_2$  acting as catalyst to take place. Most of the carbenes used today are based on Mo, W and Ru. These metals are not within the most abundant elements in earth. Therefore, substituting them for cheaper, eco-friendly and less toxic first row transition metal complexes is a desirable goal. In this way, iron appears as the best candidate, since it belongs to the same group as ruthenium. Unfortunately, the synthesis of iron carbenes is challenging and the existing species does not perform metathesis. That is, cyclopropanation is the most common process when reacting first row transition metal carbenes with olefins. Computational chemistry appears as potential technique for determining the suitable combination of ligands, oxidation state and coordination around iron that could favor the olefin metathesis reaction.

In this contribution, we study the reactivity of the existing  $[Fe]=CH_2$ , as well as a large set of possible *in silico* designed  $L_3M=CH_2$  and  $L_4M=CH_2$  carbenes. In a first stage, we calibrated the different DFT methods with the available experimental date. Afterwards, we analyzed which coordination sphere, nature of the ancillary ligands and oxidation state of iron could favor olefin metathesis instead of cyclopropanation. Results show that alkyl-containing  $\sigma$ -donating ligands promotes singlet ground state iron carbenes. However, this is not sufficient for favoring metathesis. In fact, the best combination of ligands is highly sensitive to the geometry around the metal center and coordination number.[1]



[1] E. de Brto Sá, L. Rodríguez-Santiago, M. Sodupe, X. Solans-Monfort, *Organometallics*. **35**, (2016) 3914.



## Enhanced sampling methods at the bio-inorganic interface: insights on silica biocompatibility and nanotoxicity

**Massimo Delle Piane, Nils Hildebrand, Lucio Colombi Ciacchi**

*Faculty of Production Engineering and Bremen Center for Computational Material Science, University of Bremen, Am Fallturm 1 28359, Bremen, Germany*

The interaction between biomolecules and inorganic materials has become of prominent interest in fields ranging from basic research up to industrial product design, leaving several open challenges. Among inorganic materials, the interaction of silica with biological systems is particularly complex and contradictory, particularly at the nano-level. Indeed, on the one hand, silica is at the basis of several biomineralization processes, on the other hand, the contact of some types of silica nanoparticles with the membrane of erythrocytes is known to cause its rupture.

Molecular dynamics (MD) simulations are a valuable tool in investigating these interactions. However, despite the increase in available computational resources, MD still suffers a debilitating timescale problem that greatly reduces the number of phenomena that can be investigated. Numerous enhanced sampling methods have been introduced to alleviate this problem[1], such as Metadynamics (MetaD) and Replica Exchange with Solute Tempering (REST).

We will here present examples of their applications, to shed light on the interactions between biomolecules and silica. Particularly, recent results will be shown regarding the investigation of silica-induced protein conformational changes[2] and the effects of silica nanoparticles of various size and features on membrane models of different composition (Figure 1).

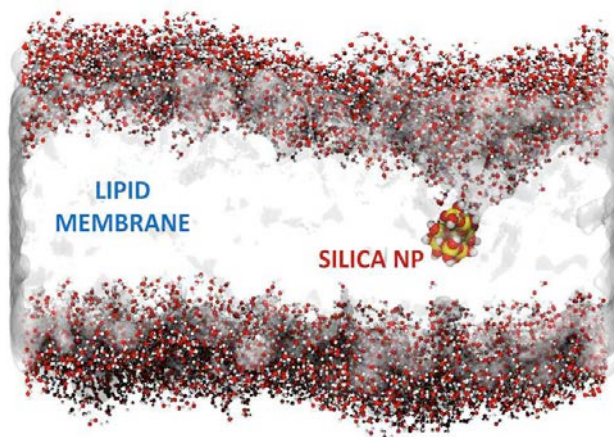


Figure 1: A small colloidal silica particle penetrating a phosphatidylcholine membrane.

- [1] T. P. Valson Omar, M. Parrinello, *Annu. Rev. Phys. Chem.* **67**, 159 (2016).
- [2] L. Derr, N. Hildebrand, S. Köppen, et al., *Biointerphases*. **11**, 011007 (2016).

## Understanding the Gas-phase Fragmentation Mechanisms of Deprotonated L-Cysteine-sulfate via Direct Dynamics Simulations.

**Veronica Macaluso<sup>1</sup>, Debora Scuderi<sup>2</sup>, M. Elisa Crestoni<sup>3</sup>, E. Martínez-Núñez<sup>4</sup>, William L. Hase<sup>5</sup> and Riccardo Spezia<sup>1</sup>**

<sup>1</sup>LAMBE, Univ Evry, CEA, CNRS, Université Paris-Saclay, Blvd. F. Mitterrand, Evry, France

<sup>2</sup>Laboratoire de Chimie Physique, UMR 8000, Université Paris Sud, Orsay, France

<sup>3</sup>Dipartimento di Chimica e Teconologie del Farmaco, Università di Roma La Sapienza, Rome, Italy

<sup>4</sup>Department of Physical Chemistry, University of Santiago de Compostela, Spain

<sup>5</sup>Department of Chemistry and Biochemistry, Texas Tech University, Lubbock (TX), USA  
veronica.macaluso@univ-evry.fr

Thiolate cystenyl residues of proteins have different roles in different cellular processes, in particular, in combatting the oxidative stress. In fact, Cys-SH functions are known as to be the major targets of peroxides species, and the associated oxidation process can induce many different post-translational modifications. The sulfenic acid seems to be the most interesting one, since has been detected in a broad range of signalling cellular mechanisms. [1] Scuderi, Crestoni and co-workers have characterized the L-cysteine-sulphate anion ( $m/z$  200) via tandem mass spectrometry with the purpose of forming the deprotonated sulfenic acid ( $m/z$  136). In particular, coupling IR-MPD spectroscopy with collision induced dissociation (CID), they investigated the structure of these ions. How the  $m/z$  136 ion, and other fragment ions obtained in gas phase as a function of collisional conditions, is an open question.

Coupling collisional dynamics simulations based on PM6-D semi-empirical Hamiltonian with DFT calculations, we have elucidated the different products suggesting the corresponding reaction mechanisms. First we were able to explain the selectivity in terms of thermodynamic *vs* kinetic control. Moreover, simulations suggested an initial common mechanism for the formation of  $m/z$  136, observed in ion traps, and the ion  $m/z$  81, which is the most abundant under linear collisional conditions. The last step is crucial to make the selection between these two ions and a roaming mechanism is at the basis of it. As in previous works [2] on roaming studies, our roaming mechanism product results to be the predominant product when performing IR-MPD experiments on the parent ion.

[1]D. S. Rehder, C. R. Borges, *Biochemistry*, **49**, 7748–7755 (2010)

[2]J. M. Bowman, *Mol Phys*, **112**, 2516-2528, (2014)

## Molecular Dynamics applied to peptide nanotubes in a membrane environment

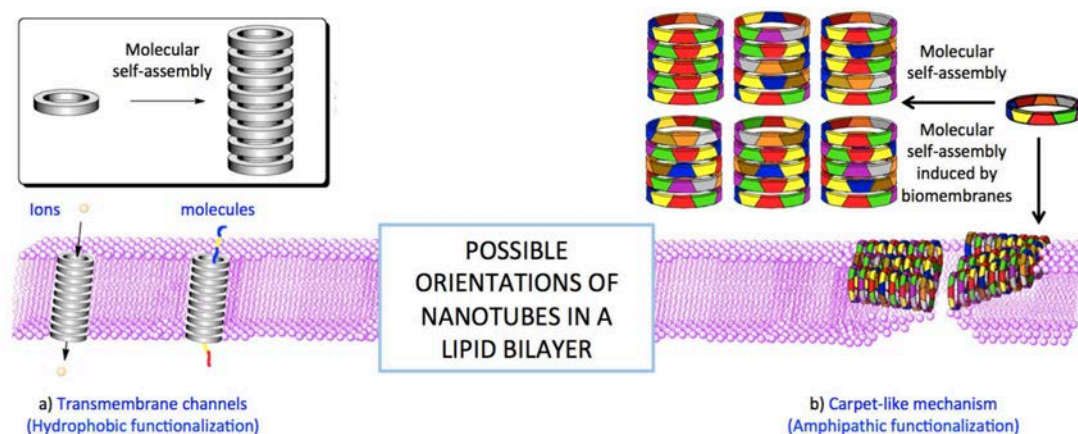
M. Calvelo,<sup>1</sup> J. R. Granja,<sup>1</sup> R. Garcia-Fandino<sup>1,2</sup>

<sup>1</sup>*Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS), University of Santiago de Compostela 15782 Santiago de Compostela, Spain*

<sup>2</sup>*CIQUP, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, R. Campo Alegre s/n, P-4169-007 Porto, Portugal.*

Self-assembling cyclic peptide nanotubes (SCPNs) have attracted a great amount of attention from the scientific community in recent years due to their important applications in biology, chemistry and material science.[1] They are based on cyclic structures that adopt a planar form with the amide groups arranged perpendicular to the plane of the cycle so that they are stacked by the formation of  $\beta$ -sheets. The radial disposition of the side chains outwards the channel modifies the external properties of the nanotube, allowing to control their formation and properties. The modulation of the external properties of SCPNs allows the design of cyclic peptides (CPs) that self-assemble into lipid membranes, changing their permeability and resistance properties.[2] Depending on the sequences the formed SCPNs can be oriented perpendicularly to the lipid membrane (hydrophobic CPs) or in a parallel fashion (amphiphilic CPs). The consequences of this orientation determine the response caused in the lipid membrane and confer them important properties, such as a high antimicrobial activity.

Using Molecular Dynamics simulations (both using atomistic-AA and coarse-grained-CG resolution) we have studied the effect of the inner-functionalization of the SCPNs cavities, as well as the modulation of their external properties when they are inserted into a lipid bilayer. Different examples carried out recently in our research group will be presented, showing the power of combining experimental and computational methods in the field of supramolecular chemistry and demonstrating the power of theoretical calculations when acting as an atomic microscope to analyze the fine details of a complex supramolecular structure.



[1] (a) A. Stavrakoudis, *Peptide*, **92**, 143 (2009). (b) A. Khalfa, *J. Phys. Chem. B*, **114**, 2676 (2010)

[2] D. Seebach, *Helv. Chim. Acta*, **80**, 173 (1997).

[3] (a) M. R. Ghadiri, *Nature*, **412**, 452 (2001). (b) L. Motiei, *Chem. Commun.*, 3693 (2009).

## Assemblage of Metal Hydrides Clusters: Theoretical Design of One and Two-Dimensional Structures for Hydrogen Storage.

C. Giraldo<sup>2</sup>, C. Z. Hadad<sup>2</sup>, W. Tiznado<sup>3</sup>, E. Osorio<sup>1</sup> and F. Ferraro<sup>1</sup>

<sup>1</sup>*Departamento de Ciencias Básicas, Universidad Católica Luis Amigó, Transversal 51A # 67B-90, Medellín, Colombia*

<sup>2</sup>*Grupo de Química-Física Teórica, Instituto de Química, Universidad de Antioquia, AA1226, Medellín, Colombia*

<sup>3</sup>*Departamento de Ciencias Químicas, Facultad de Ciencias Exactas, Universidad Andrés Bello, Av. República 275, Santiago, Chile*

Recently we have reported a theoretical design of new metal hydrides clusters based on the high stability of the  $\text{Al}_4\text{H}_7^-$  system [1]. Our results showed that the systems with the higher stability and a high percentage of hydrogen, by weight, correspond to systems where three aluminum atoms have been substituted by three Mg-H and Be-H units,  $\text{Be}_3\text{AlH}_{10}^-$  and  $\text{Mg}_3\text{AlH}_{10}^-$  systems. Interestingly, these flat and tetrahedral conformations persist after being doped with  $\text{Na}^+$  as contraion. In this work we report a theoretical study about the use of metal hydride clusters as assembly blocks for the formation a larger system, especially one and two-dimensional structures, in order to be used has hydrogen storage materials. For these purposes, the explorations on the potential energy surfaces (PES) of  $(\text{NaAl}_4\text{H}_7)_n$  and  $(\text{NaE}_3\text{AlH}_{10})_n$  clusters, whit  $\text{E}=\text{Mg-Be}$  and  $n=2-4$  systems were performed, in addition, some larger linear and circular structures were proposed to determine their stability. The results obtained in this work showed that the cluster prefer to interact through contraion, in agreement whit fukui functions regions, which allows maintaining their identity as building blocks; otherwise, its initial building blocks conformation is lost; additionally, it was found that the cluster containing beryllium is the one that more easily retains its conformation as a block. It was also found that H-L gap decreases as the size of the system increase, in agreement with Gemming et al., work on  $(\text{Mo}_3\text{S}_3)_n$  clusters [2]. On the other hand, some linear and circular structures were proposed with the aim of determining their stability; it was found that they are minima in the potential energy surface, but that they are around 30 kcal.mol<sup>-1</sup> less stable that the global minima.

[1] C. Giraldo, F. Ferraro, C. Z. Hadad, L. Ruiz, W. Tiznado and E. Osorio. *RSC Adv.* **7**, 16069, 2017.

[2] S. Gemming, G. Seifert, N. Bertram, T. Fischer, M. Gotz and G. Gantefor. *Chem. Phys. Lett.* **474**, 127, 2009.

## Alchemical Free Energy Calculations by Ensemble Dynamics: The Conveyor Belt Scheme.

David F. Hahn<sup>1</sup>, Philippe H. Hünenberger<sup>1</sup>

<sup>1</sup>Laboratory of Physical Chemistry, Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 2, 8093 Zurich, Switzerland

Molecular dynamics (MD) simulations are an important tool for studying chemical and biological processes at a molecular level. MD can be used to predict differences between different chemical environments or molecular entities by means of alchemical free energy calculations where two physical end states  $A$  and  $B$  are connected by a coupling parameter  $\lambda$  along an alchemical pathway. Most commonly these calculations are performed by thermodynamic integration (TI)[1] or Bennett's acceptance ratio (BAR)[2]. We present an alternative method based on  $\lambda$ -dynamics[3][4], which employs several copies of a system (replicas) as parts of an ensemble with an assigned periodic variable  $\Lambda$  and mass  $m_\Lambda$ . This ensemble is propagated in the  $\Lambda$ -space, simultaneously moving each replica accordingly in the mapped  $\lambda$  space. Because of force compensation, the total force on the  $\Lambda$  is significantly lower compared to the forces acting on the  $\lambda$  of a single replica and thus facilitating diffusion of each replica along the alchemical pathway. We apply the method to three model systems and compare it to TI, which reveals several advantages: (i) Instead of multiple simulations as in TI, one simulation with several replicas is sufficient, therefore the set-up is convenient. (ii) The method is easier to automatize because no prior knowledge about the curvature of the pathway is needed. (iii) Since the energy barriers are lowered in comparison to  $\lambda$ -dynamics of one system, a nearly uniform sampling is achieved along the pathway. (iv) Because the pathway is sampled continuously, there is no error due to quadrature. (v) The calculations converge faster than TI calculations, thus they are computationally more efficient.

[1] J.G. Kirkwood, *J. Chem. Phys.* **3**, 300 (1935).

[2] C.H. Bennett, *J. Comput. Phys.* **22**, 245 (1976).

[3] X. Kong, C.L. Brooks III, *J. Chem. Phys.*, **105**, 2414 (1996).

[4] N.S. Bieler, R. Häuselmann, P.H. Hünenberger, *J. Chem. Theory Comput.* **10**, 3006 (2014).

## Electron correlation from a screened Coulomb formalism

Daniel Kats<sup>1</sup>

<sup>1</sup>*Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany*

Electron correlation is an important concept which can be understood as the missing part in the mean-field treatment. Wavefunction-based approaches are widely used in quantum chemistry to compute the electron correlation. The electron correlation energy can also be calculated as an infinite sum of all possible Feynman diagrams (excluding the diagrams which correspond to the mean-field energy). Taking into account only some classes of diagrams or combinations of diagrams can yield a polynomial-scaling method applicable even to molecular systems for which many wavefunction-based methods fail. [1]

The recently introduced screened Coulomb formalism [2] can be seen as one of the ways to guide the summation of diagrams. It can be used to derive the distinguishable cluster doubles approach [3], which is usually more accurate than the coupled cluster doubles for weakly correlated systems, and gives qualitatively correct description of strongly correlated systems. [3, 4, 5]

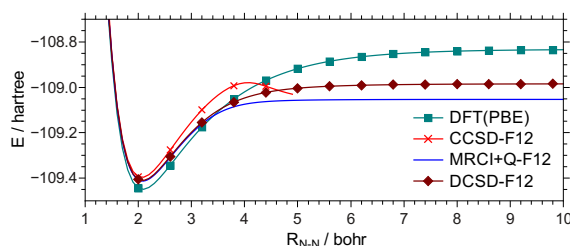


Figure 1:  $N_2$  potential energy curve using aug-cc-pVTZ basis.

In this contribution new developments will be presented which further improve the results of the distinguishable cluster approach.

- [1] R. D. Mattuck, *A Guide to Feynman Diagrams in the Many-Body Problem* (1976).
- [2] D. Kats, *J. Chem. Phys.* **144**, 044102 (2016).
- [3] D. Kats and F. R. Manby, *J. Chem. Phys.* **139**, 021102 (2013).
- [4] D. Kats, *J. Chem. Phys.* **141**, 061101 (2014).
- [5] D. Kats, D. Kreplin, H.-J. Werner, and F. R. Manby, *J. Chem. Phys.* **142**, 064111 (2015).

## Bringing DORI to analyze and understand fluxional molecules

**Benjamin Meyer<sup>1</sup>, Laurent Vannay<sup>1</sup>, Riccardo Petraglia<sup>2</sup>, Michele Ceriotti<sup>2</sup>  
and Cl  mence Corminboeuf<sup>1</sup>**

<sup>1</sup>Laboratory for Computational Molecular Design,   cole Polytechnique F  d  rale de Lausanne, CH-1015 Lausanne, Switzerland

<sup>2</sup>Laboratory of Computational Science and Modeling, Institute of Materials,   cole Polytechnique F  d  rale de Lausanne, CH-1015 Lausanne, Switzerland  
benjamin.meyer@epfl.ch

The Density Overlap Region Indicator[1] (DORI) is a density-based scalar field, which reveals covalent bonding patterns and non-covalent interactions simultaneously (Figure 1). The present work goes beyond the traditional static quantum chemistry use of scalar fields and illustrates the suitability of DORI for analyzing geometrical and electronic signatures in highly fluxional systems. Examples include a dithiocyclophane, which possesses multiple local minima featuring a different extend of  $\pi$ -stacking interactions; DORI is then employed to capture fingerprints of CH- $\pi$  and  $\pi$ - $\pi$  interactions throughout the temperature-dependent rotational processes of a molecular rotor. Finally, it serves to examine the fluctuating  $\pi$ -conjugation pathway of a photochromic torsional switch (PTS). Molecular dynamic trajectories are obtained using the REMD@DFTB framework,[2] which combines density functional tight binding in DFTB+ and replica exchange molecular dynamic as implemented in the dynamic driver i-PI.[3] Attention will be placed on post-processing the large amount of generated data and on reducing their dimensionality using DORI.

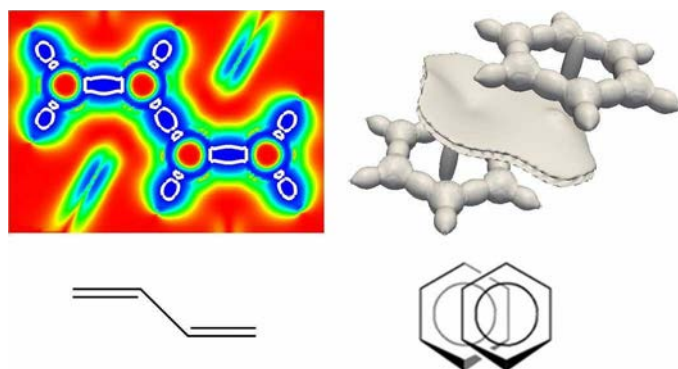


Figure 1: Two-dimensional DORI maps in the  $\sigma_h$  plane of the cyclobutadiene (left) and three dimensional DORI representation of the parallel-displaced benzene dimer (right).

- [1] P. de Silva, C. Corminboeuf, *J. Chem. Theory Comput.* **10**, 3745 (2014).
- [2] R. Petraglia, A. Nicol  i, M. D. Wodrich, M. Ceriotti; C. Corminboeuf, *J. Comput. Chem.* **37**, 83 (2016).
- [3] M. Ceriotti; J. More; D. E. Manolopoulos; *Comput. Phys. Commun.* **185**, 1019 (2014).



## Combining molecular docking and QM/MM methods for studying ligand binding to metalloproteins

**Okke Melse, Antoine Marion, and Iris Antes**

*Center for Integrated Protein Science Munich at the Department of Biosciences,  
Technische Universität München, Emil-Erlenmeyer-Forum 8, D-85354 Freising, Germany*

Combined Quantum Mechanics/Molecular Mechanics (QM/MM) studies were shown to be a valuable tool in areas of biomolecular simulations in which an explicit description of the system's electronic properties is needed, such as the prediction of spectroscopic properties or the simulation of enzymatic reactions [1]. More recently, QM/MM calculations were also evaluated for the area of computer-aided drug design, predominantly to improve the accuracy of binding free energy calculations and for the refinement of ligand binding poses. For these purposes many different variations in the free energy approaches as well as the QM methods applied were evaluated, with very varying success [2-3]. In the end, in most cases empirical, adjusting parameters were fitted to obtain satisfactory results.

We evaluated and optimized a new, combined molecular docking and QM/MM-based approach for the accurate calculation of ligand binding free energies in metal containing binding sites, which is not dependent on the use of any empirical fitting parameters. We specifically chose metalloenzymes as evaluation case as classical force fields are known to have several shortcomings in the description of metal interactions. Thus, describing the binding site with quantum mechanics should improve the description of potential polarization effects and the metal coordination. We evaluated different combinations such as calculating QM/MM interaction energies directly for optimized docking poses of the ligand or calculations of molecular dynamics-based QM/MMPBSA-based energies. In the presentation we will discuss the results obtained with the different combinations for four different metalloenzymes and present the final approach.

- [1] H. M. Senn, W. Thiel, *Angew. Chem. Int. Ed.* **48**, 1198-1229 (2009).
- [2] A. Khandelwal, S. Balaz, *Proteins: Struct., Funct., Bioinf.* **69**, 326-339 (2007).
- [3] H. Lu, X. Huang, et al., *Bioorg. Med. Chem.* **22**, 2149-2156 (2014).



## Vibrational properties of iridium and rhenium complexes in ground and excited states: Interpretation using DFT

Martin Pižl<sup>1,2</sup>, Stanislav Zálšíš<sup>1</sup>, Jan Heyda<sup>1,3</sup>, Antonín Vlček Jr.<sup>1,4</sup>

<sup>1</sup>*J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Dolejškova 3, 182 23 Prague, Czech Republic.*

<sup>2</sup>*Department of Inorganic Chemistry, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic.*

<sup>3</sup>*Department of Physical Chemistry, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic*

<sup>4</sup>*Queen Mary University of London, School of Biological and Chemical Sciences, Mile End Road, London E1 4NS, United Kingdom*

Measurements of vibrational properties are often used for characterization of complexes. In excited state, the time-resolved infrared (TRIR) spectroscopy is used for investigations of vibrational properties. In the present study, we focused on complexes containing iridium or rhenium metal atoms.

The binuclear iridium complex -  $[\text{Ir}_2(1,8\text{-diisocyanomenthane})_4]^{2+}$  - has two "deformational isomers" with different absorption at 470 nm (eclipsed) and 585 nm (twisted). Experimental photophysical data of both isomers were interpreted using DFT calculations in ground and excited states. Geometries of excited states were optimized by time-dependent DFT (TDDFT) for both singlet and triplet states.

In order to understand the character and dynamics of optically excited states DFT calculations were performed on  $[\text{Re}(\text{X})(\text{CO})_3(\text{L})]^n$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$ ;  $\text{L} = \text{bpy}$  (2,2'-bipyridine) or substituted bpy systems). Vibrational frequencies and intensities were calculated either by harmonic approach or by anharmonic one using the vibrational second order perturbation theory (VPT2) method. Molecular dynamic (MD) simulations on ground and the lowest triplet states followed by time DFT and TDDFT calculations at instant times were used for interpretation of time-dependent experimental data. Vibrational analyses of ground and excited states for both complexes are in good agreement with experimental data.

**Acknowledgements** This work was supported by the Ministry of Education of the Czech Republic (grant number LTC17052) and the COST Action CM1405.

## Molecular excitation energies from the Bethe-Salpeter equation

Xin Gui<sup>1</sup>, Christof Holzer<sup>1</sup>, Wim Klopper<sup>1</sup>

<sup>1</sup>*Institute of Physical Chemistry, Karlsruhe Institute of Technology, Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany*

The Bethe-Salpeter equation (BSE) [1] was initially derived in nuclear physics and later imported to the field of computational solid-state physics. Recently, it has been widespread for calculating molecular excitation energies and provided optimistic results in a variety of systems.[2-6] The BSE formalism is very similar to the time-dependent density functional theory (TDDFT) in the language of linear response, and thus has the same scaling with respect to system size as TDDFT. However, BSE can be applied for description of excitations that are particularly problematic for TDDFT, e.g. excitations with charge-transfer character. The BSE approach has recently been implemented in our TURBOMOLE program using a resolution-of-the-identity (RI) approximation for all two-electron integrals that are required to solve the equation.[7] Since BSE normally requires quasiparticle energies from preceding *GW* calculations as input, *GW* and BSE have often emerged together, which is known as the *GW*-BSE formalism. Here we present an extensive assessment of the performances of the *GW*-BSE approach for singlet and triplet valence and Rydberg excitations, charge-transfer transitions, and absorption spectra of transition metal complexes. We also investigate the performances of BSE with different underlying *GW* methods, since the quality of the *GW* energy levels strongly affects the BSE excitation energies.

- [1] E. E. Salpeter, H. A. Bethe, *Phys. Rev.* **84**, 1232 (1951).
- [2] D. Jacquemin, I. Duchemin, X. Blase, *J. Chem. Theory Comput.* **11**, 3290 (2015).
- [3] D. Jacquemin, I. Duchemin, X. Blase, *J. Chem. Theory Comput.* **11**, 5340 (2015).
- [4] D. Jacquemin, I. Duchemin, X. Blase, *Mol. Phys.* **114**, 957 (2016).
- [5] X. Blase, P. Boulanger, F. Bruneval, M. Fernandez-Serra, I. Duchemin, *J. Chem. Phys.* **144**, 034109 (2016).
- [6] D. Jacquemin, I. Duchemin, X. Blase, *J. Phys. Chem. Lett.* **8**, 1524 (2017).
- [7] K. Krause, W. Klopper, *J. Comput. Chem.* **38**, 383 (2017).

## Modelling the structural and optical properties of supramolecular arrays adsorbed on two-dimensional materials

**Anton S. Nizovtsev<sup>1,2</sup>, Matteo Baldoni<sup>1,3</sup>, Vladimir V. Korolokov<sup>4</sup>,  
Simon A. Svatek<sup>4</sup>, James Kerfoot<sup>4</sup>, Alex Summerfield<sup>4</sup>,  
Nicholas A. Besley<sup>1</sup>, Peter H. Beton<sup>4</sup> and Elena Besley<sup>1</sup>**

<sup>1</sup>*School of Chemistry, University of Nottingham, University Park,  
Nottingham NG7 2RD, United Kingdom*

<sup>2</sup>*Nikolaev Institute of Inorganic Chemistry SB RAS, Academician Lavrentiev Avenue, 3,  
Novosibirsk, Russia*

<sup>3</sup>*ISMN, CNR, via P. Gobetti 101, 40129 Bologna, Italy*

<sup>4</sup>*School of Physics and Astronomy, University of Nottingham, University Park,  
Nottingham NG7 2RD, United Kingdom*

Two-dimensional supramolecular assembly of organic molecules, which can be achieved on a wide range of different substrates, provides a highly flexible route to control the spatial organization of adsorbates and the chemical functionality of a surface.

We present an overview of our recent computational studies based on the classical molecular dynamics and density functional theory, which was focused on modelling the structural and optical properties of different molecular arrays adsorbed on graphene and hexagonal boron nitride (*h*BN). The following main findings are highlighted:

- (i) supramolecular organization of adsorbed alkane chains induces curvature in a graphene monolayer transferred onto a deformable substrate [1];
- (ii) supramolecular heterostructures can be formed on *h*BN surface by sequential deposition of layers with different structural properties [2];
- (iii) *h*BN surface influences the optical properties of the network formed by molecules, which are relevant for organic electronics.

We thank the Leverhulme Trust for providing financial support under the grant RPG-2016-104. EB acknowledges ERC Consolidator grant (307755 FIN).

[1] S. A. Svatek *et al.*, *Nano Lett.* **15**, 159 (2015).

[2] V. V. Korolokov *et al.*, *Nature Chem.* (2017), in press.

**Leading relativistic corrections for L=1 atomic states calculated with a finite-nuclear-mass approach and all-electron explicitly correlated Gaussian functions.**

**Monika Stanke<sup>1</sup>**

*<sup>1</sup>Institute of Physics, Faculty of Physics, Astronomy, and Informatics, Nicolaus Copernicus University, Grudziądzka 5, Toruń, PL 87-100, Poland*

We report progress in the development and implementation of quantum-mechanical methods for calculating bound ground and excited states of small atomic systems. The work concerns states with the  $L=1$  angular momentum quantum number. The method is based on the finite-nuclear-mass (non-Born-Oppenheimer; non-BO) approach and the use of all-particle explicitly correlated Gaussian functions for expanding the non-relativistic wave function of the system. The development presented here includes derivation and implementation of algorithms for calculating the leading relativistic corrections determined using the standard first-order perturbation theory as expectation values of the operators representing the corrections using the non-BO wave functions. The method is tested in the calculations of the ten lowest  $^1P$  states of the helium atom and the four lowest  $^1P$  states of the beryllium atom.

## Excited states with second order approximate internally-contracted multireference coupled-cluster linear response theory

Arne Bargholz<sup>1</sup>, Andreas Köhn<sup>1</sup>

<sup>1</sup>*Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany*

Based on previous work from e.g. Banerjee and Simmons [1], Hanauer *et. al* [2] have introduced the internally-contracted multireference coupled-cluster theory. Namely the singles-and-doubles method with and without perturbative triples (ic-MRCCSD(T) and ic-MRCCSD) as multireference analoga to the well known single reference CCSD(T) and CCSD methods. The new methods are able to accurately consider strong static correlation while improving upon the treatment of dynamic correlation over standard multireference methods like MRCISD. Yet they share the steep scaling in computational cost with their single reference analoga, ic-MRCCSD scales  $O(N^6)$  iteratively and ic-MRCCSD(T) includes an  $O(N^7)$  non-iterative step. We present a cheaper  $O(N^5)$  second order approximate internally-contracted multireference coupled-cluster theory (ic-MRCC2) which can be used to obtain excitation energies in the framework of linear response theory (compare also [3]).

We will present ground state energies and vertical excitation energies of selected molecules and compare them to CASPT2, NEVPT2 and full ic-MRCCSD and ic-MRCCSD(T) results.

- [1] A. Banerjee and J. Simons, *J. Quantum. Chem.* **2**, 207 (1981).
- [2] M. Hanauer and A. Köhn, *J. Chem. Phys.* **134**, 204211 (2011).
- [3] P. K. Samanta, D Mukherjee, M. Hanauer and A. Köhn, *J. Chem. Phys.* **140**, 134108 (2014).

## Molecular dynamics simulation steady-state prediction by electrostatics — applications in supramolecular chemistry

Jean-Noël Grad<sup>1</sup>, Daniel Hoffmann<sup>1</sup>

<sup>1</sup>*Bioinformatics and Computational Biophysics, Center for Medical Biotechnology, University of Duisburg-Essen, Universitätsstr. 7, D-45117 Essen, Germany*

Recent improvements in software and hardware have enabled computationally-tractable micro-second molecular dynamics (MD) simulation of large protein complexes, offering new insights into biological processes with slow kinetics. Nonetheless, the MD sampling problem remains a challenging obstacle[1], especially in supramolecular chemistry where the protein–polymer interface is stabilized by a multitude of weak and non-specific interactions, often leading to a combinatorial explosion of the conformational landscape accessible to the polymer. In such a situation, the MD simulation steady-state may never be reached. Two decades ago, a similar computational problem was solved using FFT-driven algorithms for protein–protein recognition based on shape complementarity and electrostatics[2, 3], allowing the exhaustive sampling of protein–protein interface energetic landscapes in a time-efficient manner. The technique was successfully transferred to protein–ligand docking and mapping[4, 5], and was recently adapted by our group into a tool for MD simulation steady-state prediction. Using electrically charged fragments of macromolecular ligands to exhaustively scan a protein surface, we could extract information to narrow down MD starting conditions or assess MD convergence. Two test cases are presented: sonic hedgehog–heparin interactions and 14-3-3/c-Raf stabilization.

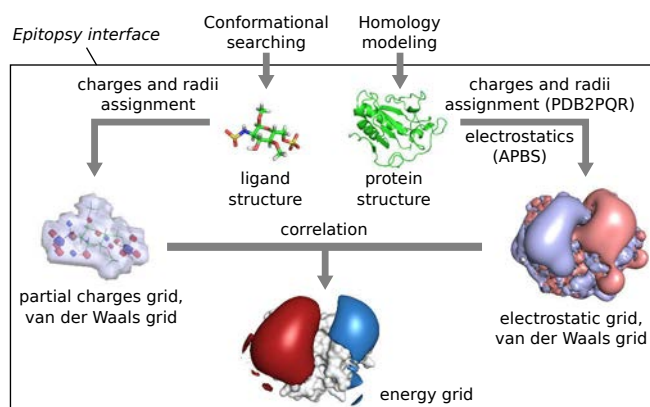


Figure 1: Computation of energy grids with our software Epitopsy. Source code available at: <https://github.com/BioinformaticsBiophysicsUDE/Epitopsy>

- [1] D. M. Zuckerman, *Annu. Rev. Biophys.* **2011**, 40, 41–62.
- [2] E. Katchalski-Katzir *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **1992**, 89, 2195–2199.
- [3] H. A. Gabb *et al.*, *J. Mol. Biol.* **1997**, 272, 106–120.
- [4] S. E. Mottarella *et al.*, *J. Chem. Inf. Model.* **2014**, 54, 2068–2078.
- [5] C. H. Ngan *et al.*, *Nucleic Acids Res.* **2012**, 40, W271–W275.

## Using DFT Methods to Understand the Chemistry of Functionalized Binary and Intermetalloid Zintl Clusters

Lukas Guggolz<sup>1</sup>, Stefan Mitzinger<sup>1</sup>, Armin Eulenstein<sup>1</sup>, Stefanie Dehnen<sup>1</sup>

<sup>1</sup>*Philipps-Universität Marburg, Fachbereich Chemie and Wissenschaftliches Zentrum für Materialwissenschaften, Hans-Meerwein-Straße, D-35043 Marburg, Germany*

In the course of our recent studies in the field of Zintl anion chemistry,<sup>[1–5]</sup> we use density functional theory (DFT) methods<sup>[6,7]</sup> to better understand this type of clusters. Our focus lies on both binary and intermetalloid Zintl anions. One of the goals of the experimental study is the reduction of the high anionic charges in order to modify the anions' chemical and physical surface properties, and thus to affect their stability and reactivity in common solvents. The calculations support the experimentalists on choosing suitable reactants.

We performed extensive and systematic computational studies on the properties of binary, tetrahedral group 13/14, 13/15, and 14/15 clusters and their possible functionalization with protons, silyl groups, and other (metal)organic substituents.

Additionally, we used DFT calculations to find the most plausible position for each element in binary Zintl clusters, depending on the electronic structure of the anion of choice. In doing so, we were also able to rationalize the protonation, and the respective positions of the hydrogen atoms in various clusters obtained by chemical synthesis.

- [1] F. Lips, R. Clérac, S. Dehnen, *J. Am. Chem. Soc.* **133**, 14168 (2011).
- [2] F. Lips, M. Hołyńska, R. Clérac, U. Linne, I. Schellenberg, R. Pöttgen, F. Weigend, S. Dehnen, *J. Am. Chem. Soc.* **134**, 1181 (2012).
- [3] R. Ababei, W. Massa, K. Harms, X. Xie, F. Weigend, S. Dehnen, *Angew. Chem.* **125**, 13786 (2013); *Angew. Chem. Int. Ed.* **52**, 13544 (2013).
- [4] S. Mitzinger, L. Broeckaert, W. Massa, F. Weigend, S. Dehnen, *Chem. Commun.* **51**, 3866 (2015).
- [5] S. Mitzinger, L. Broeckaert, W. Massa, F. Weigend, S. Dehnen, *Nat. Commun.* **7**, 10480 (2016).
- [6] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **7**, 3297 (2005).
- [7] J. M. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.* **91**, 146401 (2003).

## Can Coupled Cluster Theory Describe Polyradical Character?

Andrew M. James<sup>1</sup>, T. Daniel Crawford<sup>1</sup>, Hans Lischka<sup>2</sup>

<sup>1</sup>*Department of Chemistry, Virginia Tech, Blacksburg, Virginia, United States*

<sup>2</sup>*School of Pharmaceutical Sciences and Technology, Tianjin University, Tianjin, China*

Polycyclic aromatic hydrocarbon (PAH) systems have been the focus of many investigations in recent years. These materials are nano scale analogs to graphene, which has been shown to possess many properties that make it useful for applications in organic electronic devices. While many PAHs have closed-shell ground states, many examples exist of PAH which have open-shell and radical character in the ground state. In this work two classes of PAHs have been investigated to characterize polyradical features of their ground state electronic structure. The triangular non-Kekulé structures phenalenyl, triangulene, and a  $\pi$ -extended triangulene system with high spin ground states, and zethrene, p-quinodimethane-linked bisphenalenyl, and the Clar goblet, which have singlet-polyradical character in the ground state. Unrestricted Hartree-Fock (UHF), Coupled Cluster with singles and doubles (CCSD), and equation-of-motion CCSD (EOM-CCSD) computations have been carried out on these systems. The natural orbital occupation numbers (NOONs) have been computed to quantify the open shell character of their electronic structure in the ground, and lowest excited states. Given the expense associated with high-level CCSD calculations, the agreement between NOONs and singlet-triplet splitting with different orbital freezing schemes has been investigated. A comparison has been made to results of previous studies[1] where multi-reference methods have been used in order to probe the limitations of single-reference coupled cluster methods for chemical systems of this type.

[1] A. Das, T. Müller, F. Plasser, H. Lischka, *J. Phys. Chem. A* **120**, 1625 (2016).



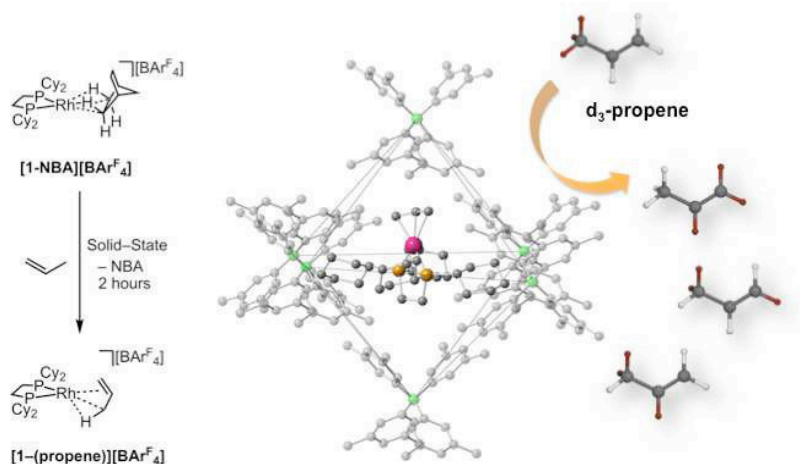
## Modeling $\sigma$ -Alkane Complexes as Precursors to Organometallic Catalysis in Solid-State.

Tobias Krämer<sup>1</sup>, Stuart A. Macgregor,<sup>1</sup> F. Mark Chadwick,<sup>2</sup>  
Alasdair I. McKay,<sup>2</sup> Andrew S. Weller<sup>2</sup>

<sup>1</sup>*Institute of Chemical Science, Heriot-Watt University, Edinburgh, EH14 4AS, UK*

<sup>2</sup>*Department of Chemistry, University of Oxford, Oxford, OX1 3TA, UK*

The crystalline solid-state environment is a versatile platform that can enable access to unstable organometallic species whose generation and stabilization might be difficult to achieve otherwise. We recently reported the targeted synthesis of well-defined  $\sigma$ -alkane complexes, e.g.  $[1\text{-NBA}][\text{BAr}^{\text{F}}_4]$  ( $[\text{Rh}(\text{Cy}_2\text{P}(\text{CH}_2)_2\text{PCy}_2)(\text{NBA})][\text{BAr}^{\text{F}}_4]$ ; Cy = cyclohexyl; NBA = norbornane;  $\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$ ), via single-crystal to single-crystal solid/gas transformations [1]. Such complexes feature a labile alkane directly coordinating to the metal center through their C–H  $\sigma$ -bonds, rendering them interesting precursors for onward solid/gas reactivity and catalysis.



Addition of small gaseous molecules such as propene or 1-butene to  $[1\text{-NBA}][\text{BAr}^{\text{F}}_4]$  in a solid/gas reaction results in the formation of the corresponding alkene complexes [2]. We used periodic electronic structure calculations in parallel with experiment in order to characterize these species structurally and spectroscopically, and modeled the processes involved in their solid/gas reactivity and catalysis.

[1] S. D. Pike, A. L. Thompson, A. G. Algarra, D. C. Apperley, S. A. Macgregor, A. S. Weller, *Science* **337**, 1648 (2012)

[2] F. M. Chadwick, A. I. McKay, A. J. Martinez-Martinez, N. H. Rees, T. Krämer, S. A. Macgregor, A. S. Weller, *Chem. Sci.*, submitted (2017)

## Molecular Basis of Ligand Interaction of GPR40/GPR120 based on FMO Calculations with Multiple Sequence Analysis

**Yuta Yamamoto<sup>1</sup>, Vladimir Sladek<sup>1,2</sup>, Sundaram Arulmozhiraja<sup>1,2</sup>,  
Kohsuke Hayamizu<sup>3</sup>, Shogo Nakano<sup>4</sup>, Sohei Ito<sup>4</sup>, Yasuo Watanabe<sup>3</sup>,  
Shizuo Yamada<sup>5</sup>, Hiroaki Tokiwa<sup>1,2</sup>**

<sup>1</sup>Department of Chemistry, Rikkyo University, 3-34-1 Nishi-Ikebukuro, Toshima, Tokyo, 171-8501 Japan

<sup>2</sup>Research Center for Smart Molecules, Rikkyo University, 3-34-1 Nishi-Ikebukuro, Toshima, Tokyo, 171-8501 Japan

<sup>3</sup>General Health Medical Center, Yokohama College of Pharmacy, 601 Matano, Totsuka, Yokohama, 245-0066 Japan

<sup>4</sup>Department of Food and Nutritional Sciences, University of Shizuoka, 52-1 Yada, Suruga, Shizuoka, 422-8526 Japan

<sup>5</sup>Center for Pharma-Food Research, University of Shizuoka, 52-1 Yada, Suruga, Shizuoka, 422-8526 Japan

Free fatty acids (FFAs) are nutrients that provide a source of energy and play an important role as signaling molecules in various cellular processes. FFA receptors (FFARs), which belong to the superfamily of GPCRs, are activated by direct binding of FFAs. FFAR1 and FFAR4, (previously designed as GPR40 and GPR120), respectively, have been demonstrated by various pharmacological studies on insulin sensitivity. However, the molecular basis of ligand interactions at the receptors still remains unclear. To elucidate the difference of interactions between carbon chain length and the number of unsaturated bonds in the FFAs, the interaction analysis of FFAR1/FFAR4 complexes with  $\omega$ -3 and  $\omega$ -6 FFAs were performed by the first-principles calculations based fragment molecular orbital (FMO) calculations combined with multiple sequence analysis. All FMO calculations were carried out at the correlated RI-MP2/cc-pVDZ level. Consensus and corresponding amino acid residues in the receptors were identified by the multiple sequence alignment analysis using our newly-developed INTMSAlign program [1]. Active site could be found in FFAR4 by the multiple correlation analysis. And Arg183 and Arg258 among the residues in the active site were identified as key residues for stable interactions of FFAs binding to FFAR1 by the interfragment interaction energy (IFIE) analysis for the FFAR1 complex with  $\omega$ -3/ $\omega$ -6 FFAs. Similar combined analysis for the FFAR4 complex with  $\omega$ -3 / $\omega$ -6 FFAs could also reveal that Arg99 contributes significantly stable interaction of FFAs to FFAR4 due to attractive electrostatic interaction with carboxyl group.

[1] S. Nakano & Y. Asano, *Sci. Rep.* **5**, 8193 (2015).

## Molecular dynamics simulation study of self-organization of carbazole dendrimer

**OneMichio Katouda<sup>1</sup>, Motomichi Tashiro<sup>2</sup>, Yutaka Imamura<sup>3</sup>**

<sup>1</sup>*RIKEN Advanced Institute for Computational Science, 7-1-26 Minatojima-minami-machi, Chuo-ku, Kobe, Japan*

<sup>2</sup>*Department of Applied Chemistry, Toyo University, 2000 Kujirai, Kwagoe, Japan*

<sup>3</sup>*Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Japan*

Dendrimers is the macromolecule consisting of three major architectural components, the central core, branch units, and peripheral end groups. Dendrimers tend to form amorphous aggregation despite of the good symmetric structure, and the tendency is significant as the generation of the dendrimer increases. Only several examples have been reported for crystalline dendrimers consisting the earlier (first- or second-) generation dendrimers. Yamamoto and his coworkers reported recently the crystalline self-assembled  $\pi$ -conjugated dendrimer framework composed of a triazine (TAZ) core and third-generation carbazole (Cz) dendrons. [1] This third-generation triazine (G3TAZ) dendrimer forms different self-assembled structures and/or morphology depending on the concentration of dendrimers and the difference of mixture ratios of chloroform good solvent and acetonitrile poor solvent. In this study, we have performed the molecular dynamics simulation study to investigate the self-organization structures depending on the concentration of dendrimers and mixture ratios of solvents. The results of radial distribution functions (RDFs) indicate that different self-assembled structures are formed depending on the difference of the mixture ratio of chloroform and acetonitrile solvents. When the ratio of chloroform is higher than acetonitrile, the RDF indicates that the self-assembled structure of G3TAZ is crystal-like structure. The RDF when the ratio of acetonitrile is higher than chloroform indicates that the more amorphous-like structure is formed.

[1] S. Nakajima, K. Albrecht, S. Kushida, E. Nishibori, K. Yamamoto, Y. Yamamoto, (private communication).

## Benchmark *Ab Initio* Conformational Energies for the Proteinogenic Amino Acids and Assessment of DFT Functionals

Manoj K. Kesharvani<sup>1</sup>, Amir Karton<sup>2</sup>, Jan M. L. Martin<sup>1,\*</sup>

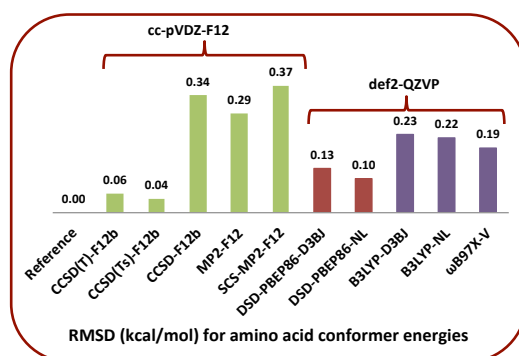
<sup>1</sup>Department of Organic Chemistry, Weizmann Institute of Science, 76100 Rehovot, Israel

Email: gershom@weizmann.ac.il

<sup>2</sup>School of Chemistry and Biochemistry, The University of Western Australia, Perth, WA 6009, Australia

The relative energies of the YMPJ [1] conformer database of the 20 proteinogenic amino acids, with N- and C-termination, have been re-evaluated using explicitly correlated coupled cluster methods. Lower-cost *ab initio* methods such as MP2-F12 and CCSD-F12b actually are outperformed by double-hybrid DFT functionals: in particular, the DSD-PBEP86-NL double hybrid performs well enough to serve as a secondary standard. Among range-separated hybrids,  $\omega$ B97X-V performs well, while B3LYP-D3BJ does surprisingly well among traditional DFT functionals. Treatment of dispersion is important for the DFT functionals: for the YMPJ set, D3BJ generally works as well as the NL nonlocal dispersion functional. Basis set sensitivity for DFT calculations on these conformers is weak enough that def2-TZVP is generally adequate. For conformer corrections to heats of formation, B3LYP-D3BJ and especially DSD-PBEP86-D3BJ or DSD-PBEP86-NL are adequate for all but the most exacting applications. The revised geometries and energetics for the YMPJ database have been made available as electronic supporting information and should be useful in the parametrization and validation of molecular mechanics force fields and other low-cost methods. The very recent dRPA75 method yields good performance, without resorting to an empirical dispersion correction, but is still outperformed by DSD-PBEP86-D3BJ and particularly DSD-PBEP86-NL.

[1] Y. Yuan, M. J. L. Mills, P. L. A. Popelier, F. Jensen, *J. Phys. Chem. A*, **118**, 7876 (2014).



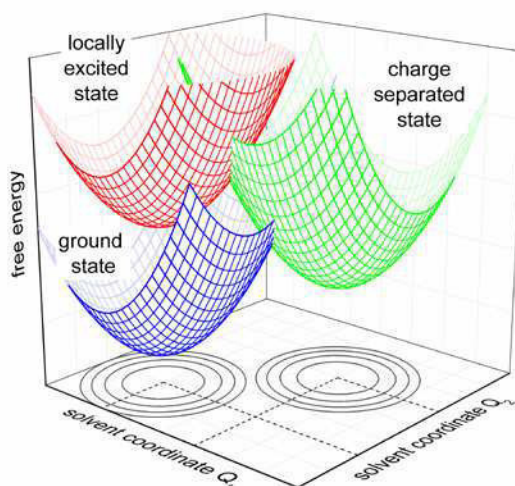
## The model of multistage non-equilibrium electron transfer reaction in non-Debye polar solvent

Serguei V. Feskov

*Volgograd State University, Universitetskiy pr., 100, Volgograd, Russia*

Ultrafast photoinduced electron transfer reactions often proceed in non-equilibrium regime with respect to solvent polarization around the reactants. In non-Debye solvents with several relaxation timescales, a single-step electron transfer (ET) is generally described with a set of solvent “relaxation” coordinates. This approach however cannot be extended to multistage ET, because non-equilibrium polarization, formed at early stages, can affect subsequent photochemical processes in donor-acceptor molecular systems.

We report here a general model of multistage non-equilibrium ET, taking into account both multimode relaxation of solvent and electronic transitions between several molecular centers. The model uses reaction coordinates of two types (“spatial” and “relaxation” polarization coordinates) and a matrix of solvent reorganization energies for construction of parabolic free energy surfaces for electronic states of the molecular system.



Efficient numerical algorithms for solution of the model equations are also proposed. The algorithms are based on the Brownian simulation technique and address the most computationally demanding tasks of the method: 1) detection of the recrossing events for all electronic and vibrational transitions in the course of the reaction; 2) calculation of transient absorption spectra in photoreactions with participation of several intramolecular vibrational quantum modes; 3) simulation of optical excitation of the system by short laser pulses with known spectral and temporal characteristics. The proposed approaches allow reducing computational complexity of the algorithm with respect to some critical parameters (number of solvent relaxation modes, number of active high-frequency vibrational degrees of freedom, etc.) and thus rising performance of computations.

The work is supported by Russian Science Foundation under the project 16-13-10122.

## Efficient Parallel Implementation of Exact Exchange for Periodic Systems within Concentric Atomic Density Fitting Approximation

Xiao Wang<sup>1</sup>, Cannada A. Lewis<sup>1</sup>, Edward F. Valeev<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061, United States*

Development of quantum chemistry methods for periodic systems, especially 2-D slabs and 3-D crystals, has been hampered for decades due to the unaffordable scaling with system size.[1] One of the obstacles is the computation of two-electron repulsion integrals, whose near-field interaction can only be computed exactly or approximated using density fitting (DF). In this work, a massively-parallel implementation of an efficient local DF method is presented in which product density is approximated using only auxiliary basis functions with the same centers as atomic orbitals (AOs) in that product. We applied this approach for the exchange term in Hartree–Fock with periodic boundary conditions (periodic HF) based on linear combinations of Gaussian-type AOs, leading to a significant decrease in the computational cost with an accuracy below millihartree per atom. Large computations such as lattice energies of 3-D systems are carried out efficiently using the new periodic HF method.

- [1] C. Müller and B. Paulus *Phys. Chem. Chem. Phys.* **14**, 7605 (2012).
- [2] D. S. Hollman, H. F. Schaefer, and E. F. Valeev *J. Chem. Phys.* **140**, 064109 (2014).
- [3] S. Manzer, E. Epifanovsky, and M. Head-Gordon *J. Chem. Theory Comput.* **11**, 518 (2015)

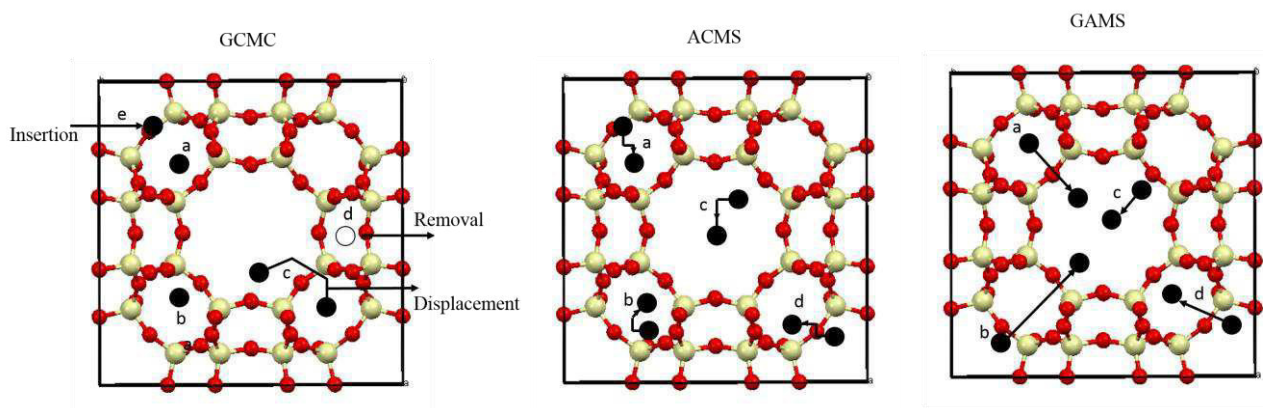
## A Novel Method For Recruiting Global Optimization Techniques For Strategically Oriented Molecular Simulation

Leila LotfiKatooli<sup>1\*</sup>, Akbar Shahsavand<sup>1</sup>, Fahimeh Nazarikatouli<sup>2</sup>

*Chemical Engineering Department, Ferdowsi University of Mashhad, Mashhad, Iran<sup>1</sup>  
Chemistry Department, Aliabad Katoul Branch, Islamic Azad University, Aliabad Katoul,  
Iran<sup>2</sup>*

*leylaalotfi@gmail.com \**

Traditional molecular simulation techniques such as Grand Canonical Monte Carlo (GCMC) strictly rely on purely random search inside the simulation box for predicting the adsorption isotherms. This blind search is usually extremely time demanding for providing a faithful approximation of the real isotherm and in some cases may lead to non-optimal solutions. A novel approach is presented in this article which does not use any of the classical steps of the standard GCMC method, such as *displacement*, *insertion* and *removal*. The new approach considers the molecular simulation problem as a global optimization challenge. The proposed approach uses popular global optimization techniques. Two different algorithms, Molecular simulation via Genetic Algorithm (GAMS) and Molecular Simulation via Ant Colony Algorithm (ACMS) are introduced to find the optimal configuration for adsorption of any adsorbate on Nano-structured adsorbent under prevailing pressure and temperature. Three various case studies used for validation of new algorithms and results illustrate the superior performances of the proposed method over the standard GCMC technique. The introduced algorithms are more complex while they are more accurate and tremendously faster.





## Controlling the Photoexcited Decay of Fe(II)-N-Heterocyclic Carbene Complexes Through Structural Modifications

Mátyás Pápai<sup>1,2</sup>, Klaus B. Møller<sup>1</sup>, György Vankó<sup>2</sup>, Tamás Rozgonyi<sup>3</sup>,  
Thomas J. Penfold<sup>4</sup>

<sup>1</sup>Department of Chemistry, Technical University of Denmark, Kemitorvet, DK-2800 Kongens Lyngby, Denmark;

<sup>2</sup>Wigner Research Centre for Physics, Hungarian Academy of Sciences, P.O. Box 49, H-1525 Budapest, Hungary

<sup>3</sup>Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, P.O. Box 286, H-1519 Budapest, Hungary

<sup>4</sup>School of Chemistry, Newcastle University, Newcastle upon Tyne, NE1 7RU, United Kingdom.

Understanding, and subsequently being able to manipulate, the excited-state decay pathways of functional transition metal complexes is of utmost importance in order to solve grand challenges in solar energy conversion and data storage. Herein, we present spin-vibronic quantum wavepacket dynamics simulations [1,2] on two functional Fe-N-heterocyclic carbene (NHC) complexes: the first discovered Fe(II)-NHC photosensitizer, [Fe(bmip)<sub>2</sub>]<sup>2+</sup> (bmip = 2,6-bis(3-methyl-imidazole-1-ylidene)pyridine) [3], and its 3-*tert*-butyl (*t*-Bu) functionalized derivative, [Fe(btbp)<sub>2</sub>]<sup>2+</sup> (btbp = 2,6-bis(3-*tert*-butyl-imidazole-1-ylidene)-pyridine). The results show that relatively minor variations in the molecular structure lead to completely different excited-state relaxation of the initially excited singlet metal-to-ligand charge transfer (<sup>1</sup>MLCT) state. In [Fe(bmip)<sub>2</sub>]<sup>2+</sup>, the ultrafast <sup>1</sup>MLCT→<sup>3</sup>MLCT intersystem crossing is followed by a rather slow <sup>3</sup>MLCT→<sup>3</sup>MC (MC = metal-centred) decay, resulting in a relatively long (>4 ps) simulated <sup>3</sup>MLCT state lifetime, in good agreement with the experimental 9 ps value [3]. On the other hand, in the case of [Fe(btbp)<sub>2</sub>]<sup>2+</sup>, the initially photoexcited <sup>1,3</sup>MLCT state relaxes to MC states on the subpicosecond timescale. This occurs because the *t*-Bu functionalization stabilizes the <sup>1</sup>MC states, enabling the <sup>1,3</sup>MLCT→<sup>1</sup>MC population transfer to occur in the near proximity of the Franck-Condon geometry, making the conversion very efficient. These simulations [1,2] demonstrate how the excited-state dynamics of these Fe(II)-NHC complexes can be controlled by comparably small changes in the ligand sphere, thus, paving the way for the design of high-efficiency transition metal-based functional molecules.

[1] M. Pápai, G. Vankó, T. Rozgonyi, T. J. Penfold, *J. Phys. Chem. Lett.*, 2016, **7**, 2009–2014.

[2] M. Pápai, T. J. Penfold, Klaus B. Møller, *J. Phys. Chem. C*, 2016, **120**, 17234–17241.

[3] Y. Liu, V. Sundström, K. Wärnmark, *Chem. Commun.*, 2013, **49**, 6412–6414.



## Structure of hyaluronan solvation sphere and its influence on the molecular shape.

**Marek Ingr<sup>1,2</sup>, Eva Kutálková<sup>1</sup>, Roman Witasek<sup>1</sup>, Václav Buš<sup>1</sup>, Josef Hrnčířík<sup>1</sup>**

<sup>1</sup>*Tomas Bata University in Zlín, Faculty of Technology, Department of Physics and Materials Engineering, Nám. T.G. Masaryka 5555, 76001 Zlín, Czech Republic*

<sup>2</sup>*Charles University, Faculty of Sciences, Department of Biochemistry, Hlavova 8/2030, 12843 Praha 2, Czech Republic*

Hyaluronan (HA), an alternating co-polymer of glucuronic acid and N-acetylglucosamine ( $[(4)\text{-}\beta\text{-D-GlcpA-(1}\rightarrow\text{3)-}\beta\text{-D-GlcpNAc-(1}\rightarrow\text{)]}_n$ ) is an important biomolecule occurring in the extracellular matrix of the connective tissues, synovial fluid, vitreous fluid of eyes, etc. It has numerous biological functions and is also a promising material for drug delivery systems and tissue engineering. Free macromolecules of HA in aqueous solutions form highly swollen and loosely packed random coils. We have recently developed a molecular-dynamics (MD) based method for modelling HA random coils [1] which revealed the dependencies of the radius of gyration on concentration of dissolved ions, in an apparent agreement with experiment. In order to study the individual interactions governing the macromolecular shape we constructed an averaged plot of the solvation-sphere atoms surrounding the monomeric units of individual types. Analyzing this plot, tiny structural differences of the HA molecule and its solvation shell can be uncovered and correlated with the solution composition and the macromolecular properties. The plot also clearly identifies the hydrophilic and hydrophobic areas on HA molecule and supports the hypothesis of partially hydrophobic behavior of this otherwise strongly hydrophilic molecule [2]. In accord with this, hydrophobic interactions between two HA chains were identified, although the structures are rather unstable. Hence, the detailed description of HA solvation shell may contribute to understanding of the macromolecular shape of this molecule and its interactions with other, especially protein, molecules.

Acknowledgment: Access to computing and storage facilities owned by parties and projects contributing to the National Grid Infrastructure MetaCentrum provided under the program “Projects of Large Research, Development, and Innovations Infrastructures” (CESNET LM2015042), is greatly appreciated. RW was supported by the Internal Funding Agency of Tomas Bata University in Zlín, project IGA/FT/2016/011.

[1] M. Ingr, E. Kutálková, J. Hrnčířík, *Carbohydr. Polym.* **170**, 289 (2017).

[2] J. Necas, L. Bartosiková, P. Brauner, J. Kolar, *Vet. Med.-Czech* **53**, 397 (2008).

## Carbon-Chlorine Multiple Bonding in Doubly and Triply Charged Chlorobenzene

Felipe Fantuzzi<sup>1</sup>, Benedikt Rudek<sup>2</sup>, Wania Wolff<sup>3</sup>, Marco A. C. Nascimento<sup>1</sup>

<sup>1</sup>*Instituto de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ 21941-909, Brazil.*

<sup>2</sup>*Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany.*

<sup>3</sup>*Instituto de Física, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ, 21941-972, Brazil.*

In free-radical halogenation of aromatics, singly-charged ions are usually formed as an intermediate. We used a proton beam to ionize chlorobenzene ( $\text{C}_6\text{H}_5\text{Cl}$ ,  $^1\mathbf{1}$ ) and investigate its stability by means of time-of-flight mass spectroscopy. However, apart from the singly-charged parent-ion and its fragments, we find a significant yield of doubly- and triply-charged parent-ions. We used high-level theoretical methods based on Density Functional Theory (DFT) at the PBE0/cc-pVTZ(-f) level and Generalized Valence Bond (GVB) to calculate the structure, relative stabilities and bonding of these chlorobenzene dications and trications. The most stable isomers (Figure 1) are distonic and exhibit unusual carbon-chlorine multiple bonding: a terminal  $\text{C}=\text{Cl}$  double bond in a formyl-like  $\text{CHCl}$  moiety ( $^1\mathbf{2}^{2+}$ ), and a cumulene-like  $\text{C}=\text{C}=\text{Cl}$  species ( $^1\mathbf{3}^{2+}$ ). The GVB calculations also revealed an excited state of  $^1\mathbf{3}^{2+}$  with a nitrile-like  $\text{C}\equiv\text{Cl}$  triple bond structure. This study paves the way for the synthesis of novel chlorine-containing compounds with multiple C-Cl bonds [1].

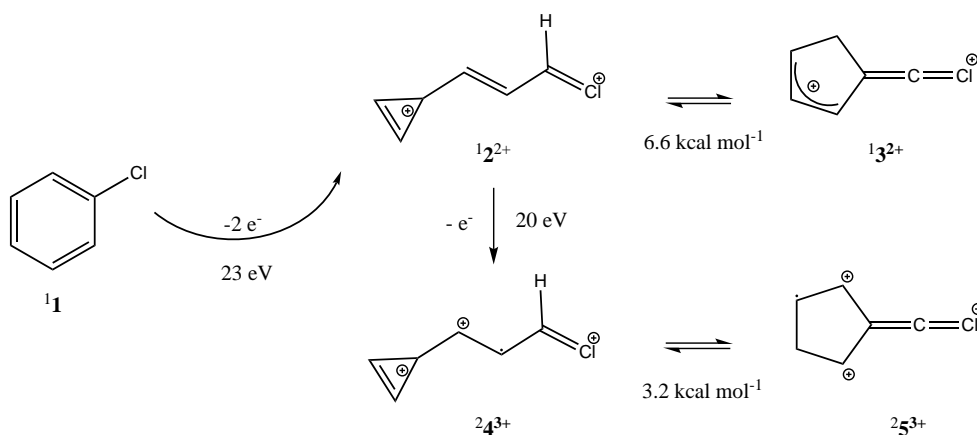


Figure 1: Most stable structures of doubly- and triply-charged  $\text{C}_6\text{H}_5\text{Cl}$ .

[1] F. Fantuzzi, B. Rudek, W. Wolff, M. A. C. Nascimento. *In preparation* (2017).

## Towards Improved Machine Learning and Semiempirical Quantum Chemical Methods

Pavlo O. Dral and Walter Thiel

*Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1,  
45470 Mülheim an der Ruhr, Germany*

Many areas of research require fast methods for computing quantum mechanical (QM) properties. Particularly useful for this purpose are semiempirical QM (SQM) methods and machine learning (ML). Because of the underlying physical model, SQM methods can be general-purpose and reasonably accurate for many molecules quite far outside the training set, while ML is generally a special-purpose technique and only as good as its training set. In our lab we improve and combine both QM and ML methods.

We introduced improvements for training and applying kernel ridge regression-based ML to generate very accurate molecular potential energy surfaces that can be used to calculate rovibrational spectra of small molecules with spectroscopic accuracy (error less than  $1\text{ cm}^{-1}$  relative to the reference *ab initio* spectrum)[1]. We also proposed two hybrid QM/ML approaches. The first one (an automatic parameterization technique) uses ML to improve the SQM Hamiltonian by adjusting semiempirical parameters[2] while the second one ( $\Delta$ -ML) employs ML to correct low-level QM methods (SQM or DFT) using reference data from high-level QM calculations[3].

Moreover, we currently develop new general-purpose orthogonalization- and dispersion-corrected SQM methods (ODMx)[4] based on the robust OMx framework[5,6]. Our validation of preliminary parameterizations shows that the new ODMx methods are more accurate than the OMx methods for many ground- and excited-state properties and for noncovalent interactions[4]. They are essentially as fast as the OMx methods.

- [1] P. O. Dral, A. Owens, S. N. Yurchenko, W. Thiel, *J. Chem. Phys.*, *accepted*.
- [2] P. O. Dral, O. A. von Lilienfeld, W. Thiel, *J. Chem. Theory Comput.* **11**, 2120 (2015).
- [3] R. Ramakrishnan, P. O. Dral, M. Rupp, O. A. von Lilienfeld, *J. Chem. Theory Comput.* **11**, 2087 (2015).
- [4] P. O. Dral, X. Wu, W. Thiel, *in preparation*.
- [5] P. O. Dral, X. Wu, L. Spörkel, A. Koslowski, W. Weber, R. Steiger, M. Scholten, W. Thiel, *J. Chem. Theory Comput.* **12**, 1082 (2016).
- [6] P. O. Dral, X. Wu, L. Spörkel, A. Koslowski, W. Thiel, *J. Chem. Theory Comput.* **12**, 1097 (2016).

**CASPT2 on-the-fly surface hopping dynamics****Jae Woo Park<sup>1</sup>, Toru Shiozaki<sup>1</sup>**

*<sup>1</sup>Department of Chemistry, Northwestern University, 2145 Sheridan Rd., Evanston, IL 60208, USA.*

We present the development of theory and algorithms that enable the efficient evaluations of the analytical nuclear gradient and derivative coupling in the framework of extended multistate complete active space second-order perturbation theory (XMS-CASPT2). With this implementation, on-the-fly condensed phase surface hopping dynamics on the XMS-CASPT2 surfaces in large systems are now routine. As an example, the nonadiabatic dynamics simulations of GFP chromophore in water will be presented.

## Insights into the Excited State Chemistry of Lanthanoid(III) Motexafins

Norah Heinz, Nils Herrmann, Michael Dolg, Xiaoyan Cao

*Institute for Theoretical Chemistry, University of Cologne, Greinstr. 4, 50939 Köln, Germany*

Texaphyrins, which can be understood as expanded porphyrins, localise at cancerous lesions and are considered to be promising drugs in treatments as radiation therapy or photodynamic therapy. Especially certain texaphyrins called motexafins containing trivalent lanthanoid ions in the center – e.g. Gadolinium, Gd- $\text{Tex}^{2+}$  – are considered to possess very promising attributes. In the presence of ascorbic acid they are expected to catalyse the generation of reactive oxygen species (ROS). When stimulated by visible light, texaphyrins are believed to play an important role as catalysts in this process. With the help of the texaphyrin an electron is transferred from the ascorbate to  $\text{O}_2$  forming  $\text{O}_2^{\bullet-}$ . This species is then used to generate  $\text{H}_2\text{O}_2$  which is known to be a potent apoptosis trigger. During the catalysis the texaphyrin – Gd- $\text{Tex}^{2+}$  – is reduced by the ascorbate species. The electron is then transferred to  $\text{O}_2$  and the catalyst is regained [1].

To understand the process of the electron transfer in detail, several properties of lanthanide(III) motexafins are analysed. Electron affinities and ionisation potentials in gas phase as well as in aqueous environment are calculated and discussed in detail. The first water coordination sphere and its effects on the molecular properties are considered. Reduction potentials are determined in order to explain the effectiveness of texaphyrin species as catalyst [3]. The results are discussed in the context of the autoxidation of ascorbic acid [2], which accounts for the uncatalysed formation of ROS in the postulated mechanism.

On the other hand emphasis is being placed on the description of the excited states of the Gd- $\text{Tex}^{2+}$  species, in order to analyse the primary step of the catalysis, namely the activation of the compound by visible light. Since the electronic structure of texaphyrins resembles the one of porphyrins and several electronic excitations in porphyrins are known to display charge transfer character, this is also expected in the case of texaphyrins. A detailed study of the excitation spectra of texaphyrins at the level of TD-DFT is presented applying different density functionals and energy-consistent scalar relativistic pseudopotentials for lanthanoids. Also the aqueous environment is taken into account to simulate *in vivo* conditions. Special focus is set on the treatment of long range correlation effects and the identification of charge transfer excitations.

- [1] D.J. Magda, Z. Wang, N. Gerasimchuk, W. Wei, P. Anzenbacher, Jr. and J.L. Sessler *Pure Appl. Chem.* **76**, 365 (2004).
- [2] N. Herrmann, N. Heinz, M. Dolg and X. Cao *J. Comput. Chem.* **37**, 1914 (2016).
- [3] X. Cao, N. Heinz, J. Zhang and M. Dolg. *submitted*.

## Orbital Locality Landscapes

Charles J. C. Scott<sup>1</sup>, David J. Wales<sup>1</sup>, Alex J. W. Thom<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of Cambridge, Cambridge*

We consider the optimisation of orthonormal molecular orbitals according to various localisation conditions[1] using techniques developed to treat potential energy landscapes.[2] We categorise the stationary points and connectivity of the landscapes resulting from different penalty functions in various molecules. We consider the chemical significance of the solutions obtained and the implications for reliably obtaining localised orbitals. While multiple stationary points and minima have been previously acknowledged as a problem in localisation procedures,[3, 4] we believe this to be the first study of the structure of the corresponding landscapes. Understanding this structure is required to obtain well-localised orbitals for general molecular systems, and hence facilitate the development of high-level local correlation methods.

- [1] B. Jansík, S. Høst, K. Kristensen, P. Jørgensen, *J. Chem. Phys.* **134**, 194104 (2011).
- [2] D. J. Wales, *Energy Landscapes*, Cambridge University Press, (2003).
- [3] J. E. Subotnik, A. Sodt, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **9**, 5522 (2007).
- [4] S. Lehtola, H. Jónsson, *J. Chem. Theory and Comput.* **9**, 5365 (2013).

## Hybrid Approach to Fermi Operator Expansion: Towards Langevin Dynamics with Linear System-Size Scaling

H. Wiebeler<sup>1</sup>, S. Mohr<sup>2</sup>, Thomas D. Kühne<sup>1</sup>

<sup>1</sup>*Dynamics of Condensed Matter, Department of Chemistry, University Paderborn, Warburgerstr. 100, 33098 Paderborn, Germany*

<sup>2</sup>*Department of Computer Applications in Science and Engineering, Barcelona Supercomputing Center (BSC-CNS), c/ Jordi Girona 29, 08034 Barcelona, Spain*

In our recent work, we introduced an improved field-theoretic approach to the grand-canonical potential suitable for linear scaling molecular dynamics using forces from self-consistent electronic structure calculations [1, 2]. This approach does not rely on the ability to localize the electronic wavefunction, so even metals can be treated.

In this work, we present an implementation of this approach into a DFT electronic structure calculation code, which is using a localized Daubechies wavelet basis [3, 4]. In particular, we investigate the possibility to substantially accelerate the computation of the interatomic forces by computing them approximately at the expense of white noise. The noisiness of the forces can then be compensated by means of a modified Langevin dynamics scheme [5].

For the purpose of demonstrating our novel approach, we also performed some tests in order to proof the linear scaling behavior of our approach with respect to Hamiltonian matrices from DFT-calculations. Furthermore, we are testing the white noise criterion by calculating the auto-correlation of the noise in the forces.

- [1] M. Ceriotti, T. D. Kühne and M. Parrinello, *J. Chem. Phys.* **129**, 024707 (2008).
- [2] D. Richters and T. D. Kühne, *J. Chem. Phys.* **140**, 134109 (2014).
- [3] S. Mohr, L. E. Ratcliff, P. Boulanger, L. Genovese, D. Caliste, T. Deutsch and S. Goedecker *J. Chem. Phys.* **140**, 204110 (2014).
- [4] S. Mohr, L. E. Ratcliff, L. Genovese, D. Caliste, P. Boulanger, S. Goedecker and T. Deutsch *Phys. Chem. Chem. Phys.* **17**, 31360 (2015).
- [5] T. D. Kühne, M. Krack, F. R. Mohamed and M. Parrinello, *Phys. Rev. Lett.* **98**, 066401 (2007).

## Esterase-2 as a fluorescent biosensor for the detection of organophosphates: electronic insights from molecular dynamics

Ingrid G. Prandi<sup>1,2</sup>, Teodorico C. Ramalho<sup>1</sup>, Tanos C. C. França<sup>2</sup>

<sup>1</sup>*Department of Chemistry, Federal University of Lavras, Av. Doutor Sylvio Menicucci, 1001, Lavras, Brazil*

<sup>2</sup>*Laboratory of Molecular Modeling Applied to the Chemical and Biological Defense, Military Institute of Engineering, Praça Gen. Tibúrcio, 80, Rio de Janeiro, Brazil*

Organophosphorus (OP) pesticides began to be employed on large scale during the World War II in order to protect soldiers from insects that transmit infectious diseases like malaria. Specifically synthesized to be toxic molecules, most OPs pesticides are not specific to a target organism, and the indiscriminate use of these substances poses a great risk to many species including humans [1]. Unfortunately, despite of some strong restrictions about the use of OP pesticides by the Food Quality Protection Act, they are still in clandestine use because of their low cost and, consequently the number of people intoxicated by OP pesticides is still high worldwide. [2,3] The first step to cure a patient that is intoxicated by an OP molecule is to identify the specific infecting compound. In the literature, previous studies show that OPs are great inhibitors of the acetylcholinesterase enzyme (AChE) [3,4]. Thus, for patient diagnostics, it may be possible to use an esterase enzyme as a biological sensor to detect OP compounds. In particular, the presence of the Esterase 2 (EST2) from *Alicyclobacillus acidocaldarius* in an environment that contains OP is able to change the fluorescence signal when light of the right wavelength falls on the sample. Indeed, experimental results show signs that the variation in the fluorescence signal is able to quantitatively identify these compounds [5,6]. In this work, we apply docking analyses, molecular dynamics simulations and quantum-mechanics-based calculations in order to study structural and fluorescence properties of four different OPs (chlorpyrifos, diazinon, paraoxon and parathion) as EST2 inhibitors. Finally, theoretical predictions are compared with experimental results in order to validate the methodology and enable its employment on other OP compounds.

- [1] L. Perezgasga, L. Sánchez-Sánchez, S. Aguila, R. Vazquez-Duhalt. *Appl Biochem Biotechnol.* **166**, 1236–1247 (2012)
- [2] R. Iyer, B. Iken, A. Leon. *Toxicol Lett.* **233**, 200–206 (2015)
- [3] B. Hileman. *Chem. Eng. News.* **78**, 34–36 (2000)
- [4] N. Bunya, K. Sawamoto, H. Benoit, S. B. Bird. *J Toxicol.* **2016**, 1-5 (2016)
- [5] P. Carullo, G. P. Cetrangolo, L. Mandrich, G. Manco, F. Febbraio. *Sensors.* **15**, 3932-3951 (2015)



## **CYLview: A Free Molecular Analysis and Representation Program for Chemists.**

**Claude Y. Legault<sup>1</sup>**

*<sup>1</sup>Department of Chemistry, Université de Sherbrooke, 2500 boul. De l'Université,  
Sherbrooke (Québec), J1K 2R1, Canada*

The efficient analysis and communication of scientific results is a vital portion of the work of any chemist. This aspect is even more important for computational chemists, due to the amount and complexity of the results obtained. Tools to maximize the efficiency of this process are thus critical. The present major challenge with the preparation of publication quality representations of structures is the need to use multiple programs to achieve the desired result. In this regard, CYLview [1] was specifically created to accelerate the evaluation and analysis of computed structures, as well as to generate in the same program high quality representations, containing all the information (e.g. bond distances, angles, atom numbering) needed for professional publications and presentations. The steady increase in computing resources has led to the study of ever larger structures that are inherently more difficult to depict; static two dimensional images of three dimensional structures over a certain size lead to a loss of spatial orientation and distracting clutter. CYLview overcomes these issues by using powerful visual cues, such as fog and focal blur. This free software has grown in popularity over the years, with now more than 2500 registered users. The current features of the program will be presented. New developments will be presented to stimulate feedback and suggestions from the researchers.

[1] C. Y. Legault, *CYLview, 1.0b*; Université de Sherbrooke (Québec), Canada;  
<http://www.cylview.org> (2009)

## Range-separated hybrid scheme combining AP1roG with density-functional theory

Odile Franck<sup>1</sup>

<sup>1</sup>*Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Toruń, Poland*

The antisymmetric product of one-reference orbital geminals (AP1roG) [1] is a geminal-based method that can be rewritten as a general pair-coupled-cluster-doubles (PCCP) wave-function. However, AP1roG, as other geminal-based methods, misses a large fraction of dynamical correlation effects. To overcome this limitation *a posteriori* corrections have been proposed such as linear coupled-cluster based methods [2] or perturbation theory based methods [3]. Another approach to include dynamical correlation to PCCD that has been proposed recently is to combine PCCD with density-functional theory (DFT) [4][5]. In this study, we combine DFT and AP1roG in a range-separated hybrid and compare this method to other *a posteriori* corrections.

- [1] P. A. Limacher, P. W. Ayers, P. A. Johnson, S. De Baerdemacker, D. Van Neck, P. Bultinck, *J. Chem. Theory Comput.* **9**, 1394 (2013).
- [2] K. Boguslawski, P. W. Ayers, *J. Chem. Theory Comput.* **11**, 5252 (2015).
- [3] P. Limacher, P. W. Ayers, P. Johnson, S. De Baerdemacker, D. Van Neck, P. Bultinck, *Phys. Chem. Chem. Phys.* **16**, 5061 (2014).
- [4] A. J. Garza, I. W. Bulik, T. M. Henderson, G. E. Scuseria, *Phys. Chem. Chem. Phys.* **17**, 33523 (2015).
- [5] A. J. Garza, I. W. Bulik, T. M. Henderson, G. E. Scuseria, *J. Chem. Phys.* **142**, 044109 (2015).

## **Electrode effects in molecular electronics: a computational perspective**

**Manuel Smeu**

*Department of Physics, Binghamton University – SUNY, 4400 Vestal Parkway East,  
Binghamton, NY 13902, United States*

Molecular electronics offers a means of achieving next generation of electronic devices, beyond semiconductor technologies, due to the high tunability and relatively inexpensive manufacturing costs of molecules. The field is now at a point where molecular junctions can be routinely fabricated and their conductance measured in the lab. From the computational perspective, the state-of-the-art is the non-equilibrium Green's function technique combined with density functional theory (NEGF-DFT) approach that provides the transmission function,  $T(E)$ , from which the conductance characteristics of the molecular junction can be obtained. The prototypical system is composed of two Au electrodes bridged by a molecule with some anchoring groups (e.g. thiol, amine). However, using a different metal (e.g. Cu, Pt, Al), or other material (e.g. carbon nanotube, graphene nanoribbon), for the electrodes results in a different alignment between the molecular orbitals and the Fermi level of the electrodes, thus yielding different transport properties. Additionally, the exact atomic configuration at the electrode/molecule interface can play a dramatic role. In this presentation, the effects on molecular conductance of different metal electrodes, their atomic orientation and configuration will be discussed, and some insights into how to obtain control over these parameters will be offered.

## The Methylsulfinyl Radical and Its Reaction with Ozone

Marissa L. Estep<sup>1</sup>, Henry F. Schaefer<sup>1</sup>

<sup>1</sup>*Center for Computational Quantum Chemistry, University of Georgia, 1004 Cedar Street, Athens, GA, USA*

The methylsulfinyl radical ( $\text{CH}_3\text{SO}$ ) serves as a key intermediate in the sulfur chemistry of the remote marine atmosphere, with its reactions leading to production of sulfuric acid and sulfates [1]. The methylsulfinyl radical is typically oxidized by either  $\text{NO}_2$  or ozone, but we focus our efforts on its reaction with ozone. We have studied the structures and fundamental modes of the ground and first excited states of the methylsulfinyl radical using coupled cluster methods, and have examined the adiabatic excitation energy of the first excited state using methods as complete as CCSDT(Q) [2]. With this background, we examine the reaction of the methylsulfinyl radical with ozone. This reaction has been the object of experimental [1, 3] and theoretical [4] studies, with the theoretical work entailing treatment of the reaction with the MP2/6-311++G(2df,p) method. Given the multiconfigurational nature of ozone, we build upon this available work by considering the possibility that the reaction complex may require treatment of both static and dynamic correlation. We examine metrics of multireference character to determine whether application of multireference methodology is appropriate for this system.

- [1] D. Borissenko, A. Kukui, G. Laverdet, G. Le Bras, *J. Phys. Chem. A* **107**, 1155 (2003).
- [2] M. L. Estep, H. F. Schaefer, *Phys. Chem. Chem. Phys.* **18**, 22293 (2016).
- [3] A. A. Turnipseed, S. B. Barone, A. R. Ravishankara, *J. Phys. Chem.* **97**, 5926 (1993).
- [4] X. Li, Y. Meng, S. Zheng, *J. Mol. Struct. THEOCM* **847**, 52 (2007).

## Computational Studies of Substituted Porphyrin-Squaraine Dyads as Chromophores for Solar Cells based on TiO<sub>2</sub>

Merlys Borges-Martínez<sup>1</sup>, Raúl Mera-Adasme<sup>1</sup>, Gloria Cárdenas-Jirón<sup>1</sup>

<sup>1</sup>*Theoretical Chemistry Laboratory, Faculty of Chemistry and Biology,  
University of Santiago de Chile (USACH), Casilla 40, Correo 33, Santiago, Chile*

Since the discovery of dye-sensitized solar cells (DSSC), the search for efficient dyes for the devices has been an active area of research. Porphyrin-based dyes have produced excellent results so far [1]. The porphyrin macrocycle can efficiently inject electrons to a semiconductor but it has a poor absorption in the visible light region [2]. Linking porphyrin with a second chromophore is expected to enhance the light-absorption properties [3]. In the present work, we studied the light-absorption properties of a dyad formed by the combination of porphyrin and squaraine (SQ), which we modified by adding of electron-donor (push) groups to porphyrinic moiety. The modifications aimed to improve electron injection properties of the chromophores toward a semiconductor, like TiO<sub>2</sub>, and induce a panchromatic light absorption.

Optimized molecular geometries were obtained at the density functional theory (DFT) using hybrid functional B3LYP and double- and triple-zeta polarized Ahlrichs basis set. Vibrational frequencies were obtained for the minimum-energy structures. The absorption spectra of the chromophore dyads and their isolated fragments were obtained using Time-Dependent DFT. Solvent effects of tetrahydrofuran (THF) were modeled with Conductor Polarizable Continuum Model (CPCM). Fourteen density functionals were evaluated in order to choose the method that better reproduced the experimental spectra. Using the chosen functional, dyads were analyzed in terms of the electronic absorption properties and parameters of photovoltaic cells.

The changes in the UV-vis spectra upon substitution of the porphyrinic ring were fundamentally in the relative intensities of absorption bands. Stronger and red-shifted SQ bands were observed for substituents with amine groups, favouring the panchromatic absorption of the dyads. Of the four models of TiO<sub>2</sub> studied, the band gap of the semiconductor was best described by the clusters with 15 and 16 TiO<sub>2</sub> units. The photovoltaic parameters and chemical potential of donor groups of dyads bonded to TiO<sub>2</sub> cluster indicated that, dyads with aromatic amines are more suited to inject electrons to a semiconductor.

**Acknowledgments.** GCJ thanks FONDECYT/CONICYT by Project N°1131002 and 1171719 for financial support. MBM thanks CONICYT-PCHA/Doctorado Nacional/2015-21150093 for PhD scholarship. RMA thanks CONICYT for financial support under Proyecto de Atracción e Inserción de Capital Humano Avanzado en la Academia PAI N° 79150043.

- [1] M. Urbani, M. Grätzel, M.K. Nazeeruddin, T. Torres, *Chem. Rev.*, **114**, 12330 (2014).
- [2] G.I. Cárdenas-Jirón, T. Baruah, R.R. Zope, *Handbook of Porphyrin Science*, **42**, 233 (2016).
- [3] J. Warnan, F. Buchet, Y. Pellegrin, E. Blart, F. Odobel. *Org. Lett.*, **13**, 3944 (2011).

# Laplace-transformed atomic and active orbital-based formulations of relativistic and multireference perturbation theories for large molecules

Benjamin Helmich-Paris<sup>1</sup>, Lucas Visscher<sup>1</sup>, Michal Repisky<sup>2</sup>, Stefan Knecht<sup>3</sup>

<sup>1</sup>*Section of Theoretical Chemistry, VU University Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands*

<sup>2</sup>*CTCC, Department of Chemistry, UIT The Arctic University of Norway, N-9037 Tromø, Norway*

<sup>3</sup>*Laboratory of Physical Chemistry, ETH Zürich, Vladimir-Prelog-Weg 2, CH-8093 Zürich, Switzerland*

We present a formulation of Laplace-transformed atomic orbital-based second-order Møller–Plesset perturbation theory (MP2) energies for two-component Hamiltonians in the Kramers-restricted formalism.[1] This low-order scaling technique can be used to enable correlated relativistic calculations for large heavy element-containing molecules. We show that the working equations to compute the relativistic MP2 energy differ by merely a change of algebra (quaternion instead of real) from their non-relativistic counterparts and feature an overhead factor of at most 16 due to inclusion of spin-orbit coupling. Our current implementation computes on 16 CPUs the Coulomb energy of a tellurium polyethylene glycol (Te-PEG-20) within 4.5 h by using 6500 and 8409 spherical Harmonic orbital and auxiliary basis functions, respectively.

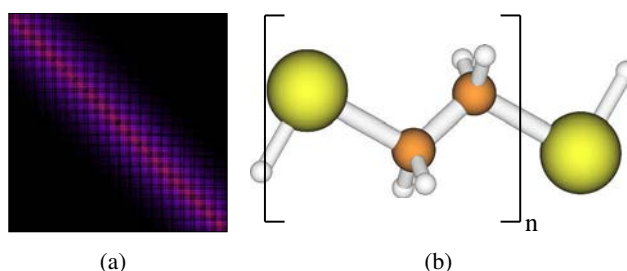


Figure 1: Real occupied pseudo-density matrix  $\underline{\mathbf{P}}^0$  (a) of Te-PEG-20 (b)

Following similar lines, Laplace transformation of energy denominators is employed to express the partially contracted  $n$ -electron valence second-order perturbation theory (NEVPT2) energies in the atomic and active molecular orbital basis.[2] As AO basis functions are inherently localized and the number of active orbitals is comparatively small, our formulation is particularly suited for a linearly scaling NEVPT2 implementation that may calculate accurate energies and properties of large open-shell molecules.

[1] B. Helmich-Paris, M. Repisky, and L. Visscher *J. Chem. Phys.* **145**, 014107 (2016).

[2] B. Helmich-Paris and S. Knecht *J. Chem. Phys.* **146**, 224101 (2017).

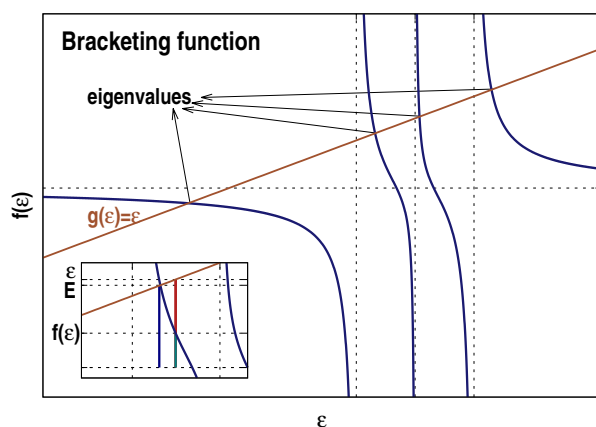
## Calculating lower bound to the energy eigenvalues of the Hamiltonian

Zsuzsanna Tóth<sup>1</sup>, Ágnes Szabados<sup>2</sup>

<sup>1</sup>*Doctoral School of Chemistry, Faculty of Science, ELTE Eötvös Loránd University, Budapest, Hungary, tzsuzsi@lowdin.chem.elte.hu*

<sup>2</sup>*Laboratory of Theoretical Chemistry, Faculty of Science, ELTE Eötvös Loránd University, Budapest, Hungary*

In quantum chemistry the usage of upper bounds to the energy is common. In contrast to upper bounds, lower bounds are barely used, because they are much more complicated and can only be applied if appropriate conditions are fulfilled.



Löwdin's bracketing function[1],  $f(\varepsilon)$  gives a lower bound if the argument  $\varepsilon$  is an appropriate upper bound. In general the argument and the value of the function „brackets” at least one eigenvalue.

In a previous publication[2] we proved, that the bracketing function has variational nature, which means that maximising the lower bound leads to exact wavefunction and energy. It leads to the idea of calculating the lower bound with better and better wavefunction in steps of a full CI iteration[3]. In each step of the

iteration we get closer and closer lower and upper bounds to the full CI energy.

In my presentation I will show an improvement over our previous method of calculating approximate but reliable lower bound. The new technique is based on the closed formula for the inverse of a block partitioned matrix[4]. This allows efficient calculation of the expansion of the lower bound, utilizing a more sophisticated zero order matrix.

[1] P.-O. Löwdin, *Phys. Rev.* **139**, A357 (1965).

[2] Á. Szabados, Zs. Tóth, *J. Math. Chem.* **52**, 2210 (2014).

[3] Zs. Tóth, Á. Szabados *J. Chem. Phys.* **143**, 084112 (2015).

[4] Zs. Tóth, P. R. Nagy, P. Jeszenszki, Á. Szabados *Theor. Chem. Acc.* **134**, 100 (2015).

## Holomorphic Hartree–Fock Theory: Beyond the Coulson–Fischer Point

**Hugh G. A. Burton<sup>1</sup>, Hamish G. H. Hiscock<sup>1,2</sup>, James D. Farrell<sup>1,3</sup>,  
Alex J. W. Thom<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, University of Cambridge, Cambridge, UK*

<sup>2</sup>*Department of Chemistry, University of Oxford, Oxford, UK*

<sup>3</sup>*Institute of Physics, Chinese Academy of Sciences, Beijing, China*

The disappearance of unrestricted Hartree–Fock (UHF) solutions at certain geometries is well studied for many molecular systems, preventing the use of UHF states as a basis for non-orthogonal Configuration Interaction (NOCI) calculations.[1] We propose a new holomorphic energy functional constructed by removing the complex conjugation of orbital coefficients from the expectation value of the Hartree-Fock energy.[2, 3] The holomorphic Hartree–Fock energy functional is complex analytic and we believe it has a constant number of stationary points across all molecular geometries. Using a revised self-consistent field (SCF) method we find a constant number of solutions for H<sub>2</sub> and LiH; where standard UHF states coalesce and disappear, their holomorphic UHF counterparts extend into the complex direction. Finally, we use the holomorphic UHF solutions of LiH as a basis for NOCI to calculate size-extensive, smooth binding curves.

[1] A. J. W. Thom and M. Head–Gordon, *J. Chem. Phys.* **131**, 124113, (2009).

[2] H. G. Hiscock and A. J. W. Thom, *J. Chem. Theory Comput.* **10**, 4795, (2014).

[3] H. G. A. Burton and A. J. W. Thom, *J. Chem. Theory Comput.* **12**, 167, (2016).



**The Prototypical Transition Metal Carbenes:  $(\text{CO})_5\text{Cr}=\text{CH}_2$ ,  $(\text{CO})_4\text{Fe}=\text{CH}_2$ , and  $(\text{CO})_3\text{Ni}=\text{CH}_2$**

**Jared D. Weidman, Marissa L. Estep, and Henry F. Schaefer III**

*Center for Computational Quantum Chemistry, University of Georgia, 140 Cedar St., Athens, GA, USA*

Transition metal carbene complexes have received interest in the field of organometallic chemistry due to their demonstrated ability to catalyze various carbon-carbon bond forming reactions. Here, we present a theoretical study of the most prototypical of such carbenes, these methylene-substituted transition metal carbonyls. These particular complexes have not been synthesized experimentally, though some similar complexes with larger carbene ligands have been synthesized. Five functionals (B3LYP, BP86, M06-L,  $\omega$ B97X, and  $\omega$ B97X-D3) were utilized along with a cc-pVTZ basis to obtain equilibrium geometries and bond dissociation energies. In addition, bonding analysis was performed to gain insight into the nature of the metal-carbene double bond.

## Contributions for the Combustion Model of Dimethyl Ether from Theoretical Calculations

Rodrigo R. V. Castro <sup>1</sup>, Vinicius N. Rocha <sup>1</sup>, Gladson de S. Machado <sup>1</sup>, Glauco Favilla Bauerfeldt<sup>1</sup>

<sup>1</sup> Departamento de Química, Instituto de Ciências Exatas, Universidade Federal Rural do Rio de Janeiro, Rodovia Br 465 km 47, Seropédica, Rio de Janeiro, Brazil

Dimethyl ether (DME) has been pointed out as a potential alternative fuel for compression ignition engines and the understanding of the combustion profile is fundamental for this discussion. In this work, a contribution for this issue is proposed by: (1) the evaluation of the combustion mechanism and identification of the key steps for the DME consumption; (2) re-evaluation of the rate coefficients for these most important reactions, on the basis of a quantum mechanical description and variational transition state theory calculations and (3) reassessment of the combustion mechanism adopting the predicted rate coefficients. The analysis of the DME combustion mechanism suggests that DME unimolecular dissociation (the only unimolecular reaction included in the original mechanism) and DME + OH bimolecular reaction are the steps with major contribution to the DME consumption, at different time scales. Since DME shows four unimolecular steps, namely dissociation ( $\text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_3\text{O} + \text{CH}_3$ ),  $\text{H}_2$  elimination (E11,  $\text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_3\text{OCH} + \text{H}_2$  and E12,  $\text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_2\text{OCH}_2 + \text{H}_2$ ) and decomposition ( $\text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_2\text{O} + \text{CH}_4$ ), the possible competition and contribution of the other unimolecular channels were quantified. The dissociation step has been described at the MRPT2/cc-pVTZ level, whereas elimination and decomposition channels have been calculated at the M06-2X/aug-cc-pVTZ level. The dissociation limit for the  $\text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_3\text{O} + \text{CH}_3$  channel has been predicted as 81 kcal mol<sup>-1</sup>. Critical energies for elimination reactions, E11 and E12, and decomposition are 85.58, 82.58 and 101.7 kcal mol<sup>-1</sup>, respectively. Barrier values suggest that E12 reaction may compete with the unimolecular dissociation channel, contributing to the formation of  $\text{H}_2$  specie, which are very important in the combustion mechanism. The bimolecular, DME + OH reaction, is also shown to be important for the consumption of the fuel and proceeds by a hydrogen abstraction mechanism, leading to methoxymethyl radical and  $\text{H}_2\text{O}$ . For such reaction, theoretical calculations have also been performed at the M06-2X/aug-cc-pVTZ level. Concerning the available literature on this bimolecular reaction, new stationary points have been located and connected to reactants and products via reaction paths, whose contribution to the global kinetics has been proved to be significant. Pre-barrier complexes have been located, stabilized by 0.76, 4.81 and 5.05 kcal mol<sup>-1</sup>. These intermediates are connected to corresponding saddle points, which lie 0.29, -0.34 and 1.57 kcal mol<sup>-1</sup>, respectively, also with respect to reactants. Canonical variational rate coefficients have been calculated for each reaction path and summed up to predict the global rate coefficients, in the range from 200 – 1500 K, in good agreement with the experimental data. The proposed kinetic data finally represent a great contribution to the literature, concerning the combustion chemistry of dimethyl ether.

## Multistructure and Multipath Kinetics Test Study: Reaction of 1-pentene + OH

Tatiane Nicola Tejero<sup>1</sup>, Glauco Favilla Bauerfeldt<sup>1</sup>

<sup>1</sup> *Departamento de Química, Instituto de Ciências Exatas, Universidade Federal Rural do Rio de Janeiro, Rodovia Br 465 km 47, Seropédica, Rio de Janeiro, Brazil*

Alkenes + OH reactions are important in the field of atmospheric chemistry and, despite all devoted efforts, several points remain yet to be explored. Here, the 1-pentene + OH reaction is described by a mechanism taking into account the reversible formation of a  $\pi$ -type prebarrier complex ( $\pi$ -PC), followed by the addition steps, which can lead to different products, considering the addition of the OH radical to each carbon atom at the double bond [1]. Moreover, several conformers of the reactants are observed. Then, the single mechanism described above should be attributed to each single conformer and the collection of the distinct mechanisms composes the so-called multipath case [2].  $\sigma$ -type intermediates can also be located and their role in the dynamics of these reactions could be clarified through a detailed and complete description of this problem. Theoretical procedures have been performed at the Density Functional Theory level, adopting the M06-2X functional along with the aug-cc-pVDZ basis set and canonical variational rate coefficients have been predicted. At the M06-2X/aug-cc-pVDZ level,  $\pi$ -PCs,  $\sigma$ -PC and saddle points lie on the ranges: -3.54 – -3.63, -2.55 – -3.59 and -2.12 – 0.12 kcal mol<sup>-1</sup>, respectively. The contributions of each different reaction channel (of each reactant conformer) to the overall kinetics have been calculated, leading to the conclusion that the inclusion of all conformers and the corresponding paths is very important to improve the final kinetic results. It has also been noted that the contributions of the intermediate  $\pi$  type for the dynamics of the reaction are the most important. This model could also explain the non-Arrhenius behavior. Global rate coefficients have been finally calculated, as a function of the temperature, by summing up individual rate coefficient weighted by the Boltzmann population of the conformer. The global rate coefficient, predicted at 298 K is  $1.54 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, in good agreement with the experimental value [3],  $2.74 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

[1] Barbosa, T. S. et al. *PCCP* **2015**, *17*, 8714.

[2] Yu, T.; et al. *Faraday Discuss.* **2012**, *157*, 59.

[3] Miller, W. H.; *The Journal Chemical Physics*, **1976**, *65*, 2216.

## **Computational Study of Isolated Glycine, Alanine and Solvated Glycine Zwitterion and Contribution to ISM Behavior**

**Neubi F. Xavier Junior<sup>1</sup>, Diego N. Jesus<sup>1</sup>, Gabriel S. S. Brites<sup>1</sup>, Leonardo Baptista<sup>2</sup>, Cristiane M. Cardoso<sup>1</sup>, Glauco F. Bauerfeldt<sup>1</sup>**

<sup>1</sup>*Departamento de Química. Instituto de Ciências Exatas. Universidade Federal Rural do Rio de Janeiro. Rodovia Br km 7, Seropédica, RJ, Brasil*

<sup>2</sup>*Departamento de Química e Ambiental, Faculdade de Tecnologia, Universidade do Estado do Rio de Janeiro, Rodovia Presidente Dutra Km 298, Resende - RJ, Brazil*

The presence of glycine in interstellar medium (ISM) is still controversial<sup>1</sup>. Although gas phase glycine has not been detected in ISM, some fragments associated to its formation and decomposition have already been identified. The solid phase (icy) glycine is, on the other hand, predominant in the ISM. In this work, the main goal is the description of the structure and reactivity of glycine in different media (gas phase and aqueous solution) aiming the contribution to the Astrochemical knowledge about the formation and decomposition of amino acids in the ISM. All calculations have been performed at the CCSD(T)/6-311++G(2d,2p)//B3LYP//6-311++G(2d,2p) level. Conformational analysis of the glycine in its neutral and radical cation forms, revealing spectra of eight and four conformers of neutral and glycine radical cation, respectively. In each case, one conformer has been shown to prevail. The study of the unimolecular reactions show that the deamination is the dominant channel among all possibilities, including decarboxylation and dissociation paths. Rate coefficients have been calculated as a function of the temperature and the energy, adopting the canonical and microcanonical variational transition state theories, respectively. The barrier energies are predicted as: 69,36 kcal/mol for decarboxylation and 44,76 kcal/mol for deamination on neutral form glycine. On glycine radical cation the barrier height estimated was 56,00 kcal/mol. A similar study has been performed for alanine. To simulate the icy medium, calculations for glycine in aqueous solution have been performed using CPCM and IEF-PCM methods. PCM parameters have been tested and chosen as those which allowed the best description of a global chemical property: the pKa's values. These results finally contribute to the understanding of the role of glycine in the ISM and the possible paths leading to its formation and decomposition in the prebiotic atmosphere and primitive Earth.

[1] Sergio Pilling et al., *Astrobiology* **13**, 79-91 (2013).

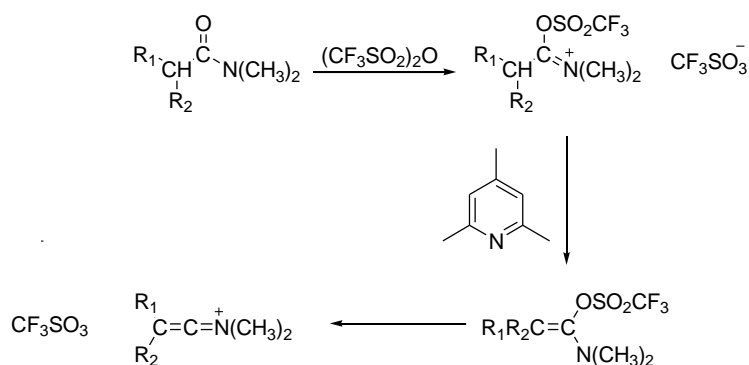
## KETENIMINIUM SALT FORMATION AND THEIR ELECTROCYCLIZATION REACTIONS

**Ulfet Karadeniz,<sup>1</sup> Gamze Tanriver,<sup>1</sup> Amandine Kolleth,<sup>2</sup> Alexandre Lumbroso,<sup>2</sup> Sarah Sulzer,<sup>2</sup> Alain De Mesmaeker,<sup>2</sup> and Saron Catak<sup>1\*</sup>**

<sup>1</sup>Bogazici University, Department of Chemistry, Bebek 34342 Istanbul, Turkey

<sup>2</sup>Syngenta Crop Protection AG, Crop Protection Research, Research Chemistry, Schaffhauserstrasse 101, CH-4332, Switzerland

Keteniminium salts are an improved alternative to their ketene analogues due to their higher electrophilicity, regioselectivity and reactivity properties. We use a DFT approach to elucidate the formation of keteniminium salts by referring to the mechanism proposed by Ghosez in 1981 (Scheme 1).<sup>[1]</sup> Depending on a previous study by E. Villedieu-Percheron et al.<sup>[2]</sup> we recently described an efficient access to 3-amino-benzothiophenes through the 6 $\pi$  electrocyclization of keteniminium intermediates.<sup>[3]</sup> As a continuation of this study, we examine the reactivity of keteniminium salts in electrocyclization reactions resulting in different heterocyclic systems. In addition to the effect of the heteroatom, the effect of the substituents on the keteniminium salt is also rationalized by the study.



**Scheme 1.** Ghosez's Mechanism for the Formation of Keteniminium Salts.<sup>[1]</sup>

[1] J. B. Falmagne, J. Escudero, S. Taleb-Sahaoui, L. Ghosez, *Angew. Chem. Int. Ed. Engl.* **20** (1981).

[2] E. Villedieu-Percheron, S. Catak, D. Zurwerra, R. Staiger, M. Lachia, A. De Mesmaeker, *Tetrahedron Lett.* **55** (2014).

[3] A. Lumbroso, J. Behra, A. Kolleth, P. Y. Dakas, U. Karadeniz, S. Catak, S. Sulzer-Mossé, A. De Mesmaeker, *Tetrahedron Lett.* **56** (2015).

**Fermionic PEPS for finite two-dimensional Hubbard models****Jheng-Wei Li<sup>1</sup>, Toru Shiozaki<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, Northwestern University, 2145 Sheridan Rd., Evanston, IL 60208, USA*

We study the finite two-dimensional Hubbard model using fermionic projected entangled pair states (fPEPS). A general procedure to account for the anti-commutative relation of fermions in tensor network states has been proposed. We demonstrate that the fPEPS ansatz is an efficient numerical approximation to explore the ground state phase diagram of the two-dimensional Hubbard model.

**Electron Delocalization in Infinite  $\sigma$ -Bonded One-dimensional Chains  
(MMe<sub>2</sub>)<sub>∞</sub>, M = Si, Ge, Sn, Pb**

**Milena Jovanovic<sup>1,2</sup>, Josef Michl<sup>1,2</sup>**

<sup>1</sup>*Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309,  
United States*

<sup>2</sup>*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech  
Republic, 16610 Prague 6, Czech Republic*

$\sigma$ -Electron delocalization in  $\sigma$ -bonded systems affects their optical properties, ionization potentials, charge and energy transfer, conductivity, and chemical reactivity. The presence or absence of  $\sigma$  delocalization is often dictated by chain conformation. We investigate  $\sigma$  delocalization in linear saturated infinite chains of atoms of silicon, germanium, tin, and lead, from the planar all-anti limit with a backbone dihedral angle  $\omega = 180^\circ$  toward the highly twisted all-syn limit  $\omega = 0^\circ$ . To describe  $\sigma$  delocalization we use band theory within the tight-binding Ladder C model, which includes only those hybrid orbitals that are involved in backbone bonding. This model has three distinct hopping integrals that describe primary, geminal, and vicinal interactions. Only the vicinal integral depends on the backbone dihedral angle. We investigate the effects of parameter values and chain conformation on electron delocalization.

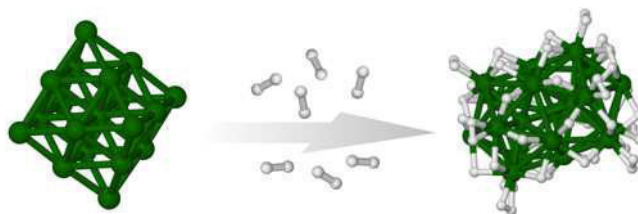
## Structural characterization of hydrogen adsorbed ruthenium clusters - toward an atomistic understanding of ammonia synthesis

Dennis Bumüller<sup>1</sup>, Anna-Sophia Hehn<sup>2</sup>, Eugen Waldt<sup>1</sup>, Reinhart Ahlrichs<sup>2</sup>,  
Manfred M. Kappes<sup>1,2</sup>, Detlef Schooss<sup>1,2</sup>

<sup>1</sup>*Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT),  
Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

<sup>2</sup>*Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 2,  
76131 Karlsruhe, Germany*

Structural characterization of ruthenium nanoparticles is essential when aiming to elucidate the catalyst's role in ammonia synthesis. In particular, the examination of small ruthenium clusters is significant and indispensable as cluster structures often differ from the bulk lattice motif. We present a combined experimental and theoretical study using trapped ion electron diffraction and density functional theory calculations to determine the structure of Ru<sub>19</sub><sup>+</sup> clusters and to analyze the effect of hydrogenation [1, 2]. Cluster structure computations are obtained from a genetic algorithm search procedure [3]. Results reveal that bare Ru<sub>19</sub><sup>+</sup> has a closed-shell octahedral fcc structure in contrast to the hcp geometry of the bulk. Adsorption of hydrogen causes the octahedral cluster to rearrange toward a bi-icosahedral motif once a load of 20 to 30 hydrogen atoms is reached. Calculations furthermore predict that hydrogen is preferentially atomically bound and favors two-fold bridge configurations. A linear dependence between adsorption energies and the relative position of the d-band centers to the Fermi level is found, confirming the bi-icosahedral cluster structure as favorable motif for hydrogen adsorption.



- [1] E. Waldt, A.-S. Hehn, R. Ahlrichs, M. M. Kappes, D. Schooss, *J. Chem. Phys.* **142**, 024319 (2015).
- [2] D. Bumüller, A.-S. Hehn, E. Waldt, R. Ahlrichs, M. M. Kappes, D. Schooss, *J. Phys. Chem. C* **121**, 10645 (2017).
- [3] C. Neiss, D. Schooss, *Chem. Phys. Lett.* **532**, 119 (2012).



## DFT Study of the Chemical-Physics Properties of a Series of New Benzoxazole Derivatives

Hayat Ayache<sup>1,2</sup>, Fazia Derridj<sup>3</sup>, Aziz Elkechai<sup>1</sup>, Dalila Hammoutène<sup>2</sup>

<sup>1</sup> LPCQ, Faculté des Sciences, UMMTO, Tizi-Ouzou, Algeria

<sup>2</sup> LTMM, Faculté de Chimie, USTHB, 16111, Algiers, Algeria

<sup>3</sup> LPCM, Faculté des Sciences, UMMTO, Tizi-Ouzou, Algeria

A new series of benzoxazole derivatives have been recently synthesized. They constitute an interesting class of chelating agents capable of coordinating metal ions such as zinc and cadmium, by giving complexes of biological interest, and which can serve as models for metallic depollution.

Structural parameters, vibrational spectra (IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and UV-Visible absorption) of these benzoxazole derivatives were performed by DFT and TD-DFT, to have an insight into their photophysical properties.

Reactivity descriptors such as ionization energy, electronic affinity, global hardness, global softness, electrophilicity, nucleophilicity and condensed Fukui functions were also determined. The calculated geometrical parameters are in good agreement with those of similar benzoxazole derivatives and the theoretical frequencies assignments confirmed the experimental measurements [1-5].

### References

- [1] C. T. Zeyrek, H. Unver, Ö. Temiz-Arpaci, K. Polat, N. O. İskeleli, M. Yildiz, *J. Mol. Struct.* **1081**, 22 (2015).
- [2] C. N. Sundaresan, S. Dixit, P. Venugopalan, *J. Mol. Struct.* **693**, 205 (2004).
- [3] H. Unver, O. T. Arpacı, M. Zengin, T. N. Durlu, *J. Mol. Struct.* **609**, 205 (2002).
- [4] A. E. H. Machado, J. A. Miranda, S. Gualardi, D. E. Nicodem, D. Severino, *Spectrochim. Acta A* **59**, 345 (2003).
- [5] F. Derridj, J. Roger, F. Geneste, S. Djebbar, H. Doucet, *J. Organomet. Chem.* **694**, 455 (2009).

## Development of *In Silico* Drug Design Techniques Based on the Fragment Molecular Orbital Method

**Kaori Fukuzawa**

*School of Pharmacy and Pharmaceutical Sciences, Hoshi University, 2-4-41 Ebara,  
Shinagawa-ku, Tokyo 142-8501, Japan*

The Fragment molecular orbital (FMO) method is one of the high-potential approach for protein - ligand interaction energy analysis in structure based drug design. By using the FMO method, detailed information on the interaction between the ligand and the target protein can be obtained based on a quantum mechanical calculation. Interaction between a ligand and each amino acid residue can also be quantitatively evaluated using the inter fragment interaction energy (IFIE). The FMO method has been applied to many protein-ligand systems, and recent activities that have evolved these research have been rapidly progressing. Here we will introduce the recent research on the development in "FMO Drug Design Consortium (FMODD)" through industry-academia-government collaboration.

By using K-computer since 2015, FMO calculation of protein-ligand complex exceeding 1,000 structures have been done so far. Correlation between calculated binding energies and IC<sub>50</sub> activity values was investigated on various types of target proteins using X-ray crystal structures from Protein Data Bank. We are preparing to store these calculation results in the IFIE database and plan to release it widely as basic data of FMO based drug design. In the future, we would like to enable rational drug design with high reliability for targets for which electronic effects are important, which cannot be solved by conventional classical approaches.

### Acknowledgement

This research has been carried out by cooperation of many collaborators involved in FMODD. A part of this research was done in activities of the FMODD, and the results were obtained using the K computer (project ID: hp170183). This work was also supported by JSPS KAKENHI Grant Number JP15K05397.

### References

- [1] "The Fragment Molecular Orbital Method" ed. Fedorov, D. G. & Kitaura K.: (Taylor & Francis/ CRC Press, Boca Raton, FL, 2009).
- [2] Fedorov, D. G., Nagata, T., Kitaura, K., *Phys. Chem. Chem. Phys.* **14**, 7562 (2012).
- [3] Tanaka, S., Mochizuki, Y., Komeiji, Y., Okiyama, Y. and Fukuzawa, K., *Phys. Chem. Chem. Phys.*, **16**, 10310 (2014).

## Construction of IFIE-database with semi-automated FMO calculation protocol

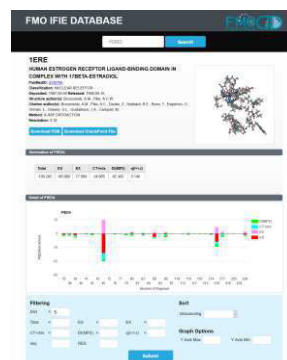
**Chiduru Watanabe<sup>1</sup>, Yoshio Okiyama<sup>1</sup>, Daisuke Takaya<sup>1</sup>, Shunpei Nagase<sup>1</sup>,  
Kikuko Kamisaka<sup>1</sup>, Hirofumi Watanabe<sup>2</sup>, Kaori Fukuzawa<sup>3</sup>, Teruki Honma<sup>1</sup>**

<sup>1</sup>*RIKEN Center for Life Science Technologies, 1-7-22 Suehiro-cho, Tsurumi-ku, Yokohama,  
Kanagawa 230-0045, Japan,*

<sup>2</sup>*Education Center on Computational Science and Engineering, Kobe University, 7-1-48,  
Minatojimaminamimachi, Chuo-ku, Kobe 650-0047, Japan*

<sup>3</sup>*Department of Physical Chemistry, School of Pharmacy and Pharmaceutical Sciences,  
Hoshi University, 2-4-41 Ebara, Shinagawa, Tokyo 142-8501, Japan*

The fragment molecular orbital (FMO) method proposed by Kitaura *et al.* enables us to efficiently perform *ab initio* quantum mechanical calculations for large biomolecules by many-body expansion technique with fragmentation. Inter-fragment interaction energy (IFIE) analysis based on FMO is able to reveal important interactions in molecular recognition such as protein-ligand binding in units of amino acid residues and a ligand. Moreover, the information of important interactions estimating from decomposed electronic energy terms (e.g. electrostatic and dispersion interactions) is quite useful for drug design. On the other hand, it is not easy to perform FMO calculations for not experienced researchers in the matter of structure preparation and FMO setting. To publicly disclose the IFIE data, we have started to comprehensively collect IFIE data and construct IFIE-database (Figure 1). However, there are limits to prepare huge amount of various protein structure data (e.g. PDB having ca. 40,000 entries of protein-ligand complex) by manual labor. Thus, we developed “semi-automated FMO calculation protocol” to efficiently carry out structure preparation and subsequent FMO calculations for multiple X-ray crystal structures. To validate the FMO protocol, we manually prepared protein structure and carry out FMO calculations using the same crystal structures. As a result, IFIE values of the FMO protocol data showed good agreement with those of manual labored data. Therefore, we confirmed that this protocol can be used for structure preparation and FMO calculations of massive protein structures. There are at present the IFIE data of 300 complexes obtained from the FMO protocol. They were registered in newly developed IFIE-database with GUI. This research was done in activities of the FMO drug design (FMODD) consortium [<http://eniac.scitec.kobe-u.ac.jp/fmodd/index.html>]. The results of FMO calculations were obtained using the K computer (project ID: hp170183).



**Figure 1 IFIE-database**

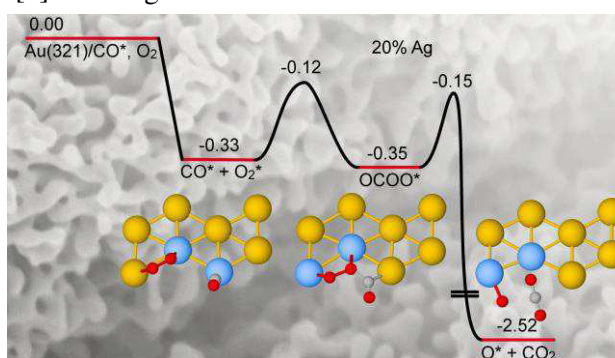
## New Insights Into Oxygen Activation On Nanoporous Gold - A Selective Catalyst For Methanol Oxidation

Wilke Dononelli<sup>1</sup>, Lyudmila Moskaleva<sup>2</sup>, Thorsten Klüner<sup>1</sup>

<sup>1</sup> IfC, Carl von Ossietzky Universität Oldenburg, 26111 Oldenburg, Germany

<sup>2</sup> IAPC, Universität Bremen, 28359 Bremen, Germany

Au-based catalysts can be used for fuel cells, the synthesis of esters or the selective oxidation of alcohols. [1] There is a high interest in this metal based catalysts because the selectivity of gold to partial oxidation products is higher than the selectivity of other metals. Especially nanoporous gold (np-Au), an unsupported form of catalytically active gold, has recently attracted considerable interest due to its potential use in the selective oxidation of alcohols like methanol. [2] Although these oxidation reactions have been investigated by several groups during the past decade, the origin of the catalytic activity of np-Au has not been understood completely. The main remaining question that we try to answer is the nature of the active sites of the np-Au. Within DFT (density functional theory) calculations, using the PBE functional as implemented in the Vienna ab initio simulation package (VASP) [3], we describe the influence of residual silver atoms in the material and try to explain possible pathways for the activation of oxygen, which is the most essential step of these oxidative coupling reactions. [1,4] Therefore a kinked Au(321) surface introduced by Moskaleva [5] represents one of the reactive surfaces of the nanoporous gold in this study. Since Zielasek *et al.* [6] experimentally found atomic oxygen at the surface of the np-Au for the reaction of CO and O<sub>2</sub> to CO<sub>2</sub>, it was estimated that first molecular oxygen is dissociated and then the atomic oxygen reacts with CO. In earlier studies, we were able to demonstrate, that this reaction only occurs if a high amount of residual silver is present at the surface. The activation barrier for the dissociation can be lowered from 1.1 eV on pure gold to 0.7 eV with silver impurities. [5] For this study, we considered a direct reaction of CO and O<sub>2</sub>, where the activation barrier can be lowered to 0.4 eV without and 0.2 eV with silver impurities (see fig., reprinted from ref. [1]). [1,4] In addition, we are able to show, that comparable reaction pathways via the direct reaction of O<sub>2</sub> with either H<sub>2</sub>O [4] or CH<sub>3</sub>OH are possible and that the role of the residual silver has not been discussed entirely correct for the last decade, since no ag is needed to activate these reactions.



[1] W. Dononelli, L. V. Moskaleva and T. Klüner, in Encyclopedia "Interface Chemistry: Surface Science and Electro-chemistry", Elsevier (2017).

[2] A. Wittstock, V. Zielasek, J. Biener, C. Friend and M. Bäumer, *Science* **327**, 319 (2010).

[3] G. Kresse and J. Hafner, *Phys. Rev. B*, **49**, 14251 (1994).

[4] W. Dononelli, M. V. Moskaleva, M. Bäumer and T. Klüner, submitted (2017).

[5] L. V. Moskaleva, V. Zielasek, T. Klüner, K. Neyman and M. Bäumer, *Chem. Phys. Lett.* **525**, 87 (2012).

[6] V. Zielasek, B. Jürgens, C. Schulz *et al.*, *Ang. Che. Int. Ed.* **45**, 8241 (2006).

**Mechanism of Nakamura's Bisphosphine Iron-Catalyzed Asymmetric C(sp<sup>2</sup>)-C(sp<sup>3</sup>) Cross-Coupling Reaction .**

**Wes Lee<sup>1</sup>, Jun Zhou<sup>1</sup>, Osvaldo Gutierrez<sup>1</sup>**

<sup>1</sup> *Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742 (USA)*

*Quantum mechanical calculations are employed to investigate the mechanism and origin of stereoinduction in asymmetric iron-catalyzed C(sp<sup>2</sup>)-C(sp<sup>3</sup>) cross-coupling reaction between Grignard reagents and  $\alpha$ -chloroesters. A coherent mechanistic picture of this transformation is revealed. These results have broad implications for understanding the mechanisms of iron-catalyzed cross-coupling reactions and rational design of novel iron-based catalysts for asymmetric transformations.*

## Theoretical Study on the Origin of the Enantioselectivity of Flexible Catalytic Systems

Miho Hatanaka<sup>1,2</sup>

<sup>1</sup>*Institute for Research Initiatives, Division for Research Strategy, Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama-cho, Ikoma, Nara, Japan, 630-0192*

<sup>2</sup>*PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan*

Highly stereoselective reactions have been achieved by using chiral catalysts, and the computational chemistry contributed to better understanding of the mechanism of such reactions. Conventional chiral catalysts usually have rigid structures and bulky side chains on chiral centers to restrict the approach directions of reactants. Therefore, only a few transition states (TSs) of stereo-determining step need to be computed to elucidate the origin of the enantioselectivity. Recently, a number of catalytic systems having flexible structures have been reported. There could be a large number of TSs that may contribute to the stereoselectivity, and a few selective TSs may not be enough. To overcome this problem, an automated exploration method called the Global Reaction Route Mapping (GRRM) is one of the most suitable strategies. [1]

We focus on aqueous C-C bond formations catalyzed by two independent metal complexes having flexible structures. [2] Unlike conventional rigid and bulky chiral catalytic systems, the approach directions of reactants were not restricted by the catalysts and we could not predict the enantioselectivity from the geometries of the prereaction complexes. Therefore, we exhaustively gathered the TSs of the stereo-determining C-C bond formation step by using the artificial force induced reaction (AFIR) method, which is one of the methods of the GRRM strategy, and succeeded in reproducing the experimental enantio excesses quantitatively. In both two catalytic systems, the origin of the enantioselectivity was not the structural bulkiness nearby the chiral centers but the asymmetric structure of the coordination sphere.

[1] (i) S. Maeda, K. Ohno, K. Morokuma, *Phys. Chem. Chem. Phys.* **15**, 3683 (2013). (ii) S. Maeda, Y. Harabuchi, M. Takagi, T. Taketsugu, K. Morokuma, *Chem. Rec.* **16**, 2232 (2016).

[2](i) M. Hatanaka, S. Maeda, K. Morokuma, *J. Chem. Theory Comput.* **9**, 2882 (2013). (ii) M. Hatanaka, K. Morokuma, *J. Am. Chem. Soc.* **135**, 13972 (2013). (iii) M. Hatanaka, K. Morokuma, *ACS Catal.* **5**, 3731 (2015).

## **Proton Transfer in Cytochrome c Oxidase - Calculation and Prediction of Transition Networks.**

**Marco Reidelbach<sup>1</sup>, Marcus Weber<sup>2</sup>, Petra Imhof<sup>1</sup>**

*<sup>1</sup>Physics Department, Free University Berlin, Arnimallee 14, 14195 Berlin, Germany*

*<sup>2</sup>Computational Molecular Design, Zuse Institute Berlin, Takustrasse 7, 14195 Berlin, Germany*

In Cytochrome c Oxidase protons are transferred from the complex surface towards the interior via two distinct channels. How the proton transfer occurs inside the channels, however, is unclear. The Transition Network Approach allows the identification of such proton transfer pathways without introducing any bias. Thereby, a pathway displaying several experimental characteristics was identified. To circumvent numerous Transition Network recalculations, e.g. for different redox-states of the enzyme complex, the Transition Network prediction using Minimum Spanning Tree sensitivities was tested and proved to be efficient.

## The Effects of Lewis acid Complexation on Type I Radical Photoinitiators

**Benjamin B. Noble<sup>1</sup>, Adam C. Mater<sup>1</sup>, Leesa M. Smith<sup>1</sup> and Michelle L. Coote<sup>1\*</sup>**

<sup>1</sup> *Australian Research Council Centre of Excellence for Electromaterials Science,  
Research School of Chemistry, Australian National University, Canberra, ACT 2601,  
Australia*

In the present work, we examine the effects of zinc chloride (ZnCl<sub>2</sub>) and aluminium chloride (AlCl<sub>3</sub>) complexation on the photochemistry of two well-known type I photoinitiators, methyl-4'-(methylthio)-2-morpholinopropiophenone (MMMP) and 2,2-dimethoxy-2-phenylacetophenone (DMPA). High-level *ab initio* calculations and experimental results demonstrate that Lewis acid complexation has a significant effect on the individual processes that comprise radical photoinitiation. Theoretical calculations predict that both Lewis acids form solution stable chelates with MMMP and DMPA. Moreover, we found experimentally that addition of ZnCl<sub>2</sub> and AlCl<sub>3</sub> significantly alters the UV-Vis spectra of both MMMP and DMPA. Time dependent density functional theory (TD-DFT) calculations demonstrate that Lewis acid complexation blue shifts the  $n\pi^*$  excitations of both DMPA and MMMP, while concurrently red shifting the  $\pi\pi^*$  transitions. Complexation also significantly alters the stability and reactivity of the photoinitiator fragment radicals. Lewis acid binding localizes and destabilizes acyl radicals, resulting in significantly increased reactivity towards methyl methacrylate (MMA). In contrast, complexation of Lewis acids dramatically reduces the reactivity of the morpholine substituted isopropyl radical and the dimethoxyphenyl radical towards MMA. Alternative complexation at the methyl ester side-chain of MMA has a beneficial effect on the reactivity of all fragments, increasing addition rate coefficients by 2–4 orders of magnitude. Some of the important implications of these findings for pulsed laser polymerization (PLP), and acetophenone photochemistry more generally are outlined.



## Advanced artificial neural network approaches to prediction of pharmacokinetic properties and toxicity of drug compounds

Eugene V. Radchenko, Vladimir A. Palyulin, Nikolay S. Zefirov

*Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory, 1/3,  
Moscow 119991 Russia*

The pharmacokinetic properties and toxicity of potential drug compounds (ADMET properties: absorption, distribution, metabolism, excretion, toxicity) critically affect their efficacy, pharmacological profile, administration protocol and safety. Thus, the optimization of these properties is an important aspect of drug discovery and development, and the ability to predict them for new structures can substantially improve the speed and efficiency of such optimization.

The artificial neural networks are a powerful nonlinear machine learning method applicable to a broad range of chemistry problems, including the QSAR/QSPR modeling. We have developed a general methodology for the prediction of ADMET parameters based on the application of artificial neural networks and fragmental descriptors to extensive and verified experimental data sets. The fragmental descriptors for a structure are the occurrence counts of the paths, cycles and branches of varied size using an hierarchical atom type classification, providing a 'holographic' representation of a molecule. During the model construction, the GPU-based deep learning and double cross-validation are used to achieve optimal performance and model predictivity. During the prediction, a graphic map highlighting the parts of a molecule that make positive or negative contributions to the predicted property is generated as an additional guidance for the ADMET optimization.

The models built by us are implemented in an integrated online service available on the Internet (<http://qsar.chem.msu.ru/admet/>). It supports convenient prediction of important properties (in particular, lipophilicity, blood-brain barrier permeability [1], human intestinal absorption [2], plasma protein binding, mutagenicity, hERG-mediated cardiac toxicity [3], aromatic hydrocarbon receptor binding, cytotoxicity, etc.) as well as qualitative and semi-quantitative estimation of their suitability for drug-like compounds. This integrated prediction system may be used in the research in various areas of medicinal chemistry and pharmacology.

This work was supported by the Russian Foundation for Basic Research (grant #15-03-09084).

### References

- [1] A.S. Dyabina, E.V. Radchenko, V.A. Palyulin, N.S. Zefirov, *Dokl. Biochem. Biophys.*, **470**, 371 (2016). [2] E.V. Radchenko, A.S. Dyabina, V.A. Palyulin, N.S. Zefirov, *Russ. Chem. Bull.*, **65**, 576 (2016). [3] E.V. Radchenko, Yu.A. Rulev, A.Ya. Safanyaev, V.A. Palyulin, N.S. Zefirov, *Dokl. Biochem. Biophys.*, **473**, 128 (2017).

## How many electrons are excited in an electronic transition?

G. M. J. Barca<sup>1</sup>, A. T. B. Gilbert<sup>1</sup>, P. M. W. Gill<sup>1</sup>

<sup>1</sup>*Research School of Chemistry, Australian National University, ACT 2601, Australia*

What am I asserting if I claim that a “singly-excited state” resulted from an electronic transition? Or, for that matter, a doubly- or a triply-excited state? In other words, what if I ask: *how many electrons are excited in an electronic transition?*

In this Poster, we address this fundamental question by introducing the excitation number,  $\eta$ , as a metric for characterising multiply excited states. We show that calculated  $\eta$  values lie very close to positive integers, leading to unambiguous assignments of the number of excited electrons. This contrasts with previously defined quantities, such as the promotion number,[1] which can lead to misassignments. We consider several examples where  $\eta$  can provide improved characterisation of excited states.[2]

[1] M. Head-Gordon, A. M. Graña, D. Maurice, and C. A. White, *J. Phys. Chem.* **99**, 14261 (1995).

[2] G. M. J. Barca, A. T. B. Gilbert, and P. M. W. Gill, *submitted*

**Photoisomerisation and electronic spectroscopy of  $\text{XC}_3\text{N}$  ( $\text{X}=\text{-CH}_3$ ,  $\text{-H}$ ). The TD-DFT perspective.**

**Marcin Gronowski<sup>1</sup>, Thomas Custer<sup>1</sup>, Robert Kolos<sup>1</sup>**

*<sup>1</sup>Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland*

Photochemical transformations of cyanoacetylene ( $\text{HC}_3\text{N}$ ) and methylcyanoacetylene ( $\text{CH}_3\text{C}_3\text{N}$ ) dispersed in noble gas matrices were the subject of intense experimental studies. For both molecules, UV irradiation leads to formation of several isomers. In spite of the fact that both molecules have the same chromophore, their photolysis products are significantly different. We try to explain the mechanisms for photochemical transformation of these molecules using quantum chemical computations.

In the first step, we studied ground state potential energy surfaces. We found transition states on them and applied IRC computations in order to determine the minimum energy path between the transition states and minima. Then, we applied time-dependent density functional theory in the Tamm-Dancoff approximation to describe excited state potential energy surfaces. The study was carried out using the vertical approximation meaning that the energies of excited states were calculated for each of the geometries obtained during ground state IRC calculations. In the final step, we optimized geometries for minima on triplet and singlet excited states.

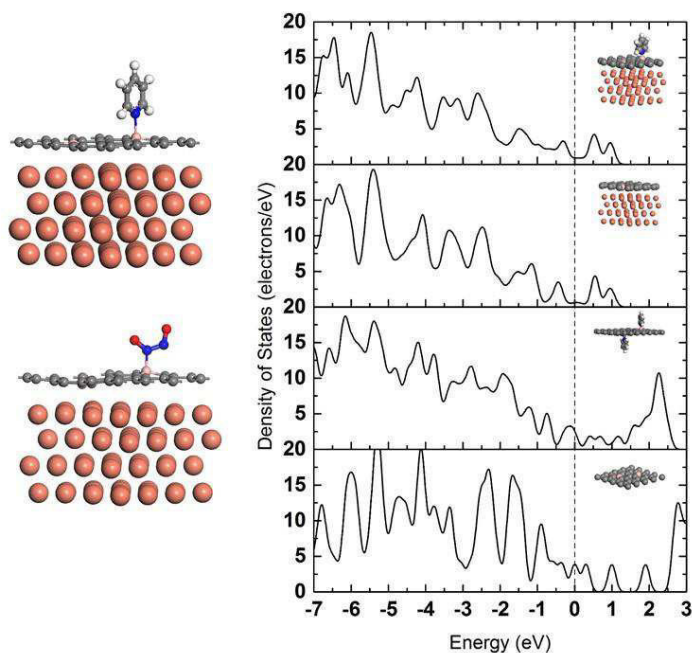
The ground and singlet excited state potential energy surfaces do not cross each other during most unimolecular transformations discussed here. This suggests that most of the chemical transformations take place on the first triplet potential energy surface. Our computations show that energies of first triplet excited states of isocyanide species are higher than for the respective cyanides. This hinders the formation of isocyanides if any other reaction channel is open, as is the case for  $\text{CH}_3\text{C}_3\text{N}$ .

## Boron-Doped Graphene for multifunctional coating – A DFT study

Valentina Cantatore and Itai Panas

*Chalmers University of Technology, Department of Chemistry and Chemical Engineering, Energy and Materials, Gothenburg, Sweden*

We describe a route to achieve multi-functional graphene coating through DFT calculations. To start with we show how chemical bonding between a copper substrate and a graphene layer can be obtained if the graphene is a priori boron doped. [1] Utilizing the well-known epitaxy between graphene and Cu(111) [2] and pair-wise binding to the Cu(111) surface through boron sites,[3] we can observe co-existence of pseudo-gap property in the graphene subsystem and, at the same time, a metallic density of states in the Cu subsystem at the common Fermi energy. Apparently a paradox is that the two subsystems, the doped graphene and the Cu surface, preserve and even recover their individual integrities upon formation of surface chemical bonds. Employing pyridine as test molecule, conditioned ability of a nucleophile to offer competitive dative bonding with the substrate for boron sites is demonstrated. It is shown also that the adsorption of small molecules on the BBG@Cu system occurs for the case of half coverage and for adsorption to boron atoms originally bound to the on-top site of Cu(111). The ability of complementary boron sites to compensate for loss of binding between on-top site and boron, resulting from said bonding to the incoming nucleophile, is emphasized. Based on these observations, the possibility to study infinite layered systems comprising FeSe monolayer and boron doped graphene is inferred and first insights on the peculiar magnetic structure of the system are showed.



[1] V. Cantatore and I. Panas, *Carbon*, **115**, 375 (2017).

[2] L. Ferrighi, M. I. Trioni and C. Di Valentina, *J. Phys. Chem. C*, **119**, 6056 (2015).

[3] V. Cantatore and I. Panas, *Carbon*, **104**, 40 (2016).

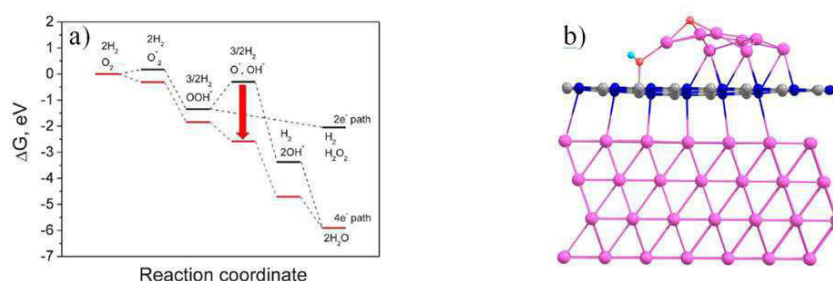
## Theoretical design of boron nitride based electrocatalysts for oxygen reduction and hydrogen evolution reactions

Andrey Lyalin<sup>1</sup>, Kohei Uosaki<sup>1</sup>, Tetsuya Taketsugu<sup>1,2</sup>

<sup>1</sup>Global Research Center for Environment and Energy based on Nanomaterials Science (GREEN), National Institute for Materials Science (NIMS), Tsukuba 305-0044, Japan

<sup>2</sup>Department of Chemistry, Hokkaido University, Sapporo 060-0810, Japan

It is demonstrated that chemically inert and insulating hexagonal boron nitride (h-BN) supported on the inert gold surface can be functionalized by interaction with the metal support and become active electrocatalysts [1,2]. It is shown that small gold clusters deposited on h-BN/Au(111) surface can provide active sites for oxygen adsorption promoting effective  $4e^-$  pathway of oxygen reduction reaction (ORR) via dissociation mechanism of OOH intermediate at the perimeter interface between the supported Au cluster and h-BN/Au surface [3]. It is also demonstrated that hydrogen evolution reaction (HER) proceeds very efficiently at the interface between Au surface and h-BN nanosheets [2]. Theoretical evaluation suggests that edge atoms of h-BN nanosheets on Au provide energetically favored sites for adsorbed hydrogen, i.e., the intermediate state of HER. Therefore it is suggested that increase in the interface area between Au and h-BN would result in increase of ORR and HER activity. This study opens a new route to develop ORR and HER catalysts based on the materials never been considered as catalytically active.



**Figure 1:** Energy diagram for ORR at BN/Au(111) (black line) and Au<sub>8</sub>@BN/Au(111) (red line) (a); optimized geometry of dissociated OOH on Au<sub>8</sub>@BN/Au(111) (b).

- [1] K. Uosaki, G. Elumalai, H. Noguchi, T. Masuda, A. Lyalin, A. Nakayama, T. Taketsugu, *J. Am. Chem. Soc.* **136**, 6542-6545 (2014).
- [2] K. Uosaki, G. Elumalai, H. C. Dinh, A. Lyalin, T. Taketsugu, and H. Noguchi, *Sci. Rep.* **6**, 32217 (2016).
- [3] G. Elumalai, H. Noguchi, A. Lyalin, T. Taketsugu, K. Uosaki, *Electrochem. Commun.* **66**, 53-57 (2016).

## Analysis of hyperfine structure in Dirac theory: anomalous increase of relativistic contraction of outer orbitals

Ayaki Sunaga, Minori Abe, Masahiko Hada

Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji-city, Tokyo, Japan

Hyperfine interaction is a magnetic interaction between an electron spin  $\hat{\mathbf{S}}$  and a nuclear spin  $\hat{\mathbf{I}}$ , and the coupling constant of the interaction is referred to as the hyperfine coupling constant (HFCC). In the framework of four-component relativistic theory, the formula of the HFCC is defined by Arratia-Perez *et al.* [1] and Malkin *et al.* [2] and so on. However, the inner product  $\hat{\mathbf{S}} \cdot \hat{\mathbf{I}}$  does not clearly appear in their definitions.

In this work, we derive a formalism which apparently includes  $\hat{\mathbf{S}} \cdot \hat{\mathbf{I}}$  when the potential of the system is spherical symmetric. Our expression of the 1<sup>st</sup> order perturbation energy due to the hyperfine interaction is as follows.

$$E = \frac{2}{3} \mu_0 g_e \beta_N g_N \beta_e \frac{1}{\alpha r_B} \frac{\hat{\mathbf{S}} \cdot \hat{\mathbf{I}}}{\hbar^2} \int_0^\infty g^\dagger(r_N) f(r_N) dr_N, \quad (1)$$

where  $g(r_N)$ ,  $f(r_N)$  are radial functions of large and small components.

By using Eq. (1) and the nonrelativistic formula of HFCC, we calculated the contribution of the relativistic effect to HFCC for Hydrogen like atom. FIG. 1 show the relativistic effect  $x$  (%), where  $x = 100(a_{\text{Rel}} - a_{\text{NR}})/a_{\text{NR}}$ .  $a_{\text{Rel}}$  and  $a_{\text{NR}}$  are the HFCC, which are obtained by using the solutions of Dirac and Schrödinger equation for Hydrogen-like atom, respectively. From FIG. 1, the values of  $x$  of 2s ~ 6s orbitals are clearly larger than 1s orbital. The reason for this is that Dirac's solution includes a term which contributes to only the relativistic contraction of the outer orbitals. The increase of the relativistic effect is accompanied by the penetration of the outer orbitals into the region of 1s orbital. This tendency can be observed in the HFCC of many-electron systems too, which will be discussed in my poster.

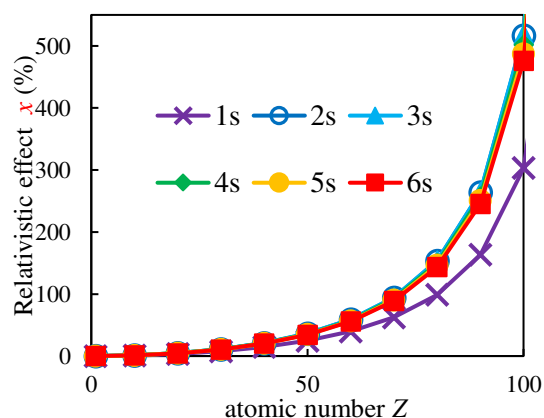


FIG. 1. Comparison of  $x$  for 1s ~ 6s orbitals for Hydrogen-like atom.

[1] R. Arratia-Perez and D. A. Case, *J. Chem. Phys.* **79**, 4939 (1983).

[2] E. Malkin, M. Repiský, S. Komorovský, P. Mach, O. L. Malkina, and V. G. Malkin, *J. Chem. Phys.* **134**, 044111 (2011).

## An Open-Source Framework for Analyzing $N$ -Electron Dynamics. Capabilities and Applications of DETCI@ORBKIT

Gunter Hermann<sup>1</sup>, Vincent Pohl<sup>1</sup>, Jean Christophe Tremblay<sup>1</sup>

<sup>1</sup>*Institut für Chemie und Biochemie, Freie Universität Berlin, Takustraße 3, Berlin 14195, Germany*

We present the capabilities of our recently published open-source framework DETCI@ORBKIT [1, 2] which is able to analyze and visualize correlated  $N$ -electron dynamics of molecular systems. In general, the program evaluates transition moments and expectations values of one-electron operators, e.g., the electron density or the electronic flux density, for explicitly time-dependent electronic wave packets that are represented as linear combinations of multi-determinantal wave functions. The wave functions are directly extracted from the output of standard Configuration-Interaction (CI) calculations at various levels of theory. Our procedure can be used to unravel the mechanistic features of a broad range of ultrafast charge migration processes in different molecular systems. To assess the robustness of the qualitative and quantitative statements concerning the dynamical details of a charge migration simulation, we investigated its convergence with respect to the electronic structure theory level and basis set size for a few benchmark systems.

Since CI calculations are not always feasible for extended systems, we extend our procedure to a non-variational hybrid method, where multi-determinantal eigenstates are obtained from linear-response time-dependent density functional theory (TDDFT). These build up a space of pseudo CI singles basis functions, which can be used to perform many-electron dynamics in strong laser fields. This combination of electronic structure methods also confers great scalability to the approach with respect to the system dimension. To validate this hybrid TDDFT/CIS scheme, we conduct a comparison of different CI methods for the laser-driven state selective excitation in a test system. The mechanistic features of the electron dynamics quantitatively coincide with the results from the higher-level electronic structure methods. In addition, the scalability of our scheme is demonstrated at the example of the broadband laser excitation in an moderate sized organic dye.

[1] V. Pohl, G. Hermann, J. C. Tremblay, *J. Comput. Chem.* **38**, 1515 (2017).

[2] G. Hermann, V. Pohl, J. C. Tremblay, *J. Comput. Chem.* **accepted**, (2017).

## Structural and spectroscopic investigation of acetyl cyanide: theory and experience

A. Bellili<sup>1\*</sup>, M. Hochlaf<sup>2</sup>, R. Linguerri<sup>2</sup>, M. Schwell<sup>3</sup>, L. Poisson<sup>4</sup>, C. Puzzarini<sup>5</sup>

<sup>1</sup> ENS de Lyon Laboratoire de Chimie UMR 5182, 46, allée d'Italie 69364 LYON, FRANCE

<sup>2</sup> Université Paris-Est, Laboratoire Modélisation et Simulation Multi Echelle, MSME UMR 8208 CNRS, 5 bd Descartes, 77454 Marne-la-Vallée, FRANCE.

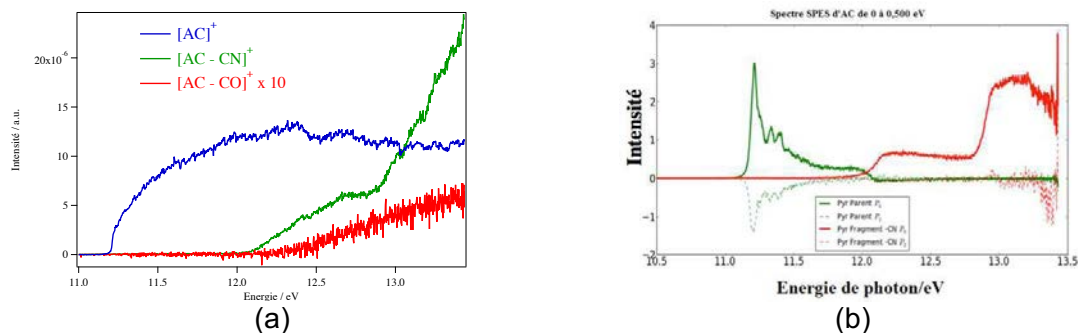
<sup>3</sup> Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR CNRS 7583, Université Paris Est Créteil and Université Paris Diderot, Institut Pierre Simon Laplace, 61 Avenue du Général de Gaulle, 94010 Créteil, FRANCE

<sup>4</sup> Laboratoire Francis Perrin, URA 2453, CEA, IRAMIS, SPAM, Laboratoire Interactions Dynamique et Lasers, F-91191 Gif-sur-Yvette, FRANCE.

<sup>5</sup> Dipartimento di Chimica "Giacomo Ciamician", Università di Bologna, Via F. Selmi, Bologna, ITALY.

In this combined theoretical and experimental work [1,2], we are interested in the photoionization, the spectroscopy and dynamics of acetyl cyanide molecule ( $\text{H}_3\text{CCOCN}$  denoted AC) cations and neutral [3]. The molecule is prebiotic and relevant for astrochemistry. It is one product of Strecker reaction [4], which is originally a realistic scenario for the formation of amino acids in interstellar medium (ISM).

We present the results of measurements performed in the synchrotron SOLEIL (DESIRS beamline) [5], where we measured the photoelectron photoion coincidence (PEPICO) spectra and the SPES spectra of acetyl cyanide. In-vacuum temperature-controlled oven was applied to promote the intact neutral species into the gas phase. The PIPICO and SPES spectra of AC are given below.



**Figure1:** (a) PIPICO (b) SPES spectra of acetyl cyanide obtained with 500 meV threshold electron resolution.

The SPES spectrum presents rich structures corresponding to the population of the vibrational levels of the cations in their ground and the electronic excited states. The assignment of these features was investigated with the help of state-of-the-art ab initio calculations. In addition, we explored the potential energy surface (PES) of acetyl cyanide and its cation using standard CCSD(T) and explicitly correlated CCSD(T)-F12 methods and more precise methods as CCSD(T)/CBS+CV. A set of specific spectroscopic parameters (vibration and rotation) was also calculated. The performed calculations included enolic tautomers which can be formed within the covered excitation energies and were studied in this work. This study allowed us to provide high resolution spectroscopic data which are essential for the interpretation of astrophysical observations.

[1] Bellili et al., The Journal of Chemical Physics 141, 134311 (2014)

[2] Bellili et al., The Journal of Chemical Physics 143, 184314 (2015)

[3] Danger et al., ApJ 535, A47, 1 (2011).

[4] Pouilly et al., Phys Chem Chem Phys. 12, 3566 (2010)

[5] <http://www.synchrotronsoleil.fr/portal/page/portal/Recherche/LignesLumiere/DESIRS>

\*The calculations were realized at Université Paris-Est Marne-La-Vallée, Laboratoire Modélisation et Simulation Multi Echelle, MSME UMR 8208 and Dipartimento di Chimica "Giacomo Ciamician", Università di Bologna.



## Exciton relaxation dynamics in photoexcited cycloparaphenylenes

Ljiljana Stojanović<sup>1</sup>, Felix Plasser<sup>2</sup>, Thomas Niehaus<sup>3</sup>, Rifaat Hilal<sup>4</sup>, and Mario Barbatti<sup>1</sup>

<sup>1</sup>Aix Marseille Univ, CNRS, ICR, Marseille, France ([ljiljana.stojanovic@univ-amu.fr](mailto:ljiljana.stojanovic@univ-amu.fr))

<sup>2</sup>Institute for Theoretical Chemistry, University of Vienna, Vienna, Austria

<sup>3</sup>Univ Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, Lyon, France

<sup>4</sup>Chemistry Department, Faculty of Science, KAU, Jeddah, Saudi Arabia

Cycloparaphenylenes (CPPs) are the shortest subunits of the single-walled armchair carbon nanotubes. In the last several years, they have received a significant attention due to potential applications in bottom-up synthesis of nanotubes. They have unusual photophysical properties, markedly distinct from linear paraphenylenes. For example, they are characterized by broad, featureless, size-independent absorption spectra, unusual size impact on photoluminescence spectra, and relaxation lifetimes in nanosecond time domain. We studied the 3-ps relaxation dynamics of [8]CPP and [10]CPP in the gas phase using surface hopping simulations based on the TD-DFTB potential energy surfaces. The properties of excitons occurring during dynamics are analyzed based on transition density matrices.

The relaxation dynamics of [8]CPP is featured by a series of delocalized charge-transfer excitons, whereas in the case of [10]CPP localized “self-trapping” excitons also occur. The localization of excitons is accompanied by significant dihedral angle distortions around sequences of rings on which they are localized. In the case of [8]CPP, significant ring strain prohibits formations of localized excitons.

The simulated emission spectra from the dynamics results confirm its experimentally found multi-peaked structures. We find that the relaxation from the  $S_1$  state, which is a dark state in the Frank-Condon region, becomes allowed due to symmetry breaking induced by electron-phonon couplings. The specific multi-peaked emission spectra arise from the relaxation processes from different local minima on the  $S_1$  surfaces.

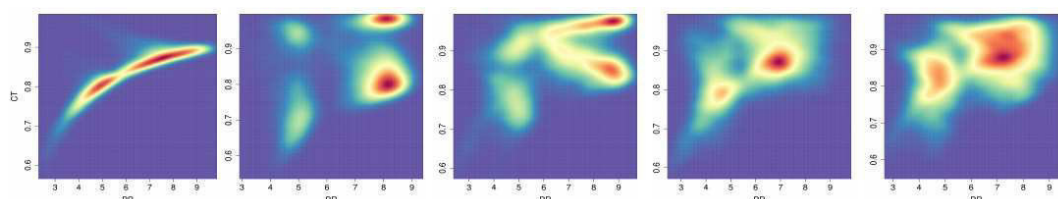


Figure 1. The correlation plots of participation ratio and charge transfer number distributions in different adiabatic states of [10]CPP.

## Water Adsorption On Gold Nanoparticles: A Theoretical Study

**Chen Hui CHAN<sup>1</sup>, Elise DUMONT<sup>1</sup>, David LOFFREDA<sup>1</sup>**

*<sup>1</sup>Laboratoire de Chimie, Ecole Normale Supérieure de Lyon and CNRS, 46 allée d'Italie,  
69364 Lyon Cedex 07, FRANCE.*

The applications of Gold Nanoparticles for enhancing hadrontherapy performance is very promising. This success have been demonstrated by highly active *in vivo* and *in vitro* experimental studies. High Z-AuNPs contribute to radiosensitization effect, making tumor cells more responsive to ionizing radiation. Upon water radiolysis, AuNPs generate secondary electrons and reactive oxygen species (ROS) which favor hadrontherapy by amplifying the damages and improving local dose enhancement.

In this work, we use theoretical approaches to study the mechanism of generation of ROS by AuNPs and provide atomic level insight into water/AuNPs interface. In particular, we aim at rationalizing the interaction of water molecule with AuNPs as a function of the size, and to determine the most stable positions of water on these nanoparticles. By using Density Functional Theory (DFT), we computed adsorption energies of single water molecule on AuNPs. To do so, we have considered metallic clusters having a truncated octahedron structure, with a diameter ranging from 0.9 to 3.3nm. The interaction energy of water on AuNPs has been decomposed into covalent and dispersive (Van der Waals forces) contributions. Our preliminary results show that the most competitive adsorption sites for water are top positions, essentially at the corners of the clusters. The adsorption strength of water progressively decreases inversely with respect to the nanoparticle size. The stability loss is significant since the adsorption energy is roughly reduced by a factor of two. This suggests weaker solvation effects at larger nanoparticle sizes.

Apart from this interesting DFT analysis, those interaction energies between water and AuNPs are key parameters for future theoretical developments related to radiochemistry in collaboration with colleagues from Institut de Physique Nucléaire in Lyon.

This project is funded by Labex PRIMES (ANR 11-LABX-0063, PhD fellowship awarded to C.H.Chan).

## Knockout driven reactions in porphyrin molecules and butadiene clusters

Giovanna D'Angelo<sup>1,2,3</sup>, Michael Gatchell<sup>1</sup>, Linda Giacomozzi<sup>1</sup>, Henrik Cederquist<sup>1</sup>, and Henning Zettergren<sup>1</sup>

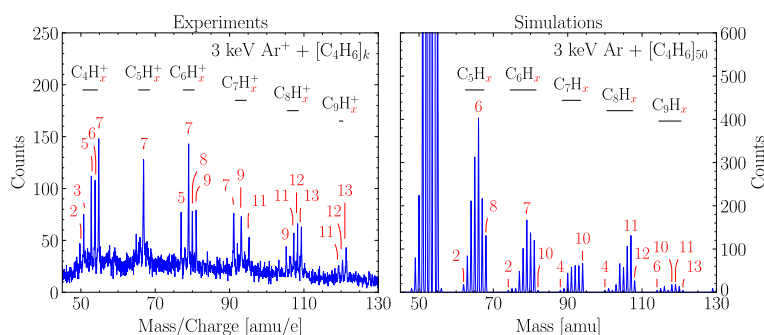
<sup>1</sup>Department of Physics, Stockholm University, Stockholm, SE-106 91, Sweden

<sup>2</sup>Faculdade de Ciências, Universidade do Porto, Porto, 4169-007, Portugal

<sup>3</sup>Departamento de Química, Universidad Autónoma de Madrid, Madrid, 28049, Spain

Recent studies on collisions between energetic ions/atoms and PAHs, fullerenes or their clusters have demonstrated the importance of prompt atom knockout in Rutherford-like scattering for molecular processing [1]. Such processes may lead to molecular growth, due to the formation of highly reactive fragments that very efficiently form new covalent bonds with surrounding molecules [1]. This type of energetic processing can be of importance for, e.g., the origin and evolution of complex molecules in space [2].

Here we present the modeling of keV-ion impact on butadiene clusters [3] and of collisions between tetraphenyl-porphyrin (TPP) ions and Ne or He atoms at 50-80 eV center-of-mass collision energies [4]. We have performed classical Molecular Dynamics simulations to model entire collision sequences, i.e. the initial knockout event and the subsequent fragmentation or molecular growth processes inside molecular clusters. Figure 1 shows a comparison between experimental and simulated mass spectra for collisions with butadiene clusters. The spectra clearly suggest the presence of molecular growth within the clusters and that this is driven by prompt carbon knockouts. We are currently investigating possible secondary fragmentation pathways, specific to collisions with atoms or ions, by means of density functional theory based methods.



**Fig.1** Experimental (left) and simulated (right) mass spectra for collision of  $C_4H_6$  cluster with  $Ar^+$ .

- [1] M. Gatchell and H. Zettergren, *J. Phys. B*, **59**, 162001 (2016).
- [2] A. G. G. M. Tielens, *Rev. Mod. Phys.* **85**, 1021-1081 (2013).
- [3] M. Gatchell et al., *Phys. Chem. Chem. Phys.* (in press) (2017).
- [4] L. Giacomozzi et al., *Phys. Chem. Chem. Phys.* (in press) (2017).

## QM/MM Studies of Reactive Intermediates in Solution: Diphenylcarbene in Solvent Mixtures

Pandian Sokkar<sup>1,2</sup>, Walter Thiel<sup>1</sup>, Elsa Sanchez-Garcia<sup>1,2</sup>

<sup>1</sup>Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany

<sup>2</sup>Universität Duisburg-Essen, 45117 Essen, Germany

**Abstract:** Carbene chemistry is a multifaceted research area by virtue of the highly spin-dependent reactivity of carbenes. In particular, the reactivity of diphenylcarbene ( $\text{Ph}_2\text{C}$ ) intrigues researchers owing to the variety of possible reaction pathways depending on whether the spin-configuration is either a singlet or a triplet state. Singlet carbenes are assumed to insert into O-H bonds, whereas triplet carbenes insert into C-H bonds. In this work, we investigate singlet  $\text{Ph}_2\text{C}$  reaction pathways in different solvent environments (acetonitrile, methanol, 2-butanol and the binary mixtures of acetonitrile and methanol), using QM/MM molecular dynamics simulations and optimizations. Our results indicate that H-bonding in protic solvents stabilizes the singlet over the triplet state of  $\text{Ph}_2\text{C}$  (Figure). We identify two mechanisms by which the singlet  $\text{Ph}_2\text{C}$  inserts into the O-H bond of alcohols in explicit solvent environment. Transient absorption spectroscopy studies further confirm our findings. [1]

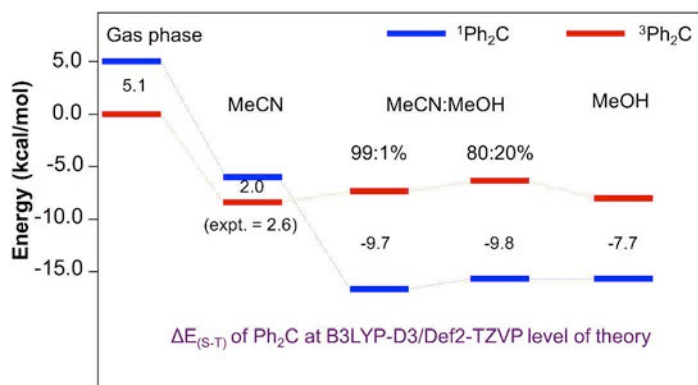


Figure. Relative energies of  $^1\text{Ph}_2\text{C}$  and  $^3\text{Ph}_2\text{C}$  in different solvent environments

[1] J. Knorr, P. Sokkar, S. Schott, P. Costa, W. Thiel, W. Sander, E. Sanchez-Garcia, P. Nuernberger, *Nat. Commun.* **7** (2016).

## Time-dependent extension of the long-range corrected density functional based tight-binding method

**J.J. Kranz<sup>1</sup>, V. Lutsker<sup>2</sup>, A. Dominguez<sup>3</sup>, B. Aradi<sup>4</sup>, T. Frauenheim<sup>4</sup>, M. Elstner<sup>1</sup>, T. A. Niehaus<sup>5</sup>**

<sup>1</sup>*Institute of Physical Chemistry, Karlsruhe Institute of Technology, Germany*

<sup>2</sup>*Department of Theoretical Physics, University of Regensburg, Germany*

<sup>3</sup>*Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany*

<sup>4</sup>*BCCMS, University of Bremen, Germany*

<sup>5</sup>*Institut Lumière Matière, Université de Lyon, France*

Although time-dependent density functional theory usually provides a good compromise between accuracy and computational performance for excited state properties, there are still many applications for which a further reduced computational cost is desirable. Such applications include, for example, quantum molecular dynamics simulation in excited states or calculations on large extended nano structures. The time-dependent density functional tight-binding[1] (TD-DFTB) semi-empirical method has been used successfully over years to tackle such problems. The conventional DFTB method is based on an approximation to DFT with an underlying GGA functional, and it thus inherits all shortcomings of such functionals. While a change of functional is straightforward in DFT, in DFTB it requires considerable alternations if the mathematical form deviates from that of a GGA functional.

Recently, a version of DFTB with a long-range corrected functional has been brought forward[2]. It is based on a tight-binding kind of approximation of the Hartree-Fock exchange integrals and a self-consistent determination of the one particle density matrix, rather than merely of atomic charges. We present a formulation and implementation of linear response TD-DFTB derived from this ground-state theory[3]. The resulting theory is similar in form to other recent empirical extension of TD-DFTB[4] to include HF exchange, but fully consistent, with HF exchange included in both ground state and the linear response calculation.

Results of benchmark calculations are presented to assess the performance of the method. It is shown that, as for full DFT, range separated functionals can solve problems, such as an incorrect description of excitations involving charge-transfer or spatially extended states.

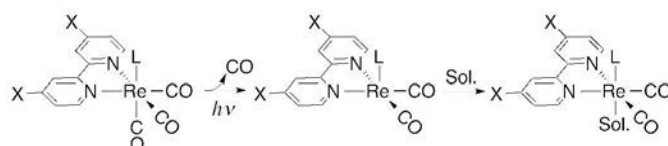
- [1] Niehaus T. A., Suhai S., Della Sala F., Lugli P., Elstner M., Seifert G. and Frauenheim T. *Phys. Rev. B*, 63(8), 085108 (2001).
- [2] Lutsker, V., Aradi B., and Niehaus T. A. *J. Chem. Phys.*, 143(18), 184107 (2015).
- [3] Kranz J. J., Elstner M., Aradi B., Frauenheim T., Lutsker V., Dominguez Garcia A. and Niehaus T. A. *J. Chem. Theory Comput.*, 13(4), 1737 (2017)
- [4] Humeniuk A. and Mitrić R. *J. Chem. Phys.*, 143(13), 134120 (2015).

## Mechanism of the photochemical ligand substitution of *fac*-[Re<sup>I</sup>(bpy)(CO)<sub>3</sub>(PR<sub>3</sub>)]<sup>+</sup> complex

Kenichiro Saita<sup>1</sup>, Satoshi Maeda<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Faculty of Science, Hokkaido University, Kita 10 Nishi 8, Kita-ku, Sapporo, 060-0810, Japan*

The mechanism of the CO ligand dissociation of *fac*-[Re<sup>I</sup>(bpy)(CO)<sub>3</sub>P(OMe)<sub>3</sub>]<sup>+</sup> has theoretically been investigated [1], as the dominant process of the photochemical ligand substitution (PLS) reactions of *fac*-[Re<sup>I</sup>(bpy)(CO)<sub>3</sub>PR<sub>3</sub>]<sup>+</sup>, by using the (TD-)DFT method. The PLS reactivity can be determined by the topology of the T<sub>1</sub> potential energy surface, since the photoexcited complex is able to decay into the T<sub>1</sub> state by internal conversions (through conical intersections) and intersystem crossings (via crossing seams) with sufficiently low energy barriers [2]. The T<sub>1</sub> state has a character of the metal-to-ligand charge-transfer (<sup>3</sup>MLCT) around the Franck-Condon region, and it changes to the metal-centered (<sup>3</sup>MC) state as the Re-CO bond is elongated and bent. The equatorial CO ligand has a much higher energy barrier to leave than that of the axial CO, so that the axial CO ligand selectively dissociates in the PLS reaction. The single-component artificial force induced reaction (SC-AFIR) search [3] reveals the CO dissociation pathway in photostable *fac*-[Re<sup>I</sup>(bpy)(CO)<sub>3</sub>Cl] as well, however, the dissociation barrier on the T<sub>1</sub> state is substantially higher than that in *fac*-[Re<sup>I</sup>(bpy)(CO)<sub>3</sub>PR<sub>3</sub>]<sup>+</sup> and the minimum-energy seams of crossings (MESXs) are located before and below the barrier. The MESXs have also been searched in *fac*-[Re<sup>I</sup>(bpy)(CO)<sub>3</sub>PR<sub>3</sub>]<sup>+</sup> and no MESXs were found before and below the barrier.



Scheme 1. Photochemical ligand substitution (PLS) reaction of *fac*-[Re<sup>I</sup>(bpy)(CO)<sub>3</sub>L]<sup>n+</sup>.

- [1] K. Saita, Y. Harabuchi, T. Taketsugu, O. Ishitani, S. Maeda, *Phys. Chem. Chem. Phys.* **18**, 17557 (2016).
- [2] Y. Harabuchi, J. Eng, E. Gindensperger, T. Taketsugu, S. Maeda, C. Daniel, *J. Chem. Theo. Comp.* **12**, 2335 (2016).
- [3] S. Maeda, Y. Harabuchi, M. Takagi, T. Taketsugu, K. Morokuma, *Chem. Rec.* **16**, 2232 (2016).

**Vibrational Density Matrix Renormalization Group****Alberto Baiardi<sup>1</sup>, Christopher J. Stein<sup>2</sup>, Vincenzo Barone<sup>1</sup>, Markus Reiher<sup>1</sup>**<sup>1</sup>*Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy*<sup>2</sup>*ETH Zürich, Laboratorium für Physikalische Chemie, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland*

Variational approaches for the calculation of vibrational wave functions and energies are a natural route to obtain highly accurate results with controllable errors. However, the unfavorable scaling and the resulting high computational cost of standard variational approaches limit their application to relatively small molecules. Here, we demonstrate how the density matrix renormalization group (DMRG) can be exploited to optimize vibrational wave functions (vDMRG)[1] expressed as matrix product states. We study the convergence of these calculations with respect to the size of the local basis of each mode, the number of renormalized block states, and the number of DMRG sweeps required. We demonstrate the high accuracy achieved by vDMRG for small molecules that were intensively studied in the literature. We then proceed to show that the complete fingerprint region of the sarcosyn-glycin dipeptide can be calculated with vDMRG.

- [1] A. Baiardi, C.J. Stein, V. Barone, M. Reiher, arXiv:1703.09313 [physics.chem-ph] (2017).

## Molecular Response to Strong Magnetic Fields: Excitation Energies and Anapole Moments

Sangita Sen<sup>1</sup>, Erik Tellgren<sup>1</sup>

<sup>1</sup>*Centre for Theoretical and Computational Chemistry/University of Oslo, Sem Sælands vei 26, 0371 Oslo, Norway*

The response of a molecule to weak external magnetic fields is well characterized by the perturbative definition of its magnetic moments, susceptibilities, etc. In the regime of strong magnetic fields, of the order of  $10^5\text{T}$ , the Coulombic and magnetic interactions become competitive and neither can be considered a perturbation on the other. Rare early studies include those on He and Li atoms[1, 2] but molecules remain largely unexplored. Such situations are often encountered under astrophysical conditions such as in highly magnetised white-dwarfs and neutron stars. The spectroscopic signatures of atoms and molecules under such extreme conditions is important to astrophysicists for studying these celestial bodies. In this work, we investigate the modulation of molecular excitation energies by external magnetic fields of this order of magnitude. The excitation energies are computed by linear response using the Random Phase Approximation on a mean field wave-function optimized in the presence of a finite magnetic field. Moreover, while electric and magnetic moments and susceptibilities are commonly computed and measured, moments which couple to the curl of the magnetic field, have been largely neglected ever since they were first considered by Zel'dovich[3] and named “anapoles”. They are distinct from the usual magnetic moments arising out of a perturbative expansion in the magnetic field and can be visualised instead as arising from a toroidal dipole[4, 5]. We have studied the orbital and spin effects on the anapole susceptibilities of molecules at the SCF level. The RHF theory is used to investigate the orbital effects[6] while the 2-component General Hartree-Fock (GHF) theory is used to study the spin and orbital effects in conjunction. We believe that a thorough study of the microscopic interactions affecting the anapole susceptibilities will throw significant light on the quantum mechanism of intramolecular interactions involving toroidal molecular structures in nature.

- [1] Becken, W., Schmelcher, P. and Diakonov, F. K., *J. Phys. B* **32**, 1557 (1999).
- [2] Al-Hujaj, O.-A. and Schmelcher, P., *Phys. Rev. A* **70**, 33411 (2004).
- [3] Zel'dovich, I. B., *J. Exptl. Theor. Phys.* **33**, 1531 (1957).
- [4] Lazzeretti, P., *Theor. Chim. Acta* **87**, 59 (1993).
- [5] Faglioni, F., Ligabue, A., Pelloni, S., Soncini, A. and Lazzeretti, P., *Chem. Phys.* **304**, 289 (2004).
- [6] Tellgren, E. I. and Fliegl, H., *J. Chem. Phys.* **139**, 164118 (2013).

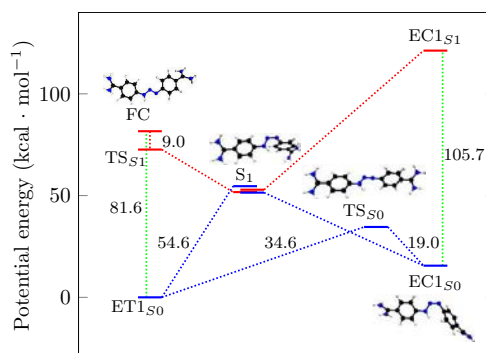


## QM/MM Polarizable Embedded RI-CC2 analytical gradients: Deexcitation Pathways of a Triazene Compound in Complex Environments

Alireza Marefat Khah<sup>1</sup>, Christof Hättig<sup>1</sup>

<sup>1</sup>*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Universitätsstraße 150, D-44801 Bochum, Germany*

Berenil (diminazene aceturate) is a DNA minor groove binder with an extremely low fluorescence quantum yield. We have studied the electronic excited state pathways of berenil using the *ab initio* ADC(2) method in combination with Conductor-like screening model (COSMO) in order to include the solvent effect within the continuum approximation. With analyzing the Natural Transition Orbitals (NTOs) and the Intrinsic Reaction Coordinate (IRC) paths, a bicycle-pedal type deexcitation mechanism and a conical intersection between ground and the S1 excited states could be identified [1]. Furthermore, the QM/MM Polarizable-Embedding which parti-



tions the molecular environment to polarizable point multipoles has been combined with the HF, the TDDFT [2] and the Coupled Cluster theory [3]. Within an ongoing project, the PERI-CC2 implementation of excitation energy is extended for molecular gradients for ground and excited states. The latter development would make it possible for us to study the excited state relaxation of berenil when it binds to DNA and/or proteins and would help us to understand the solvent role on the deexcitations with atomistic resolution.

[1] L. Grimmelsmann, et. al. J. Phys. Chem. Lett., 2017, 8, 1986.

[2] J. M. Olsen, et. al.; J. Chem. Theory Comput., 2010, 6, 3721.

[3] K. Sneskov, et. al.; J. Chem. Phys., 2011, 134, 104108.

**On-the-fly *ab initio* semiclassical dynamics of floppy molecules:  
Resonance Raman spectra of ammonia**

**Sébastien Reynaud<sup>1</sup>, Sergey V. Antipov<sup>1</sup>, Jiří Vaníček<sup>1</sup>**

*<sup>1</sup>Laboratory of Theoretical Physical Chemistry, Institut des Sciences et Ingénierie  
Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015, Lausanne,  
Switzerland*

We investigate the performance of on-the-fly *ab initio* dynamics combined with the thawed Gaussian approximation for computing vibrationally resolved resonance Raman spectra and excitation profiles of ammonia [1]. The employed approach does not require any a priori knowledge of the potential energy surface and, contrary to the popular global harmonic approximations, can account for the anharmonicity of the potential. Ammonia is chosen as a well-known example of a floppy molecule, which exhibits a large amplitude motion. Comparing the results with the experiment [2], we show that despite the strong anharmonicity of the potential, the on-the-fly *ab initio* thawed Gaussian approximation captures the main features of the resonance Raman spectrum. Moreover, within the employed approach the intensities of the combination bands are in a better agreement with experimental ones than those based on the global harmonic approximation [3].

[1] S. Reynaud, S. V. Antipov, and J. Vaníček, *In preparation*.

[2] L. D. Ziegler and B. Hudson, *J. Phys. Chem.* **88**, 1110-1116 (1984).

[3] D. W. Silverstein and L. Jensen, *J. Chem. Phys.* **136**, 064110 (2012).

## **A Novel Correlation between the Activity of *Candida antarctica* Lipase B and Differences in Binding Free Energies of Organic Solvent and Substrate**

**S. D. Banik<sup>1</sup>, M. Nordblad<sup>2</sup>, J. M. Woodley<sup>2</sup>, G. H. Peters<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, Technical University of Denmark*

<sup>2</sup>*Department of Chemical and Biochemical Engineering, Technical University of Denmark*

The ability of enzymes to operate in organic solvent is now widely accepted. The selection of solvent medium is challenging which allows the modulation of enzyme activity. For rational selection of organic medium, it is important to understand the effect of organic solvent molecules on enzyme structure and the enzymatic reaction on a molecular level. To gain such insight, we combined experimental kinetics studies with full atomic molecular dynamics simulations and found a novel correlation between the activity of *Candida antarctica* lipase B (CALB) and the binding of the solvent/substrate molecules in the active site region of CALB. We have investigated the influence of four organic solvents hexane (HEX), methyl tertiary butyl ether (MTBE), acetonitrile (ACN) and tertiary butanol (TBU) on the catalytic activity of CALB for the esterification reaction. Our study shows that these organic solvents do not alter the conformation of CALB. Rather the solvent effects ascribed by binding of solvent molecules to the enzyme active site region and the solvation energy of substrate molecules in the different solvents. Polar solvent molecules compete with the substrate to bind to the active site of region CALB resulting in an inhibitory effect which is also confirmed by the binding free energies for the solvent and substrate molecules estimated from the simulations. Consequently, the catalytic activity of CALB decreases in polar solvents. This effect is significant, and CALB is over 10 orders of magnitude more active in nonpolar solvents (HEX and MTBE) than in the polar solvents (ACN and TBU). TBU molecules show an exceptional behavior since the solvent molecule forms an extensive hydrogen bond network within the CALB active site suggesting that solvent molecules rich on hydrogen acceptors and donors are poor solvents when used for lipase-catalyzed esterification reactions.

[1] Q. Wu, P. Soni, M. T. Reetz, *J. Am. Chem. Soc.* 135, 1872 (2013).

[2] P. Adlercreutz, *Chem. Soc. Rev.* 42, 6406 (2013).

[3] S. Dutta Banik, M. Nordblad<sup>2</sup>, J. M. Woodley<sup>2</sup>, G. H. Peters, *ACS Catalysis*. 6, 6350 (2016).

## The Independent Gradient Model: a tool derived from the NCI approach to analyze molecular interactions.

C. Lefebvre<sup>1</sup>, G. Rubez<sup>1,2,3</sup>, H. Khartabil<sup>1</sup>, J-C. Boisson<sup>2</sup>, J. Contreras-García<sup>4,5</sup>, E. Hénon<sup>1</sup>

<sup>1</sup>ICMR UMR CNRS 7312, URCA, Moulin de la Housse, Reims, France

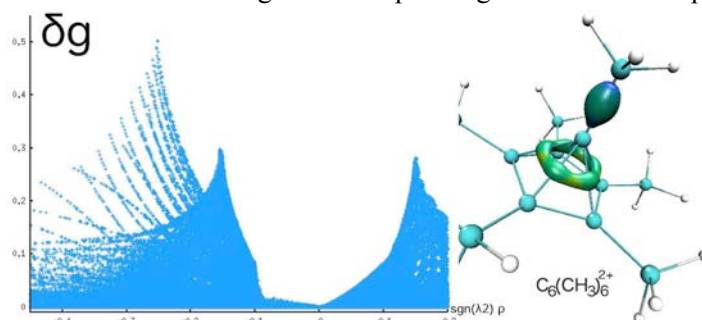
<sup>2</sup>CreSTIC EA 3804, URCA, Moulin de la Housse, Reims, France

<sup>3</sup>ATOS/BULL company, 1 rue de Provence, Echirolles, France

<sup>4</sup>Sorbonnes Universités, UPMC Univ. Paris 06, UMR CNRS 7616, Laboratoire de Chimie Théorique, Paris, France

<sup>5</sup>CNRS UMR 7616 Laboratoire de Chimie Théorique, Paris, France

An electron density (ED)-based methodology has been developed for the identification and visualization of molecular interactions using either pro-molecular density or ED derived from a single-determinant wave function. The expression of the ED gradient in terms of atomic components furnishes the basis for the Independent Gradient Model (IGM). This model leads to a density reference for non interacting atoms/fragments where the real density is preserved whilst ED gradient interaction turns off. Founded on this ED reference function that features an exponential decay also in interference regions, IGM model provides a way to identify and quantify the net ED gradient attenuation due to interactions. A new descriptor  $\delta g$  is derived to extract the signature of interactions present in an NCI plot, the parent NCI methodology developed by W. Yang *et al.* in 2010 [1]. Using an intra/inter uncoupling scheme, a descriptor ( $\delta g^{inter}$ ) is proposed that uniquely defines interfragment interaction regions. Then, an attractive feature of the IGM methodology [2] is to provide a workflow that automatically generates data composed solely of interfragment interactions for drawing the corresponding 3D isosurface representations.



[1] E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen and W. Yang, *J. Am. Chem. Soc.* **132**, 6498 (2010).

[2] C. Lefebvre, G. Rubez, H. Khartabil, J-C. Boisson, J. Contreras-García and E. Hénon, *PCCP*, submitted

## Replica-Exchange Enveloping Distribution Sampling (RE-EDS): Parallel Energy-Offset Estimation and Efficient Local Round-Trip Time Optimisation

Dominik Sidler<sup>1</sup>, Arthur Schwaninger<sup>1</sup>, Michael Cristofol-Clough<sup>1</sup>, Sereina Riniker<sup>1</sup>

<sup>1</sup>Laboratory of Physical Chemistry, ETH Zurich, Vladimir-Prelog-Weg 2, 8093 Zurich, Switzerland

Replica-exchange enveloping distribution sampling (RE-EDS) allows the efficient estimation of free-energy differences between multiple end-states from one molecular dynamics (MD) simulation [1]. In EDS, a reference state is sampled, which can be modified by two kinds of parameters, i.e. smoothness parameter and energy offsets, such that all end-states are sufficiently sampled [2]. It can be shown in practise that the choice of the energy offsets can be decoupled from the smoothing parameter distribution problem [3]. As a result, the development of a parallel energy-offset estimation (PEOE) algorithm became possible, which allows the highly efficient determination of the energy offsets [3]. In order to address the smoothness parameter distribution problem, a local round-trip time optimisation (N-LRTO) algorithm is introduced [4]. It is specially designed to deal with highly complex potential energy surfaces. This situation typically occurs for challenging real world applications, e.g. the slowly adapting environment in a protein pocket. Applying PEOE and N-LRTO to a RE-EDS system consisting of nine small-molecule inhibitors, in a complex with phenylethanolamine N-methyltransferase (PNMT), allows the accurate calculation of 36 free-energy differences in parallel [4].

- [1] J. Lee, B. T. Miller, A. Damjanovic, B. R. Brooks, *J. Chem. Theory Comput.* **10**, 2738-2750 (2014).
- [2] C. D. Christ, W. F. van Gunsteren, *J. Chem. Phys.* **126**, 184110 (2007).
- [3] D. Sidler, A. Schwaninger, S. Riniker, *J. Chem. Phys.* **145**, 154114 (2016).
- [4] D. Sidler, M. C. Clough, S. Riniker, *J. Chem. Theory Comput.* (online) DOI: 10.1021/acs.jctc.7b0028 (2017).

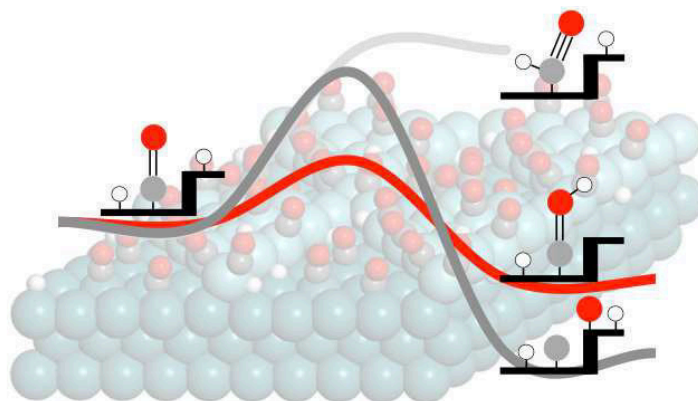
## Carbon Monoxide Activation on Ru Surfaces under Reaction Conditions from *Ab Initio* Molecular Dynamics Simulations

Lucas Foppa<sup>1</sup>, Marcella Iannuzzi<sup>2</sup>, Christophe Copéret<sup>1</sup> and Aleix Comas-Vives<sup>1</sup>

<sup>1</sup>Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir Prelog Weg 1, CH-8093 Zürich, Switzerland.

<sup>2</sup>Institute of Physical Chemistry, University of Zurich, Winterthurerstrasse 190 CH-8057 Zurich, Switzerland.

The first elementary step of Fischer-Tropsch Synthesis (FTS), the conversion of syngas (CO/H<sub>2</sub> mixture) to hydrocarbons used in the gas-to-liquid chain, consists in the activation of carbon monoxide triple bond on CO-covered surfaces of metallic catalysts (Ru, Co, Fe) [1,2]. Since FTS activity and selectivity depend on CO cleavage, the elucidation of reaction mechanisms and active sites for this transformation has been an active research topic in computational chemistry, with static DFT approaches playing a central role [1-4]. Nevertheless, it remains challenging to evaluate multiple reaction pathways simultaneously while capturing co-adsorbate interactions and entropic effects at reaction temperatures (> 300°C), acknowledged to affect the choice of activation mechanism [3,4]. Herein, we use an *ab initio* molecular dynamics (AIMD) approach to study the direct and hydrogen-assisted CO activation on Ru surface models representing flat and stepped terminations of metal catalysts. Our results point out to the previously unrecognized role of step-edges in hydrogen-assisted mechanisms and illustrate how AIMD can be used to study complex surface reaction networks.



- [1] L. Foppa, C. Copéret, A. Comas-Vives, J. Am. Chem. Soc. **138**, 16655 (2016). [2] B. T. Loveless, C. Buda, M. Neurock, E. Iglesia, J. Am. Chem. Soc. **135**, 6107 (2013). [3] G. T. K. Gunasooriya, A. P. van Bavel, H. P. C. E. Kuipers, M. Saeys, ACS Catal. **6**, 3660 (2016). [4] S. Liu, Y.-W. Li, J. Wang, H. Jiao, Catal. Sci. Technol. **6**, 8336 (2016).

## Refined approach to the cellularization of the semiclassical Herman-Kluk propagator

Sergey V. Antipov<sup>1</sup>, Jiří Vaníček<sup>1</sup>

<sup>1</sup>*Laboratory of Theoretical Physical Chemistry, Institut des Sciences et Ingénierie  
Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015, Lausanne,  
Switzerland*

The semiclassical Herman-Kluk Initial Value Representation (HK-IVR) is a well-established approximation to the quantum evolution operator. The approximation is based on classical trajectories and incorporates quantum effects, such as tunneling, coherence, and zero-point energy, into the dynamics. However, the direct application of the HK-IVR approach to large scale systems is computationally unfeasible due to the oscillatory nature of the integrand involved. A common way of dealing with this problem is based on application of the Filinov filtering (cellularization) [1, 2] technique to smooth out the oscillatory behavior of the integrand.

Here we present a refined cellularization scheme for the HK-IVR propagator [3], which employs the inverse Weierstrass transform and optimal scaling of the cell size with the number of cells, and was previously only used in the context of the dephasing representation [4]. In the new methodology the size of the sampling weight for the cell centers correlates with the size of cells, allowing for effective sampling of the phase space covered by the initial state of the system. The main advantage of the presented approach is that, unlike the standard Filinov filtering, it converges to the original HK-IVR result in the limit of an infinite number of trajectories. We illustrate the performance of the refined cellularization scheme by calculating autocorrelation functions and spectra of both integrable and chaotic model systems.

[1] N. Makri and W. H. Miller, *J. Chem. Phys.* **89**, 2170-2177 (1988).

[2] E. J. Heller, *J. Chem. Phys.* **94**, 2723-2729 (1991).

[3] S. V. Antipov and J. Vaníček, *In preparation*.

[4] E. Zambrano, M. Šulc, and J. Vaníček, *J. Chem. Phys.* **139**, 054109 (2013).

## Local control theory with an approximate treatment of the molecule-field interaction

**Julien Roulet<sup>1</sup>, Jiří Vaníček<sup>1</sup>**

*<sup>1</sup>Laboratory of Theoretical Physical Chemistry, Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015, Lausanne, Switzerland*

The advance of pulse shaping technology has opened the field of laser control of chemical reactions. The local control theory [1] belongs among the most efficient approaches to control since this technique does not require an iterative procedure. Instead, the control field is computed on the fly, using the instantaneous dynamics of the system, and guarantees an increase (or decrease) of a target observable that commutes with the system Hamiltonian. In our case, this observable is the population of a selected electronic state.

Recently, Patoz and Vaníček have implemented [2] geometric integrators of arbitrary order of accuracy for treating the nonadiabatic quantum dynamics of a molecule interacting with a time-dependent electromagnetic field. In particular, this suite of algorithms allows both an exact treatment of the interaction as well as an arbitrary combination of the time-dependent perturbation theory, Condon, rotating wave, and ultrashort pulse approximation.

Here we present an implementation of the local control theory using the above four approximations for the molecule-field interaction, since the exact treatment of the interaction with the electromagnetic-field can be computationally expensive. We investigate the validity of these approximations to the local control on several model systems, and analyze the influence of the approximations on the dynamics of the studied systems as well as on the computational cost of the local control simulation.

[1] V. Engel, C. Meier, and D. J. Tannor, *Adv. Chem. Phys.* **141**, 29 (2009)

[2] A. Patoz and J. Vaníček, in preparation.



## Probing the orientation of recombinant protein A on a membrane using computational infrared spectroscopy.

**Ana V. Cunha<sup>1</sup>, Thomas L.C. Jansen<sup>1</sup>**

<sup>1</sup>*Zernike Institute for Advanced Materials, University of Groningen  
Nijenborgh 4, 9747 AG, Groningen, The Netherlands*

Homologous recombination is the primary mediator mechanism in DNA repair and thus essential for the survival of cells. Recombinant proteins (RecA) are the molecular motors involved in this process, intervening in numerous processes in eukaryotic cells. However, *in vitro* experiments show that RecA may become inactive when interacting with phospholipids [1]. Our goal is to make use of computational spectroscopy techniques to probe the orientation of such protein (RecA, see Fig. 1(a) and 1(b)) on a membrane. The infrared spectra in the amide I region are calculated by combining classical molecular dynamics simulations with quantum mechanical response function calculations [2-3]. In this study, we examine recombinant protein A (RecA) oriented in two directions [1], one parallel to the membrane (active, Fig. 1(a)), and another perpendicular to the membrane (inactive, Fig. 1(b)). The theoretical linear spectra show that the parallel oriented protein is slightly redshifted compared to the perpendicularly oriented one, see Fig. 1(c). This difference arises as a consequence of the interaction between the protein and the phospholipid membrane, potentially enabling the experimental distinction between the active and inactive configurations.

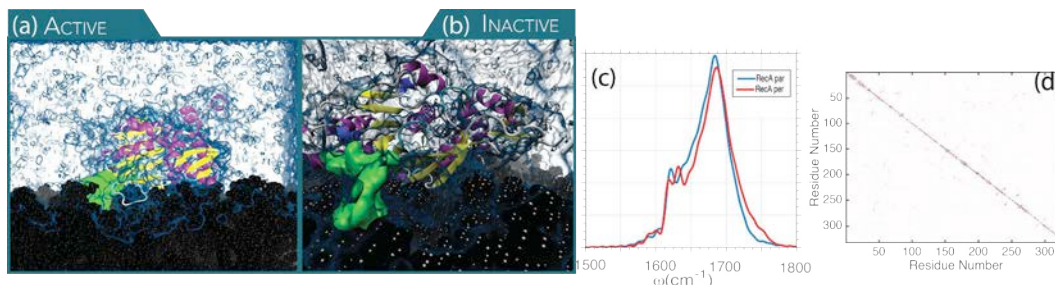


Fig. 1. (a) RecA protein with parallel orientation to the membrane. (b) RecA protein with perpendicular orientation to the membrane. (c) Predicted linear infrared spectra of RecA in both orientations. (d) Map of the difference energies of the vibrational Hamiltonian.

- [1] M. Rajendram, *et. al.*, *Mol. Cell.*, **60**,374–384 (2105).
- [2] C. Liang, T.L.C. Jansen, *J. Chem. Theo. Comp.*, **8**, 1706 (2012).
- [3] T.L.C. Jansen, J. Knoester, *J. Chem. Phys.*, **124**, 044502 (2006).

## Color-tuning mechanism in vision from a theoretical perspective

**B.B. Kamorzin, A.V. Scherbinin, A.V. Bochenkova**

*Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Russia*

A single chromophore, retinal in the protonated Schiff base form (PSBR), is responsible for absorption of light of different wavelength in visual Opsin proteins. Currently, the wavelength-tuning mechanism and the color span of the individual photoreceptors are far from being understood. This is largely due to the fact that the intrinsic photophysical properties of the bare chromophore, *i.e.*, its ‘color’ and photoabsorption spectral shape, remain to be resolved and the important reference for the so-called Opsin shift is still missing. Here, we aim at correlating a remarkably broad absorption profile of the isolated PSBR chromophore (450–650 nm) found experimentally [1] with a wide range of absorption energies observed in visual (425–560 nm) and archaeal (480–590 nm) Rhodopsins, as well as at providing a benchmark value for the most intense vibronic transition in the isolated chromophore that will help to understand the origin of the protein “Opsin” shift.

A highly accurate multiconfiguration quasi-degenerate perturbation theory, XMCQDPT2 [2], has been used for constructing a geometry-relaxed adiabatic potential that hinders intra-molecular internal rotation of the  $\beta$ -ionone ring of the isolated PSBR chromophore. The  $S_0$ - $S_1$  photoabsorption profile has been calculated by explicitly taking into account large-amplitude, highly anharmonic ground-state nuclear motion of the  $\beta$ -ionone ring. A rather flat topography of the ground-state potential energy surface along this soft mode is shown to be responsible for substantial non-equilibrium contributions to the gas-phase spectrum, which is found to be very sensitive to temperature variations. Our results potentially lead to a disclosure of one of the wavelength-tuning mechanisms operational in color vision.

This work has been supported by the Russian Science Foundation (project no. 17-13-01276). We thank the Supercomputing Center of the M.V. Lomonosov Moscow State University for providing high performance computing resources.

[1] Rajput, J., Rahbek, D. B., Andersen, L.H., Hirshfeld, A., Sheves, M., Altoè, P., Orlandi, G., and Garavelli, M., *Angew. Chem., Int. Ed.* **49**, 1790 (2010).

[2] Granovsky, A. A., *J. Chem. Phys.* **134**, 214113 (2011).

## **Accurate prediction of protein-ligand binding using molecular dynamics-based docking and QM/MM methods**

**Manuel Glaser, Okke Melse, Chen Zheng, Antoine Marion, and Iris Antes**

*Department of Life Sciences and Center for Integrated Protein Science, Technical University of Munich, Emil-Erlenmeyer-Forum 8, 85354 Freising*

Protein-ligand interactions are crucial for many important biological processes and thus the selective inhibition of disease relevant proteins is one of the major strategies for drug design in pharmaceutical industry. In this context computer-based methods are routinely used to screen large compound libraries for the identification of potential drug candidates. Thus many sampling and scoring methods have been developed for this purpose over the last two decades, which perform very well for „classical“ drug design applications, namely predicting the binding of non-covalently bound small molecule-based ligands to specific target proteins [1, 2]. Nevertheless, these approaches experience considerable limitations for the prediction of covalently bound inhibitors, ligands binding to metal containing binding sites, and very flexible ligands like peptides or macrocycles. In addition, the calculation of quantitatively accurate ligand binding affinities is still a challenge in the field. We are developing new and optimizing existing approaches for these areas of applications [3-7]. Thereby our focus is on the improvement of classical molecular docking approaches by the use of biophysical sampling methods and QM/MM approaches. We will present several case studies, which show how the accuracy of protein-ligand binding predictions can be improved considerably by the new, combined approaches for e.g. covalently bound inhibitors or metal-containing binding sites.

### **References:**

- [1] S.M. Song, S.J. Lim, J.C. Tong, *Brief. Bioinform.* **10**(5), 579 (2009)
- [2] X. Huang, S.Z. Grinter, X. Zou, *Phys. Chem. Chem. Phys.* **12**(40), 12899 (2012).
- [3] C. Hartmann, I. Antes, T. Lengauer, *Proteins* **74**(3), 712 (2009).
- [4] I. Antes, I., *Proteins* **78**(5), 1084 (2010).
- [5] M. Marcinowski, M., M. Rosam, M., C. Seitz, J. Elferich, J. Behnke, C. Bello, M.J. Feige, C.F. Becker, I. Antes, I., J. Buchner, *J. Mol. Biol.* **425**(3), 466 (2013).
- [6] M. Zachmann, G. Mathias, I. Antes, *ChemPhysChem* **16**(8), 1739 (2015).
- [7] M. Schneider, M. Rosam, M. Glaser, A. Patronov, H. Shah, K.C. Back, M.A. Daake, J. Buchner, I. Antes, *Proteins* **84**(10), 1390 (2016).

## **Symmetric Proton Transfer Routes in the Membrane Domain of Respiratory Complex I.**

**Andrea Di Luca, Ana P. Gamiz-Hernandez, Ville R. I. Kaila**

*Department of Chemistry, Technical University of Munich, Lichtenbergstr. 4, Garching, Germany*

Complex I (NADH:quinone oxidoreductase) of the respiratory chain has a fundamental role in the energy conversion of living organisms, contributing to the generation of the proton motive force across membranes. By using the energy from quinone reduction, it catalyses the pumping of four protons. Recently resolved structure from different organisms revealed new details of the enzyme structure, but access points of protons and mechanism of pumping are still elusive. Structural features of the membrane domain, as the long horizontal axis of charged residues or internal symmetry of the antiporter-like subunits, are likely to play a role in the proton transfer (pT) process. We perform large-scale classical MD simulation of transient putative states of the enzyme to identify proton transfer routes in the antiporter-like subunit of complex I, and suggest a possible mechanism of pumping [1]. Steps of the proposed mechanism are investigated with MD replica-exchange umbrella sampling (REUS), QM/MM dynamics and continuum electrostatic calculation for one antiporter-like subunit. Our results suggest that the position of the proton channels are similar for the three antiporter-like subunits and symmetry-related, accordingly to the internal symmetry of the subunits. We also show how a conserved Lys-Glu pair in each antiporter-like subunit forms a key element in the proton pumping mechanism.

- [1] A. Di Luca, A. P. Gamiz-Hernandez, V. R. I. Kaila, *PNAS* (submitted)

**Aggregates of quadrupolar dyes: the role of intermolecular interactions.****O. Uranga, D. Casanova\*, F. Castet\***

*<sup>1</sup>Department of Science and Technology of Polymers/ Facultad de Química/ University of  
the Basque Country (UPV/EHU)  
Paseo Manuel Lardizabal 4, 20009, Donostia, Spain*

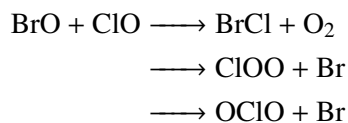
Recently, it has been shown that supramolecular aggregates provide a wide range of photophysical properties such as aggregation-induced fluorescence or phosphorescence, which can be optimized for use in a large number of applications: optoelectronics, detection of biochemical process, imaging, lightening or photovoltaic energy conversion. Optimizing these properties in view of designing devices with increased performances requires a fundamental understanding of properties of the isolated molecules together with a detailed characterization of intermolecular interactions. We present a theoretical investigation of small aggregates of quadrupolar (D- $\pi$ -A- $\pi$ -D) charge-transfer dyes, with attention focused on the role of intermolecular interactions in determining their optical properties. We tackle the theoretical issue by adopting a localized diabatic model, which describe an isolated molecule in terms of a minimal number of electronic states. The approach is applied to curcuminoid dyes, a family of chromophores with weak quadrupolar character. The method is validated against experiment. Time dependent density theory rationalize the strong ultra-excitonic effects recurrently observed in the experimental optical spectra of aggregates of highly polarizable quadrupolar dyes, offering a valuable tool to exploit the supramolecular design of material properties.

## Theoretical Study of the BrO + ClO Cross Reaction

**Adam S. Abbott, Kevin B. Moore III, Henry F. Schaefer III**

*Center for Computational Quantum Chemistry, 1004 Cedar St., University of Georgia, Street  
Address, Athens, GA, USA*

Pathways stemming from the reaction of BrO and ClO radicals are of great interest due to their integral role in stratospheric ozone depletion. An abundance of free halogen radicals, which readily convert ozone to diatomic oxygen, are produced through three pathways:



Detailed mechanisms of the above reactions have hitherto been insufficiently characterized in the literature. In this work, optimized geometries and harmonic vibrational frequencies for key stationary points on the potential energy surface have been obtained with high level coupled cluster theory. In the future, these findings will be used to reduce the current uncertainty in regard to the rate constants and branching ratios through theoretical kinetic treatments.

## Structural Distortions Accompanying Non-Covalent Interactions

Herzain I. Rivera-Arrieta<sup>1,2</sup>, Justin M. Turney<sup>2</sup> and Henry F. Schaefer III<sup>2</sup>

<sup>1</sup>*Instituto de Física, Universidad Nacional Autónoma de México, Ciudad de México 04510, México*

<sup>2</sup>*Center for Computational Quantum Chemistry, Department of Chemistry, The University of Georgia, Athens, Georgia 30602-2556, U.S.A.*

Non-covalent interactions can be seen as one of the most important forces in nature, as they domain many fundamental phenomena in chemistry and biology. The nature of these weak forces makes difficult to study them for both, theoretically and experimentally [1]. Neglect of the structural distortions suffered by the constituent molecules, as a result from these weak interactions, is a common practice when examining a potential energy surface (PES).

The methane-water complex, which can be seen as the simplest hydrophobic interaction, is a remarkable model system that has been widely studied [2-4]. Unfortunately, none of these studies had quantified the magnitude of the intramolecular distortions for each molecule, nor the energy associate with them.

Herein, in order to obtain the definite answer about the magnitude of the distortions and their energetic effects, focal point analyses (FPAs), which already have shown to be able to achieve subchemical accuracy [5], were performed on the minima structures of the PES. For the FPAs calculations, coupled cluster methods up to perturbative quadruples [CCSDT(Q)] level of theory were considered.

Our results indicate that the difference in the interaction energies ( $\Delta D_e$ ) between fully optimized and monomer fixed structures, always lies in the order of 0.02 kcal mol<sup>-1</sup> [6]. This study showed beyond any reasonable doubt, that neglect of the monomer relaxation while scanning a weakly bound noncovalent system, is a reasonable approximation for points other than the minima.

- [1] K. Müller-Dethlefs, P. Hobza, *Chem. Rev.* **100**, 143 (2000).
- [2] K. Patkowski, *J. Chem. Phys.* **138**, 154101 (2013).
- [3] C. Qu, R. Conte, P. L. Houston, J. M Bowman, *Phys. Chem. Chem. Phys.* **17**, 8172 (2015).
- [4] D. Cappelletti, A. Bartocci, F. Frati, L. F. Roncatti, L. Belpassi, F. Tarantelli, P. Aiswarya, E. Arunan, F. Pirani, *Phys. Chem. Chem. Phys.* **17**, 30613 (2015).
- [5] M. S. Schuurman, S. R. Muir, W. D. Allen, H. F. Schaefer, *J. Chem. Phys.* **120**, 11586 (2004).
- [6] H.I. Rivera-Arrieta, J.M. Turney, H.F. Schaefer, *J. Chem. Theory Comput.* **13**, 1478 (2017).

## Solubility of diclofenac in water: interplay between intra- and intermolecular hydrogen bonds

Mariana Kozłowska<sup>1,2</sup>, Paweł Rodziewicz<sup>1</sup>, Anna Kaczmarek-Kedziera<sup>3</sup>

<sup>1</sup>*Institute of Chemistry, University of Białystok, Ciołkowskiego 1K, 15-245 Białystok, Poland*

<sup>2</sup>*Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany*

<sup>3</sup>*Faculty of Chemistry, Nicholas Copernicus University, Gagarina 7, 87-100 Toruń, Poland*

Diclofenac (DCL) is a widely known and commonly used nonsteroidal anti-inflammatory drug with the best inhibition activity of the COX-2 (cyclooxygenase) enzyme [1]. Due to its simple, but specific, structure, DCL is similar to the original COX-2 substrate, i.e. arachidonic acid, therefore, provides a good fit to the enzyme pocket to inhibit the inflammation process [2,3]. On the one hand, DCL possesses an excellent inhibition ability, but on the other hand, diclofenac has low solubility in water in its unionized form [4]. The latter fact causes the usage of higher doses of the drug for a desirable anti-inflammatory effect, which is connected with undesirable side effects in the gastro-intestinal tract after its oral administration. Therefore, different modifications of DCL are made, nowadays, to increase its water solubility [5].

Why diclofenac has poor solubility in water? Is it due to the strong solute-solute interactions, which prevent the solvation of the drug, or low water affinity? There is no direct answer on this important question in the current literature. It all depends on the nature of the interactions between the drug and the solvent. The understanding of these interactions opens a new perspective for effective drug modifications that increase the diclofenac solubility and decrease the drug intake, therefore, undesirable side effects. In the present work, we focus on understanding the interplay between DCL-DCL and DCL-solvent interactions, based on different intra- and intermolecular interactions in water, including hydrogen bonds. For this purpose, we use a model of the solvated monomer and dimer of diclofenac and first principles molecular dynamics simulations, performed using the Car-Parrinello scheme at the finite temperature corresponding to water ambient conditions.

*The authors gratefully acknowledge the financial support of National Science Centre, Poland, grant number UMO-2014/13/B/ST8/04342. Computations were carried out at the Computer Center of University of Białystok.*

- [1] B. Cryer, M. Feldman, *Am. J. Med.* **104**, 413 (1998).
- [2] A.R. Sallmann, *Am. J. Med.* **80** (4B), 29 (1986).
- [3] S. W. Rowlinson et al., *J. Biol. Chem.* **278**, 45763 (2003).
- [4] A. Fini, G. Fazio, G. Feroci, *Int. J. Pharm.* **126**, 95 (1995).
- [5] R. Altman, B. Bosch, K. Brune, P. Patrignani, C. Young, *Drugs* **75**, 859 (2015).



## Can orbital-based decomposition of nonlinear optical properties unveil the role of electron correlation?

**Sebastian P. Sitkiewicz<sup>1,\*</sup>, Josep M. Luis<sup>4</sup>, Eduard Matito<sup>1,2,3</sup>**

<sup>1</sup>*Donostia International Physics Center (DIPC), Euskadi, Spain*

<sup>2</sup>*Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU), Euskadi, Spain*

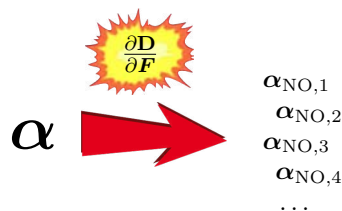
<sup>3</sup>*IKERBASQUE, Basque Foundation for Science, Bilbao, Euskadi, Spain*

<sup>4</sup>*Institut de Química Comp. i Catàlisi, Depart. de Química, Univ. Girona, Catalonia, Spain*

*\*sebastian.p.sitkiewicz@gmail.com*

Traditionally, the nonlinear optical properties (NLOPs) are defined as the contributions to the energy in terms of Taylor expansion with respect to the external electric field [1]. While most development studies devoted to higher-order dipole properties focus in finding the best methodology for their computations, the number of tools to analyze their nature is limited. Within this small group, the most popular are based on the Mulliken-type [2] and real-space electron density partitioning [3]. Although very useful for experimentally oriented studies, the atomic partitioning of NLOPs has not showed yet their utility for comparison of performance of quantum chemical methodologies. The role of electron correlation in NLOPs is usually analyzed from the sum over states (SOS) methodology, that represents the electrical response in terms of excited states of the system using the perturbational theory [1, 4]. Unfortunately, the SOS methodology is known to provide wrong estimates of NLOPs, except for FCI computations.

In this talk, a new orbital decomposition scheme of NLOPs is presented. Based on the derivatives of the reduced one-particle density matrix with respect to the magnitude of external electric field, the partitioning combines the informational aspects of SOS and the fully coupled description of the NLOP. We will analyze two systems that suffer from different electron correlation types: singlet diradicals (static correlation) and polymeric/conjugated systems (dynamic correlation).



- [1] J. O. Hirschfelder, W. Brown, S. T. Epstein, *Adv. Quant. Chem.* **1964**, 1, 255
- [2] M. Nakano, I. Shigemoto, S. Yamada, K. Yamaguchi *J. Chem. Phys.* **1995**, 103, 4175
- [3] N. Otero, C. Van Alsenoy, C. Pouchan, P. Karamanis *J. Comput. Chem.* **2015**, 36, 1831
- [4] B. Champagne, D. H. Mosley, *J. Chem. Phys.* **1996**, 105, 3592

**Excited State Gradients for a State-Specific Continuum Solvation Approach:  
a Lagrangian TDDFT formulation of VEM.**

**C. A. Guido<sup>1,2\*</sup>, G. Scalmani<sup>3</sup>, B. Mennucci<sup>4</sup>, D. Jacquemin<sup>1,5</sup>**

<sup>1</sup>*Laboratoire CEISAM - UMR CNRS 6230, Université de Nantes, 2 Rue de la Houssinière,  
44322 Nantes Cedex 3, France.*

<sup>2</sup>*Laboratoire MOLTECH - UMR CNRS 6200, Université de Angers, 2 Bd Lavoisier 49045  
Angers Cedex, France.*

<sup>3</sup>*Gaussian, Inc., 340 Quinipiac Street, Building 40, Wallingford, Connecticut, 06492,  
USA.*

<sup>4</sup>*Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Moruzzi 13,  
56124 Pisa, Italy.*

<sup>5</sup>*Institut Universitaire de France, 103, bd Saint-Michel, F-75005 Paris Cedex 05, France.*

*\*ciro.guido@univ-nantes.fr*

The accurate modeling of the environment response is a fundamental challenge for accurately describing the photophysics and photochemistry of molecules both in solution and in more complex embedding. [1] When large rearrangements of the electron density occur after an electronic transition, state-specific formulations, such as the Vertical Excitation Model [2], are necessary to achieve a proper modeling of the processes. Such a state-specific model is fundamental not only to obtain accurate energies, but also to follow the geometrical relaxation accompanying the evolution of the excited-states. [3] This study presents the analytical expression of the gradients of the Vertical Excitation Model approach by a Lagrangian formulation in the TD-DFT framework. [4] Representative organic chromophores in solution are used to test the reliability of the implementation and provide comparisons with the linear response description.

[1] B. Mennucci, S. Caprasecca, and C. A. Guido, in *Advances in Physical Organic Chemistry*, edited by I. H. Williams and N. H. Williams (Academic Press), Vol. **50**, pp. 203-241 (2016); J. Tomasi, B. Mennucci, and R. Cammi, *Chem. Rev.* **105**, 2999 (2005).

[2] A. V. Marenich, C. J. Cramer, D. G. Truhlar, C. A. Guido, B. Mennucci, G. Scalmani, and M. J. Frisch, *Chem. Sci.* **2**, 2143 (2011).

[3] C. A. Guido, D. Jacquemin, C. Adamo, and B. Mennucci, *J. Chem. Theory Comput.* **11**, 5782 (2015).

[4] C. A. Guido, G. Scalmani, B. Mennucci, D. Jacquemin, *J. Chem. Phys.* **146**, 204106 (2017).

## Coherent Dynamics in Photoexcited Azobenzene: Ultrafast Decay Resolved by sub-20-fs Pump-Probe Spectroscopy and Theoretical Simulations

Artur Nenov<sup>1</sup>, Rocio Borrego-Varillas<sup>2</sup>, Francesco Segatta<sup>1</sup>, Irene Conti<sup>1</sup>,  
Javier Segarra-Martí<sup>3</sup>, Aurelio Oriana<sup>2</sup>, Lucia Ganzer<sup>2</sup>, Shaul Mukamel<sup>4</sup>,  
Giulio Cerullo<sup>2</sup>, Marco Garavelli<sup>1</sup>

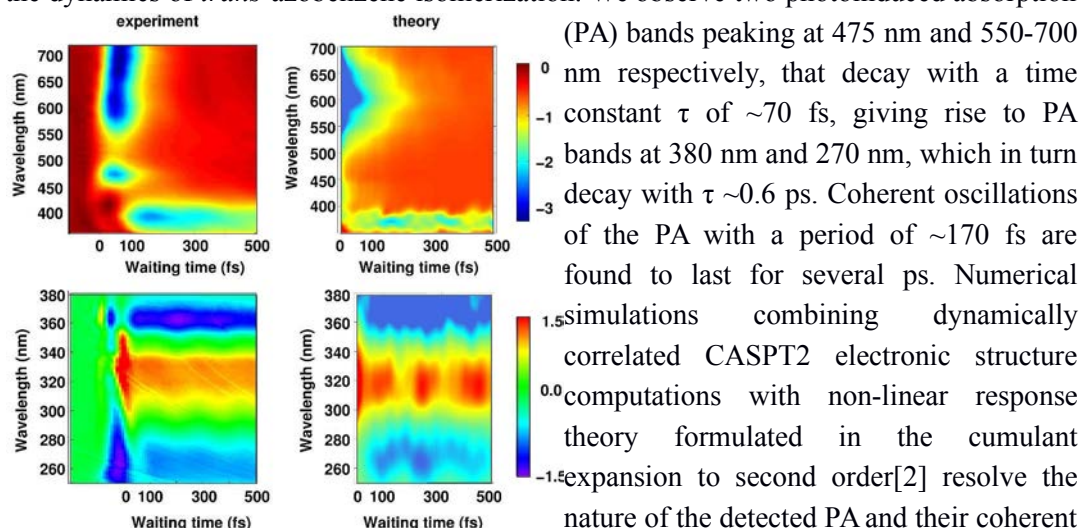
<sup>1</sup>Dipartimento di Chimica Industriale, Università degli Studi di Bologna, Viale del  
Risorgimento 4, I-40136 Bologna, Italy

<sup>2</sup>Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, I-20133  
Milano, Italy

<sup>3</sup>Laboratoire de Chimie, ENS de Lyon, CNRS, Université Lyon, F-69342 Lyon, France

<sup>4</sup>Department of Chemistry, University of California, Irvine, CA 92697-2025, USA

We use femtosecond pump-probe electronic spectroscopy in the VIS/UV range with sub-20-fs time resolution[1], combined with ab initio quantum mechanics simulations, to study the dynamics of *trans*-azobenzene isomerization. We observe two photoinduced absorption



bands peaking at 475 nm and 550-700 nm respectively, that decay with a time constant  $\tau$  of  $\sim 70$  fs, giving rise to PA bands at 380 nm and 270 nm, which in turn decay with  $\tau \sim 0.6$  ps. Coherent oscillations of the PA with a period of  $\sim 170$  fs are found to last for several ps. Numerical simulations combining dynamically correlated CASPT2 electronic structure computations with non-linear response theory formulated in the cumulant expansion to second order[2] resolve the nature of the detected PA and their coherent dynamics. The 475 nm and 550-700 nm bands are assigned to the bright  $S_2(\pi\pi^*)$  state, while the 380 nm and 270 nm bands are fingerprints of the  $S_1(n\pi^*)$  state. Mixed quantum-classical molecular dynamics simulations at CASPT2 level demonstrate that the ultrafast dynamics can be rationalized by an efficient  $S_2(\pi\pi^*) \rightarrow S_1(n\pi^*) \rightarrow \text{GS}$  non-adiabatic transfer involving predominantly the Franck Condon active modes NN stretching and CNN bending. Latter give rise to the oscillatory features observed in the pump-probe spectra.

[1] R. Borrego-Varillas, A. Candéo, D. Viola, M. Garavelli, S. De Silvestri, G. Cerullo and C. Manzoni, *Opt. Lett.* **38**, 3849-3852 (2014).

[2] S. Mukamel, *Principles of nonlinear optical spectroscopy*, O.U.P, New York (1995).

## Atmospheric Photoisomerization Interference in the Gas-Phase Oxidation of *E,E*-2-4-Hexadienal with OH: The Ketene-Aldehyde Equilibrium

Rene Pfeifer<sup>1</sup>, Felipe Fantuzzi<sup>1</sup>, Ricardo R. Oliveira<sup>1</sup>

<sup>1</sup>*Instituto de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ 21941-909, Brazil.*

Aldehydes are major pollutants formed from the combustion of fossil fuels. In the atmosphere, they react mainly with hydroxyl (OH) radicals during the day and with nitrate (NO<sub>3</sub>) radicals by night. The *E,E*-2,4-hexadienal compound is an unsaturated conjugated aldehyde, usually a by-product of the toluene photo-oxidation [1]. It can undergo through a rapid isomerization process when it is subjected to sunlight. This isomerization is a reversible process, and it leads to the formation of ketene-type compounds [2]. In this work, the mechanism of the competitive gas-phase addition of OH to the different double bonds of *E,E*-2,4-hexadienal and to the related ketene-type isomerization products was studied using Density Functional Theory (DFT) at the MO6-2X/cc-pVDZ level. The geometries of all structures were optimized without any restrictions. Vibrational frequency calculations were used to characterize the stationary points as intermediates (all frequencies are real) or as transition states (one imaginary frequency confirms the first-order saddle point configuration). The rate coefficients of each path were obtained using Transition State Theory (TST). All calculations were performed with the GAUSSIAN 09 program [3]. The results show that the reactions are exoergic, and that the OH addition to the double bond that is more distant from the aldehyde group is the most favorable from the thermodynamic point of view.

- [1] Colmenar, I., Martín, P., Cabañas, B., Salgado, S. & Martínez, E. *Atmos. Environ.* **99**, 159–167 (2014).
- [2] O'Connor, M. P., Wenger, J. C., Mellouki, A., Wirtz, K. & Muñoz, A. *Phys. Chem. Chem. Phys.* **8**, 5236–5246 (2006).
- [3] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, *et al.* *Gaussian 09, Revision E.01*. Gaussian, Inc., Wallingford CT (2009).

## **Dissipative particle dynamics study of poly(N-isopropylamide) with carboxylic and dodecyl terminal groups in aqueous solutions**

**Karel Šindelka<sup>1</sup>, Zuzana Limpouchová<sup>1</sup>, Miroslav Štěpánek<sup>1</sup>, Karel Procházka<sup>1</sup>**

<sup>1</sup>*Charles University, Faculty of science, Dept. of physical and macromolecular chemistry, Hlavova 8, Prague, Czech Republic*

We performed a parametric study of self-assembly of diblock copolymer imitating PNIPAm-C12 which was proposed as a component of various thermoresponsive drug delivery systems [1]. The focus was placed on the effect of the length of the soluble poly(N-isopropylamide) block and the charge of the carboxylic group (i.e. different pH). We also studied associative behaviour of PNIPAm-C12 in solutions containing surfactant carrying either the same or opposite charge. The simulations were performed using the computational simulation method known as the dissipative particle dynamics [2] with explicit electrostatics [3]. This highly coarse-grained method is similar to molecular dynamics and is well suited for investigation of complex systems. We compared the simulation results with experimental measurements of light and X-ray scattering [4] and found a satisfactory agreement at the qualitative and semi-quantitative level.

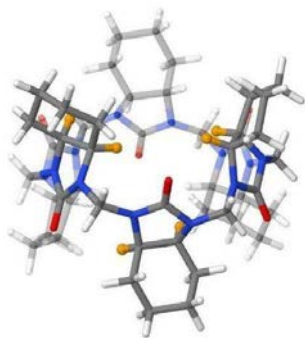
- [1] Z. J. Dai, T. Ngai, *J Polym. Sci. A: Polym. Chem.* **51**, 2995 (2013).
- [2] R. D. Groot, P. B. Warren, *J. Chem. Phys.*, **107**, 4423 (1997).
- [3] K. Procházka, K. Šindelka, X. Wang, Z. Limpouchová, M. Lísal, *Mol. Phys.*, **114**, 3077 (2016).
- [4] J. Škvarla, J. Zedník, M. Šlouf, S. Pispas, M. Štěpánek, *Eur. Pol. J.*, **61**, 124 (2014).

## Template-catalysed formation of cyclohexanohemicucurbiturils

Triin Narva, Riina Aav, Toomas Tamm

<sup>1</sup>*Department of Chemistry and Biotechnology, Tallinn University of Technology  
Ehitajate tee 5, 19086 Tallinn, Estonia*

Cyclohexanohemicucurbiturils (CycHC) are a family of host molecules that can bind a variety of small-sized anions within their cavity. Several cycHC's are chiral [1], which makes them stand out among the wide variety of hosts known in supramolecular chemistry. The synthesis of cycHC's involves use of a template – a small anion such as  $\text{Cl}^-$  or  $\text{HCOO}^-$ . The size of the cycHC formed is determined by the dimensions of the template.



**cycHC**

A new variety of cycHC's, composed of all-*cis* cyclohexanourea monomers, has recently been synthesized and characterized in our group. Their cavities are not closed like those of *trans* isomers, but tube-like, able to accommodate larger guests.

In this work equilibria between, and formation of, various stereoisomers of all-*cis*-cycHC were studied computationally using DFT at BP86/def-TZVP level. Role of the chloride template anion in the oligomerization reaction was found to be more important than previously reported. While earlier study of macrocyclisation mechanism of chiral cycHCs [1] had found a reaction barrier of 64 kJ/mol in the carbon-nitrogen bond formation step, in the presence of a chloride ion template the reaction step was found to proceed without any barrier. This finding better explains the ease of chain propagation and depropagation in the interconversion of various cycHC isomers.

This work has been supported by Estonian Research Council grants PUT692 and PUT1683.

- [1] E. Prigorchenko, M. Öeren, S. Kaabel, M. Fomitšenko, I. Reile, I. Järving, T. Tamm, F. Topic, K. Rissanen, R. Aav, *Chem. Comm* **51**, 10921 (2015).

## Variational Transition State Theory Study of Radical Reactions

Hui Zhang,<sup>1,2</sup> Lu Gao,<sup>1</sup> and Xuefei Xu<sup>1,\*</sup>

<sup>1</sup>*Center for Combustion Energy, Tsinghua University, Beijing 100084, China*

<sup>2</sup>*State Key Laboratory of Chemical Resource Engineering, Institute of Materia Medica, College of Science, Beijing University of Chemical Technology, Beijing, 100029, China*

**Abstract:** Radical reactions play important role in combustion, atmospheric chemistry, and interstellar chemistry. We take the two radical reactions as examples, H plus benzene and OH plus methanol, to introduce our recent work on variational transition state theory (VTST) study of radical reactions. Based on an accurate potential energy surface, we calculate accurate rate constants in a broad temperature range by including tunneling with small-curvature tunneling (SCT) approximation, including multistructural and torsional anharmonicity with multistructural and torsional (MS-T) method, and including anharmonicity of high-frequency mode of transition state structure by using a system-specific scaling factor of frequencies. For the pressure-dependent reactions, we use system-specific quantum RRK theory calibrated by variational transition state theory to estimate the falloff effect. The results show good agreement with the experimental observation.

### References:

- [1] J. L. Bao, J. Zheng, D. G. Truhlar, *J. Am. Chem. Soc.* 138, 2690–2704 (2016).
- [2] J. Zheng, R. Meana-Pañeda, D. G. Truhlar, *J. Am. Chem. Soc.* 136, 5150–5160 (2014).

## Different QM/MM approaches to study enzymatic reactions: ppGalNAcT2 glycosyltransferase

**Pavel Janoš<sup>1,2</sup>, Tomáš Trnka<sup>1,2</sup>, Stanislav Kozmon<sup>1,3</sup>, Igor Tvaroška<sup>1,3</sup>, Jaroslav Koča<sup>1,2</sup>**

<sup>1</sup>*Central European Institute of Technology (CEITEC), Masaryk University, 62500 Brno, Czech Republic*

<sup>2</sup>*Faculty of Science-National Centre for Biomolecular Research, Masaryk University, 62500 Brno, Czech Republic*

<sup>3</sup>*Institute of Chemistry, Slovak Academy of Sciences, 845 38 Bratislava, Slovak Republic*

Glycosyltransferases are enzymes that catalyze the formation of glycosidic bonds. Polypeptide UDP-GalNAc transferase 2 (ppGalNAcT2) is a metal dependent retaining glycosyltransferase. It catalyzes the transfer of GalNAc moiety from UDP-GalNAc to the hydroxyl group of either threonine or serine residue on the target protein. We use the ppGalNAcT2 as a case study to compare different QM/MM methodologies that can provide reaction paths, transition state information and either free energy or potential energy of an enzymatic reaction. [1]

The methods used include QM/MM Ab Initio MD at the DFT level using CPMD coupled with either metadynamics (MTD) or String Method (STM). The STM is used to derive the minimum free energy reaction path. The geometrical features of the free energy path and the energy profile are compared with minimum potential energy path obtained at much lower computational cost using Nudged Elastic Band (NEB) method. The MTD provides the free energy surface of the reaction. This surface represents a rough overview of the reaction and can confirm the physical relevance of optimized paths or potentially provide an initial guess for path optimization methods. As a validation of the suitability of DFT for the study of glycosyltransferase enzymatic reactions, we compared several widely used functionals with high-level DLPNO-CCSD(T)/CBS data using the potential energy profile from NEB.

[1] P. Janoš, T. Trnka, S. Kozmon, I. Tvaroška, J. Koča, JCTC 12, 6062-6076 (2016)



## On-the-fly *ab initio* semiclassical evaluation of absorption spectra of polyatomic molecules beyond the Condon approximation

Aurélien Patoz<sup>1</sup>, Tomislav Begušić<sup>1</sup>, Jiří Vaníček<sup>1</sup>

<sup>1</sup>Laboratory of Theoretical Physical Chemistry, Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

The time-dependent approach to spectroscopy [1] allows, in contrast to the much more common time-independent approaches, evaluating electronic spectra very easily without using the Born-Oppenheimer or global harmonic approximations. Whereas the exact molecular quantum dynamics requires a global potential energy surface, and thus scales exponentially with the number of degrees of freedom, an alternative, on-the-fly semiclassical dynamics overcomes this problem and at the same time preserves the accuracy of simulated spectra of a wide range of chemical systems [2,3]. Recently, an even simpler, single-trajectory on-the-fly *ab initio* method based on Heller's thawed Gaussian approximation [4,5] (OTF-AI-TGA) was implemented as a means to simulate electronic absorption, emission, and photoelectron spectra within the Condon approximation [6,7]. Here we present an extension of this method by employing the Herzberg-Teller approximation, which, in contrast to the Condon approximation, allows a linear dependence of the transition dipole moment on nuclear coordinates. Not only does this approach make it possible to simulate symmetry-forbidden transitions, it also provides the means to quantitatively and rigorously evaluate the contribution of the Herzberg-Teller term to the spectra. Furthermore, the on-the-fly scheme does not require invoking a global harmonic approximation, and hence describes the most important anharmonicity effects. This extended version of the OTF-AI-TGA is applied to evaluate the absorption spectra of benzene and phenyl radical. Calculated spectra reproduce the experimental data and are much more accurate than the standard global harmonic approaches. Our results indicate that in the phenyl radical, including anharmonicity effects is more important than including the Herzberg-Teller contribution, while in benzene, the Herzberg-Teller vibronic contribution is essential, since the transition is electronically forbidden and the Condon approximation yields a zero spectrum.

- [1] Eric J. Heller, *Acc. Chem. Res.*, **14** (12), 368 (1981).
- [2] J. Tatchen and E. Pollak, *J. Chem. Phys.*, **130**(4), 041103 (2009).
- [3] M. Ceotto et al., *J. Chem. Phys.*, **130** (23), 234113 (2009).
- [4] Eric J. Heller, *J. Chem. Phys.*, **62** (4), 1544 (1975).
- [5] Soo-Y. Lee and Eric J. Heller, *J. Chem. Phys.* **76**, 3035 (1982).
- [6] M. Wehrle, M. Šulc, and J. Vaníček, *J. Chem. Phys.* **140**, 244114 (2014).
- [7] M. Wehrle, S. Oberli, and J. Vaníček, *J. Phys. Chem. A* **119**, 5685 (2015).

## AlgoGen : a program to perform Molecular Docking with Full Quantum Refinement (DFQR)

H. Khartabil<sup>1,3</sup>, G. Merieux<sup>1</sup>, J-C. Boisson<sup>2</sup>, E. Hénon<sup>1</sup>

<sup>1</sup>ICMR UMR CNRS 7312, URCA, Moulin de la Housse, Reims, France

<sup>2</sup>CRéSTIC EA 3804, URCA, Moulin de la Housse, Reims, France

<sup>3</sup>Campus Universitaire des Ardennes, 4 bd Jean Delautre, Charleville-Mézières, France

Molecular docking is a widely used technique to search for new drugs in medicinal and pharmaceutical fields. It can describe the best orientation of a ligand interacting with a biological macromolecule such as protein and enzyme. To do so, a scoring function is needed in order to determine the strength of the protein-ligand association, and to rank ligands. Standard scoring functions do not appropriately consider the electron polarization and charge-transfer. In order to overcome this drawback, our new approach is based on using docking along with quantum chemistry. In this regard, we have developed AlgoGen [1], which is a software application that combines the benefits of exploratory docking using empirical Vina scoring function [2], and Full Quantum Relaxation Refinement of the protein-ligand system (Fig. 1).

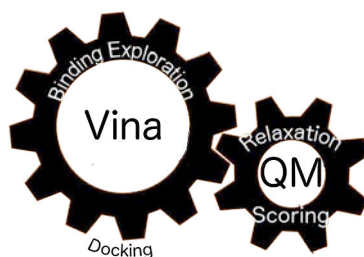


Fig. 1 Docking with Full Quantum Refinement

Recently, we have enhanced AlgoGen by developing jBox, a user-friendly Graphical Interface for ligand and protein pre-processing. Efficient detection of ligand-metal coordination by AlgoGen will be presented.

Acknowledgements to Pr R. Plantier and Dr M. Muzard (ICMR, University of Reims Champagne-Ardenne).

[1] C. Barberot, J-C. Boisson, S. Gerard, H. Khartabil, E. Thiriot, G. Monard, E. Hénon, *Comput. Theor. Chem.* **1028**, 7 (2014).

[2] O. Trott, A. J. Olson, *J. Comput. Chem.* **31**, 455 (2010).

## **Efficient Eigensolvers for Linear Response Time-Dependent Density Functional Theory**

**Eugene Vecharynski<sup>1</sup>, Jiri Brabec<sup>1,2</sup>, Meiyue Shao<sup>1</sup>, Niranjan Govind<sup>3</sup>, Chao Yang<sup>1</sup>**

<sup>1</sup>*Lawrence Berkeley National Laboratory, Computational Research Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720*

<sup>2</sup>*J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, CZ-18223 Prague 8, Czech Republic*

<sup>3</sup>*Pacific Northwest National Laboratory, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352*

We present two efficient iterative algorithms for solving the linear response eigenvalue problem arising from the time dependent density functional theory. Although the matrix to be diagonalized is nonsymmetric, it has a special structure that can be exploited to save both memory and floating point operations. In particular, the nonsymmetric eigenvalue problem can be transformed into an eigenvalue problem that involves the product of two matrices  $M$  and  $K$ . We show that, because  $MK$  is self-adjoint with respect to the inner product induced by the matrix  $K$ , this product eigenvalue problem can be solved efficiently by a modified Davidson algorithm and a modified locally optimal block preconditioned conjugate gradient (LOBPCG) algorithm that make use of the  $K$ -inner product. The solution of the product eigenvalue problem yields one component of the eigenvector associated with the original eigenvalue problem. It is shown that the other component of the eigenvector can be easily recovered in an inexpensive postprocessing procedure. As a result, the algorithms we present here are more efficient than existing methods that try to approximate both components of the eigenvectors simultaneously. In particular, our numerical experiments demonstrate that the new algorithms presented here consistently outperform the existing state-of-the-art Davidson type solvers by a factor of two in both solution time and storage.

## Compressed Representations of Dispersion Interactions and Long-Range Electronic Correlation

Jérôme F. Gonthier<sup>1</sup>, Pauline J. Ollitrault<sup>1</sup>, Martin Head-Gordon<sup>1</sup>

<sup>1</sup>*Kenneth S. Pitzer Center for Theoretical Chemistry, Department of Chemistry, University of California, Berkeley, California 94720, USA*

Dispersion interactions arise purely from long-range electronic correlation. Thus, in spite of being the weakest intermolecular force, they are present in all non-covalent dimers and are quantitatively significant in many cases, playing a significant role in complex extended assemblies such as proteins and DNA.

Detailed studies and understanding of electron correlation lead to very efficient and accurate representations using for example explicitly correlated or local methods. Low-rank accurate approximations of the full pair correlation space are now commonly available for short-range electron correlation.[1] Here, we investigate the existence and accuracy of a compressed representation for long-range electron correlation. In particular, we extract dispersion amplitudes from the CCSD doubles amplitudes in a localized orbital basis. Application of Singular Value Decomposition to the corresponding unfolded tensor[2] yields a set of two-particle geminal functions that we further analyze in terms of their occupied and virtual components.

Our investigation reveals that long-range correlation possesses compressed representations much more compact than those of short-range correlation. We identify the dominant geminal functions and reveal which set of virtual orbitals underlies them, a set that is thus particularly suited to describe dispersion. We validate the robustness of our observations in various small and medium-sized systems, and explore pathways to obtain *a priori* virtual orbitals tailored for dispersion interactions.

In addition to qualitative and quantitative insights into the compressed representation of long-range correlation, this study offers a way to obtain a well-defined dispersion energy in the basis set limit, which is invaluable to energy decomposition schemes relying on Hilbert-space partitions.[3]

[1] C. Riplinger, F. Neese, *J. Chem. Phys.* **138**, 034106 (2013).

[2] G. J. O. Beran, M. Head-Gordon, *J. Chem. Phys.* **121**, 78 (2004).

[3] J. Thirman, M. Head-Gordon, *J. Chem. Phys.* **143**, 084124 (2015).

## State-of-the-art solvation free energy modelling – add more physics and do without fudge factors

Lars Sandberg<sup>1</sup>

<sup>1</sup>*Science for Life Laboratory, Drug Discovery and Development Platform & Department of Organic Chemistry, Stockholm University, Box 1031, 17121 Solna, Sweden*

The solvation free energy is essential to model with good accuracy in many areas of biology, chemistry and physics. Here we will calculate the change in free energy of a solute molecule transferred from gas phase to water solvent, the solvation free energy. The free energy is obtained from using a relevant system Hamiltonian in combination with statistical mechanics, and it is important to sample phase space sufficiently well. One helpful approach is to describe the solvent in the continuum limit, i.e. by an implicit solvent model. The focus can now be to represent and sample the solute molecule more thoroughly. The objectives for the implicit solvent model implemented here are

1. Include all physical effects liable to molecular solvation
2. Applicable to molecules found in biological and organic chemistry
3. Model parameters of solvent and solute:
  - Introduce as few model parameters as possible
  - Introduce no/few adjustable parameters fitted to experimental hydration free energy data
  - Parameters are fully transferable with explicit solvent free energy calculations
4. Calculated free energies of solvation are
  - better or comparable to the accuracy of the golden standard of explicit solvent free energy calculations
  - made with chemical accuracy, commonly defined as thermochemical predictions within 4.2 kJ/mol (1 kcal/mol)

We have calculated solvation properties in water for a set of several hundreds of organic molecules and compared with available experimental data. The predicted solvation enthalpies, entropies, and free energies show a good accuracy (mean error < 4 kJ/mol) and precision (standard deviation of mean errors between 1-3 kJ/mol) for most functional groups. However, a few functional groups that form strong hydrogen bonds (electron-donor-acceptor complex) with the first solvation shell waters will result in an additional stabilising charge-delocalisation energy. This physical effect is not part of any classical implicit (nor classical explicit) solvent model and that is why systematic errors occur. If we solvate the solute-water complex and include the polarisation stress relief from first principle, the need for corrections are shown to be much reduced.

## Thermodynamic modelling of mesophase pitch for the development of high-performance carbon fibers

Caio César Ferreira Florindo<sup>1</sup>, Adalberto Bono Maurizio Sacchi Bassi<sup>1</sup>

<sup>1</sup>*Department of Physical Chemistry/Institute of Chemistry/ University of Campinas, José de Castro Street – University City, Campinas, Brazil*

In order to obtain high-performance carbon fibers (HPCFs) with excellent mechanical, thermal and electrical properties, it is important to control the spinning process, since molecular shape and orientation of the mesophase pitch is determined, almost exclusively, at this process [1]. In this study, one proposes a mesoscopic continuum mathematical model for mesophase pitch-based carbon fibers, in order to describe how the mesophase regions orientation distributions influence the behavior of the pitch in homogenous flows. By using the continuity condition for the orientation distribution function (ODF) of the mesophase pitch, one can obtain a new homogenous non-linear evolution equation for ODF. This work shows only two-dimensional solutions for two types of flow: (1) simple shear flow and (2) planar elongational flow. Solutions for three-dimensional flows are also obtained, but the findings will not be displayed here. In the two-dimensional approximation, all mesophase regions are parallel to the shear plane. Thus, the angle between the shear direction and the mesophase region orientation completely specifies its orientation state. In general, the ODF shows higher and narrower probability density peaks at higher shear and elongation rates. Meanwhile, the orientation angles of the mesophase regions at low shear and elongation rates are higher than for high shear and elongation rates. The solutions for the mesophase regions show that the system behaves like shear thinning, that is, its viscosity decreases as the shear rate increases. The numerical solutions for the new homogeneous non-linear equation proposed in this work show orientation angle values strictly close to those experimentally obtained by Hamada *et al.* [2]. All calculations were performed by the Mathematica software (version 11.0).

**Acknowledgments:** FAPESP (Grant 2016/08563-2).

### References:

- [1] D. Edie, M. Dunham, *Carbon* **27**, 5 (1989).
- [2] T. Hamada, M. Furuyama, Y. Sajiki, T. Tomioka, M. Endo, *J. Mater. Res.* **5**, 06 (1990).

## Hydrogenation of phenyl substituted unsaturated functional groups by d<sup>5</sup> and d<sup>6</sup> metal substituted PNP complexes

Zhihong Wei, Kathrin Junge, Matthias Beller, Haijun Jiao\*

*Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Straße 29a,  
Rostock, Germany*

**Abstract:** Catalytic hydrogenations of unsaturated functional groups are very important in organic synthesis and play key roles in the production of numerous bulk products and intermediates in the chemical and pharmaceutical industry. One of the promising examples is the aliphatic pincer chelating PN<sup>H</sup>P ligand [PN<sup>H</sup>P = (*i*Pr<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NH)] in conjugation with transition metals for various types of bifunctional heterolytic H<sub>2</sub> transformation on the basis of the effective metal-ligand cooperation. In our previous work, we explored the hydrogenation of CH<sub>3</sub>-C≡N, Ph-CO<sub>2</sub>CH<sub>3</sub> and Ph-CHO by using the d<sup>8</sup>-M<sup>II</sup> PNP pincer complexes (M = Fe, Ru, Os).[1] Herein, the structures and stability of the d<sup>5</sup> and d<sup>6</sup> metal substituted PNP pincer amido M<sup>5</sup>(NO)<sub>2</sub>(PNP)/M<sup>6</sup>(NO)(CO)(PNP) and amino HM<sup>5</sup>(NO)<sub>2</sub>(PN<sup>H</sup>P)/HM<sup>6</sup>(NO)(CO)(PN<sup>H</sup>P) complexes [M<sup>5</sup> = V, Nb and Ta, M<sup>6</sup> = Cr, Mo and W] complexes as well as their hydrogenation mechanisms for phenyl substituted unsaturated functional groups have been explored and compared at the B3PW91 level of density functional theory. Under H<sub>2</sub> environment, the computed structure and stability of the Mo and W complexes are in agreement with the experimental results.[2-4] For the designed Cr- as well as V-, Nb- and Ta-PNP complexes, the conjugated complexes can form equilibrium and fulfills the criteria of metal-ligand cooperated bifunctional hydrogenation catalysts. For the hydrogenation of Ph-C≡N, Ph-CH=NH, Ph-CH=NH-Ph, Ph-CH=N-CH<sub>2</sub>Ph, Ph-C≡CH, Ph-CH=CH<sub>2</sub>, Ph-CHO and Ph-CO-CH<sub>3</sub>, the reaction prefers either a two-step or one-step mechanism for the hydridic M-H and protonic N-H transfer. The computed barrier in the increasing order of PhCHO < Ph-C≡N < Ph-C≡CH < Ph-CH=NH < Ph-COCH<sub>3</sub> ≈ Ph-CH=CH<sub>2</sub> < Ph-CH=N-Ph < Ph-CH=N-CH<sub>2</sub>-Ph. These results clearly demonstrate that the designed d<sup>5</sup> metal substituted PNP pincer-type complexes can be promising new catalysts for the hydrogenation reactions. The d<sup>6</sup> metals of Mo complexes have higher catalytic activity than that of W and the designed Cr complex. The d<sup>5</sup> metal of Nb is more active than V and Ta as well as the d<sup>6</sup> metal of Mo. All of these provide the basis for experimental proofs.

- [1] H. Jiao, K. Junge, E. Alberico and M. Beller, *J. Comput. Chem.* **37**, 168 (2016).
- [2] Z. Wei, K. Junge, M. Beller and H. Jiao, *Catal. Sci. & Technol.* **7**, 2298(2017).
- [3] S. Chakraborty, O. Blacque and H. Berke, *Dalton Trans.* **44**, 6560(2015).
- [4] S. Chakraborty and H. Berke, *ACS Catal.* **4**, 2191(2014).

## Adsorption and activation of water on cuboctahedral Rh and Pt nanoparticles

Andrey S. Bazhenov<sup>1</sup>

<sup>1</sup>*Nanoscience Centre, Department of Chemistry, University of Jyväskylä,  
P.O. Box 35, FI-40014 Jyväskylä, Finland*

Transition metal catalysts find nowadays their application in major industrial processes to obtain sustainable chemicals and renewable fuels. Activation of water has been suggested to play a key role in the water-gas shift and multiple reforming processes, being in some cases acknowledged as the rate-determining step. Since the industrial catalysts operate at the nanoscale, atomic-level understanding of the water activation on relevant transition metals could provide useful information for rational design of catalysts with higher activity and selectivity.

We present a density functional theory study of the water activation on selected noble metals, where the metals are represented by  $M_{55}$  and  $M_{147}$  ( $M = \text{Rh}, \text{Pt}$ ) cuboctahedral nanoparticles accompanied by the extended (100), (111) and (211) surfaces, mimicking facets and edges of the nanoparticles. We systematically evaluate adsorption and activation of a single water molecule on each relevant surface site of each structural model.

Our findings [1] indicate that both Rh and Pt are nearly equally active towards the water activation, which is reflected in a difference of  $<0.10$  eV in adsorption and transition state energies between the two metals. Moreover, in the case of the nanoparticle models, we observe strong linear dependences of adsorption and transition state energies on the centres of the d-band projected onto the corresponding surface sites and on the generalized coordination numbers, which quantify the surface site coordination accounting for their first coordination spheres. These trends do not withhold for the extended surface models, hinting their insufficiency in describing the electronic and structural properties of the nanoparticles in the chosen size regime. The difference between Rh and Pt is observed in the stability of the dissociated water, which is higher in the case of Rh. These results are qualitatively in line with the experimental evidence of lower thermodynamic stability of Pt oxides.

[1] A. S. Bazhenov, L. Lefferts, K. Honkala, *J. Phys. Chem. C* **121**, 4324 (2017).



## Symmetric dissociation and excited states with Selected Configuration Interaction with Truncation Energy Error

César X. Almora-Díaz<sup>1</sup>, Alejandro Ramírez-Solís<sup>1</sup>, Carlos F. Bunge<sup>2</sup>

<sup>1</sup>*Department of Physics, Centro de Investigación en Ciencias, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001 Chamilpa 62209 Cuernavaca, Morelos, México*

<sup>2</sup>*Department of Teoretical Physics, Instituto de Física, Universidad Nacional Autónoma de México, Apdo. Postal 20-364, México 01000, México*

*A priori* Selected Configuration Interaction with Truncation Error [1,3] for molecular systems and CI by parts [4] are used to approximate the total nonrelativistic electronic ground state energies of water, C<sub>2</sub> and N<sub>2</sub> at equilibrium geometry and at geometries where bond lengths are elongated until dissociation. On N<sub>2</sub> we use a double zeta basis set, in H<sub>2</sub>O we use up to triple zeta quality basis sets, and with C<sub>2</sub> we use up to quadruple zeta basis sets. In each case we compare our all electron results of CISDTQ, CISDTQQnSx (CI-6X) and CI up to octuple excitations (CI-8X) with available results of Coupled Cluster, DMRG and other high-level electronic structure methods. In all cases CI-8X results matched converged DMRG results to within 100 microHartree. CI-6X results present Non Paralellity Errors (NPE) smaller than 1 kcal/mol. Energy values obtained within a model space (S01) up to 10 times smaller than total selected configuration space which differ up to 4 milliHartree to the total CI energy keep NPEs within the so called chemical accuracy. Finally, we compare results (within selected S01 spaces) of excited states on carbon dimer with DMRG calculations using a cc-pvdz basis set, we found that NPEs are smaller than 100 microHartree.

[1] C.F. Bunge, *J. Chem. Phys.* **125**, 014107 (2006).

[2] C.X. Almora-Díaz, *J. Chem. Phys.* **140**, 184302 (2014).

[3] C.X. Almora-Díaz, H.I.Rivera-Arrieta, C.F. Bunge *Adv. Quant. Chem.* **72**, 129 (2016).

[4] C.F. Bunge and R. Carbo-Dorca, *J. Chem. Phys.* **125**, 014108 (2006).

## An interpolation approach for the choice of polarization functions when using Gaussian basis sets

Fernando Ratuchne,<sup>1</sup> Ana Cristina Mora,<sup>2</sup> Ricardo Celeste,<sup>1</sup> Albérico B. F. da Silva<sup>2</sup>

<sup>1</sup>Universidade Estadual de Centro-Oeste, Departamento de Química, Campus Cedeteg, CEP 85040 - 080, Guarapuava - Paraná, Brasil

<sup>2</sup>Departamento de Química e Física Molecular, Instituto de Química de São Carlos, Universidade de São Paulo, C. P. 780, 13560 - 970, São Carlos - SP, Brasil

In the generation of basis sets, usually the primitive set is constructed for the free atom in its ground state and the description of the outer part of the electron density distribution is generally poor [1], so the addition of higher angular momentum functions (polarization functions) in the body of the primitive set of exponents improves the performance of a basis set in the molecular environment [2][3]. In this work, we have used a methodology based on the interpolation of Gaussian basis sets exponents to be used for the choice of polarization functions with any Gaussian basis set. The Gaussian primitive functions were generated here by using the polynomial Generator Coordinate Hartree-Fock (PGCHF) method [4] for Ga through Kr and the general contraction method was used for the construction of contracted Gaussian basis sets of 6Z quality in the valence. Polarization functions were added to the contracted bases by explicit optimization and also by interpolation of the exponents. The performance of the contracted basis sets, augmented with polarization functions obtained by interpolation, was tested in CISD and B3LYP calculations for the total energy of the systems Se, Se<sub>2</sub> and Se<sub>6</sub> and the results were compared with the total energy values obtained from explicit optimized exponents. The results obtained with the PGCHF Gaussian basis sets augmented with interpolated polarization functions are in good agreement with the ones augmented with explicit optimized polarization functions (exponents). The interpolation strategy can be useful to generate polarization functions for any Gaussian basis set in different series of atoms of the periodic table.

[1] T. H. Dunning, *J. Chem. Phys.* **90**, 1007 (1989).

[2] F. Jensen, *J. Chem. Phys.* **115**, 9113 (2001).

[3] F. Jensen, *J. Chem. Phys.* **138**, 014107 (2013).

[4] R. C. Barbosa and A. B. F. da Silva, *Mol. Phys.* **101**, 1073 (2003).

## Theoretical $pK_a$ calculations of difficult cases for thermodynamic cycles: amino acids and peptides.

Rodrigo Casasnovas<sup>1</sup>, Sebastià Sastre<sup>1</sup>, Francisco Muñoz<sup>1</sup>, Juan Frau<sup>1,2</sup>

<sup>1</sup>*Departament de Química, Institut Universitari d'Investigació en Ciències de la Salut (IUNICS), Universitat de les Illes Balears, Palma de Mallorca 07122, Spain*

<sup>2</sup>*Instituto de Investigación Sanitaria de Palma (IdISPA), 07010, Palma, Spain*

Accurate prediction of  $pK_a$  values is a current challenge in computational chemistry. The traditional approach employs thermodynamic cycles (TC) combining gas-phase energies calculated with high ab initio methods, and solvation energies calculated with continuum solvent models [1-5]. TCs are difficult to apply to amino acids and peptides because the most stable protonation states and conformations differ between gas phase and aqueous solution. Our group has applied an alternative to TCs consisting of an isodesmic reaction (IR) proton exchange reaction in solution. We have successfully applied the IR to the prediction of  $pK_a$  values of common organic molecules [6], carbon acids [7-9] and metal complexes [9, 10]. Here we apply the IR to the  $pK_a$  calculation of amino acids and peptides obtaining mean absolute errors of 0.5-1.0  $pK_a$  units for  $pK_{a1}$  ( $\alpha$ -carboxyl)  $pK_{a2}$  ( $\alpha$ -amino) and  $pK_{a3}$  (sidechain groups) of a broad set of amino acids and peptides [11].

- [1] R. Casasnovas, J. Ortega-Castro, J. Frau, J. Donoso, F. Muñoz, *Int. J. Quantum Chem.* **114**, 1350 (2014).
- [2] P. G. Seybold, G. C. Shields, *WIREs Comput. Mol. Sci.* **5**, 290 (2015).
- [3] J. Ho, M. L. Coote, *WIREs Comput. Mol. Sci.* **1**, 649 (2011).
- [4] J. Ho, M. L. Coote, *Theor. Chem. Acc.* **125**, 3 (2010).
- [5] Ho, J. *Phys. Chem. Chem. Phys.* **17**, 2859 (2015).
- [6] S. Sastre, R. Casasnovas, F. Muñoz, J. Frau *Theor. Chem. Acc.* **132**, 1310 (2013).
- [7] R. Casasnovas, D. Fernandez, J. Ortega-Castro, J. Frau, J. Donoso, F. Muñoz, *Theor. Chem. Acc.*, **130**, 1 (2011).
- [8] R. Casasnovas, M. Adrover, J. Ortega-Castro, J. Frau, J. Donoso, F. Muñoz *J. Phys. Chem. B*, **116**, 10665 (2012).
- [9] R. Casasnovas, J. Ortega-Castro, J. Frau, J. Donoso, F. Muñoz, *J. Phys. Chem. B*, **117**, 2339 (2013).
- [10] R. Casasnovas, J. Ortega-Castro, J. Donoso, J. Frau, F. Muñoz, *Phys. Chem. Chem. Phys.* **15**, 16303 (2013).
- [11] S. Sastre, R. Casasnovas, F. Muñoz, J. Frau, *Phys. Chem. Chem. Phys.* **18**, 11202 (2016).

## Automatic differentiation in quantum chemistry: Application in fully variational Hartree-Fock

Teresa Tamayo-Mendoza<sup>1,\*</sup>, Christoph Kreisbeck<sup>1</sup>, Alán Aspuru-Guzik<sup>1</sup>

<sup>1</sup>*Department of Chemistry and Chemical Biology, Harvard University, University,  
12 Oxford St, Cambridge, MA 02138*

<sup>\*</sup>*ttamayomendoza@g.harvard.edu*

Automatic differentiation (AD) is a tool that allows us to calculate derivatives of implemented functions with respect to all of their parameters up to machine precision, without having to add in any other explicit functions[1]. Since it is easy to use and accurate, AD has great potential in quantum chemistry where accurate derivatives are required to compute molecular properties and optimizations[2]. Because, even though some of these derivatives have well established explicit equations, implementing them on electronic structure methods or response functions can be both time-consuming and non-trivial. First steps have already been taken toward including AD in quantum chemistry algorithms to circumvent these issues[3].

In this poster, we show how automatic differentiation can be used to compute arbitrary gradients throughout a complete quantum chemistry method with respect to any input parameter. We describe an implementation of a fully autodifferentiable Hartree-Fock (HF) algorithm. We have selected HF for two reasons: (i) it is the starting point of many electronic correlation methods, and (ii) it features mathematical functions, including eigenvectors and special functions, which are also present in more accurate methods. Finally, we present results from embedding these gradient calculations within an optimization procedure to assemble a fully variational HF method. Using the floating Gaussian framework[4], this implementation minimizes the SCF-energy with respect to all parameters of the Gaussian basis functions and molecular geometries.

- [1] A. Griewank, A. Walter, *Evaluating Derivatives, Principles and Techniques of Algorithmic Differentiation*, second edition, SIAM Philadelphia, (2008).
- [2] C. H. Bischof, and M. Bücker, (Ed.: J. Grotendorst), *NIC Series*, **3**, 315 (2000).
- [3] U. Ekström, L. Visscher, R. Bast, A. Thorvaldsen, and K. Ruud, *J. Chem. Theory Comput.*, **6**, 1971 (2010).
- [4] T. Helgaker, and J. Almlöf, *J. Chem Phys.* **89**, 4889 (1988).

## Why does MP2 outperform MP3 and how can we improve perturbation theory?

Reinhold F. Fink<sup>1</sup>

<sup>1</sup>*Institute of Physical and Theoretical Chemistry, University of Tuebingen,  
Auf der Morgenstelle 18, 72076 Tuebingen, Germany*

We show analytically and numerically that the performance of second and third order Møller-Plesset perturbation theory (MP2 and MP3, respectively) can be rationalized and that the obtained insight opens an avenue for improved perturbation theories. An analysis of the wave functions obtained from configuration interaction (CI), coupled-cluster (CC) theory, and perturbation theories points to systematic and relatively large deviations of the first order MP wave function from exact full CI or accurate CC counterparts [1]. It is shown that MP2 profits from a systematic error cancellation due to, respectively, an underestimation and overestimation of singlet- and triplet-coupled double excitations to electron correlation. The underlying reasons for this error are explained and it is shown that it is reduced by spin-component-scaled (SCS) MP2 [2, 3].

We demonstrate that a similar error cancellation as in MP2 does not appear in MP3 due to the variational character of third order perturbation theory. Finally, it is demonstrated that retaining the excitation-degree (RE) perturbation theory [4, 5] provides much better wavefunctions than MP2 and that these errors can be further reduced by combining the unperturbed Hamiltonians of MP and RE.

- [1] R. F. Fink, *J. Chem. Phys.* **145**, 184101 (2016).
- [2] S. Grimme, *J. Chem. Phys.* **118**, 9095, (2003).
- [3] S. Grimme, L. Goerigk, and R. F. Fink, *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2**, 886, (2012).
- [4] R. F. Fink, *Chem. Phys. Lett.* **428**, 461 (2006).
- [5] R. F. Fink, *Chem. Phys.* **356**, 39, (2009).

## Binary mixtures of ionic liquids with a common anion: a molecular dynamics study

Iuliia V. Voroshylova<sup>1,2</sup>, Elisabete S. C. Ferreira<sup>1,2</sup>, André Melo<sup>2</sup>,  
Carlos M. Pereira<sup>1</sup>, M. Natália D.S. Cordeiro<sup>2</sup>

<sup>1</sup>LAQV@REQUIMTE/<sup>2</sup>CIQUP, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal

Ionic liquids (ILs) are promising materials with a number of possible applications, ranging from catalytic and reaction media to plausible electrolytes for batteries and supercapacitors. Nevertheless, ILs present some known drawbacks, such as relatively high viscosity and low conductivity. Recently, it has been proposed a way of overcoming these drawbacks by mixing different ILs, which allows a fine-tuning of their physicochemical properties [1]. Experimental studies show that the most pronounced effect on physical and chemical properties, first of all, on capacitance, occurs in ILs mixtures with small additions of IL with a different anion [2, 3].

In this study we carried out molecular dynamics (MD) simulations to understand at the molecular level the causes for some mixtures of ILs having quasi-ideal behaviour, while other mixtures showing quite large deviations from ideality. Towards this goal, we have simulated three ILs mixtures with a common cation, *i.e.*: [BMIM][FAP]/[BMIM][PF<sub>6</sub>], [BMIM][PF<sub>6</sub>]/[BMIM][TFSI] and [BMIM][FAP]/[BMIM][TFSI] (Fig. 1), in a wide concentration range, reproducing the experimentally studied ones [3]. The simulations of these three pure ILs were also carried out for comparison purposes. The excess molar volume of the mixtures is estimated and discussed. The MD results were further analysed in terms of radial distribution functions (centre-of-mass and atom-atom), running coordination numbers and hydrogen-bonds-like interactions.

**Acknowledgements.** This work received financial support from Fundação para a Ciência e Tecnologia (FCT, Lisbon, Portugal) through postdoctoral research grants with the reference SFRH/BPD/97918/2013 and SFRH/BPD/90343/2012.

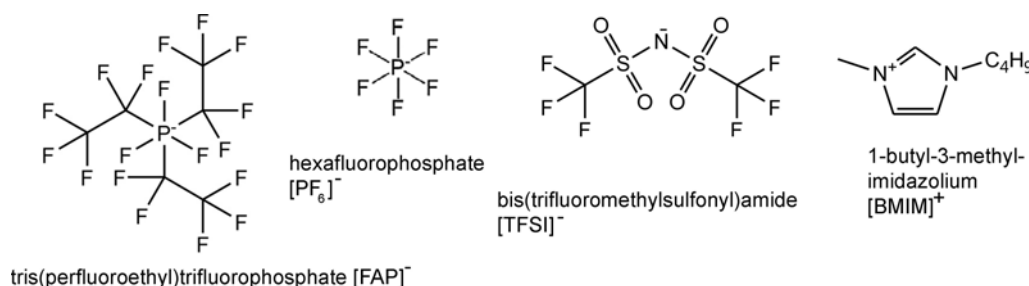


Fig. 1. Structural formulas of the ions of the studied ionic liquids.

- [1] S. Cha S. and D. Kim, *Phys. Chem. Chem. Phys.*, **17**, 29786 (2015).
- [2] R. Costa, C. M. Pereira and A. F. Silva, *Electrochem. Comm.*, **57**, 10 (2015).
- [3] R. Costa, I. V. Voroshylova, M. N. D. S. Cordeiro, C. M. Pereira and A. F. Silva, *Electrochem. Acta*, in press (2017)

## Nonlinear optical properties from TDDFT: trials and tribulations

Shane Parker<sup>1</sup>, Filipp Furche<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of California Irvine, 1102 Natural Sciences II Irvine, CA, USA*

Nonlinear response theory plays a central role in theoretical materials chemistry and applications of nonlinear response theory within time-dependent density functional theory (TDDFT) are increasingly important, from the calculation of nonlinear optical properties used to characterize complex materials to the excited-state properties and couplings needed to simulate non-adiabatic molecular dynamics. I will present an efficient implementation of the TDDFT quadratic response function, including the computation of excited state absorption spectra of perylene diimide dimers, two-photon absorption spectra of twisted conjugated porphyrins, and hyperpolarizability of octupolar calixarenes. Distressingly, recent descriptions of unphysical divergences in excited-state properties[1] and the inconsistent behaviors of multiphoton processes[2] near single-photon absorption resonances have called into question the general applicability of existing nonlinear response theories. Finally, using the aforementioned systems as examples, I will sketch the successes and failures of existing nonlinear response methods and discuss possible routes for resolving the deficiencies in nonlinear response theories.

## References

- [1] S. M. Parker, S. Roy, F. Furche, *J. Chem. Phys.* **2016**, *145*, 134105.
- [2] Z. Hu, J. Autschbach, L. Jensen, *J. Chem. Theory Comput.* **2016**, *12*, 1294–1304.

## Challenges and procedures towards automated flow chemistry

Loïc M. Roch,<sup>1</sup> and Alán Aspuru-Guzik<sup>1</sup>

<sup>1</sup>*Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, MA, USA*

Over the past decade new technologies and machines have profoundly changed the way we work, addressing constraints encountered in research lab, such as budget and waste minimization.<sup>[1]</sup> Pioneered by the pharmaceutical industry, the incorporation of high-throughput screening to continuous flow chemistry emerged as a valuable tool for a more rational search process of the *Application Space* (*A.S.*) towards an efficient and automated synthesis of new promising organic candidates.<sup>[2-4]</sup>

However, given the multidimensionality of the search space to idealize and maximize specific features of the system under study, *e.g.*, yield of the reaction, electrochemical properties, photophysical properties, etc., a combinatory approach to that vast *A.S.* is not viable. As such, artificial intelligence appears as a method of choice for a faster characterization of the *A.S.* Consequently, bridging the gap between automated procedures and machine learning algorithms becomes a necessity to guide and optimize flow processes.

Herein, we present the challenges and procedures towards automated flow chemistry.

- [1] S. V. Ley, D. E. Fitzpatrick, R. J. Ingham, and R. M. Myers, *Angew. Chem. Int. Ed.*, **54**, 3449 (2015).
- [2] B. J. Reizman and K. F. Jensen, *Acc. Chem. Res.*, **49**, 1786, (2016).
- [3] C. A. Nicolaou, I. A. Watson, H. Hu and J. Wang, *J. Chem. Inf. Model.*, **56**, 1253 (2016).
- [4] A. G. Godfrey, T. Masquelin and H. Hemmerle, *Drug Discov. Today*, **18**, 795 (2013).



## Relativistic effects on NMR spectroscopic parameters of atoms belonging to Hydrogen-bonds

**Teresita Santa Cruz and Gustavo A. Aucar**

*Physics Department, Natural and Exact Science Faculty, Northeastern University of Argentina and Institute of Modeling and Innovation on Technology, IMIT CONICET-UNNE, Corrientes, Argentina*

Relativistic effects on NMR spectroscopic parameters were usually considered on molecular systems where hydrogen bonds, HB, were not part of it [1,2]. What we present here is an study on which are the main patterns of such effects on two HB containing systems: malonaldehyde and Schiff basis, where the oxygen atom was replaced by selenium. We analyzed the magnitude and the origin of such parameters in the process of proton transmission.

One of the main relativistic effects on light atoms is due to the proximity of a heavy-atom, an effect named heavy-atom effect on light atoms (HALA) [3,4]. This is mainly of Spin-orbit (SO) type for magnetic shieldings, and until now it was only well-defined for covalent bonds. We show here that relativistic effects on both NMR spectroscopic parameters are transmitted through HB.

For shieldings, when the hydrogen atom that belongs to the HB is close to the heavy atom, SO effects are larger than Spin-free, SF, effects. The opposite happens when that hydrogen is close to the light atom.

When the proton is transferred from a light donor to a heavy acceptor there is an increase of the relativistic effect and also a change of the sign of this effect.

A similar pattern is observed for J-couplings among Se and H, being the SF contribution the largest one in the whole process of hydrogen transference.

- [1] G. A. Aucar, R. H. Romero, A. F. Maldonado, *Int. Rev. on Phys. Chem.* **29**, 1(2010).
- [2] P. Pyykkö, *Chem. Rev.* **112**, 371 (2012).
- [3] P. Pyykkö, A. Görling, and N. Rösch, *Mol. Phys.* **61**, 195 (1987).
- [4] M. Kaupp, O. L. Malkina, V. G. Malkin, and P. Pyykkö, *Chem. Eur. J.* **4**, 118 (1998).

Mechanisms of surface O removal by H<sub>2</sub> and CO activation on Fe and Co surfaces

Shaoli Liu and Haijun Jiao

*State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, Shanxi 030001, China;**Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Strasse 29a, 18059 Rostock, Germany ([haijun.jiao@catalysis.de](mailto:haijun.jiao@catalysis.de))*

Water chemistry on solid surfaces is of central importance to a broad range of scientific and technological processes, such as corrosion, electrochemistry, nanoparticle self-assembly, environmental chemistry, lubricants and heterogeneous catalysis. However, molecular mechanisms of water interaction with solid-state surfaces are poorly understood. An atomic level investigation into water-metal interaction is necessary for understanding the mechanisms of many heterogeneous catalytic reactions. On the basis of DFT and atomistic thermodynamics we studied H<sub>2</sub>O dissociative adsorption on Fe(110), Fe(100) and Fe(111) surfaces; and different mechanisms as well as surface OH and O have been found. For the water-gas shift reaction on these surfaces no BEP relationship can be found. In addition, surface O removal by H<sub>2</sub> and CO the activation on several iron cobalt surfaces has been investigated; and the mechanisms depend on Co crystal phases. These results provide the basis for understanding the experimental observation.

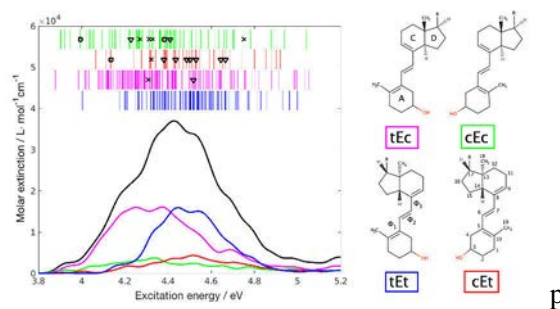


Figure 1: Wavelength and conformational dependency of tachysterol photochemistry [3].

## The quantum biology of vitamin D – Insights from non-adiabatic dynamics

**Enrico Tapavicza<sup>1</sup>, Travis Thompson<sup>1</sup>, Cecilia Cisneros<sup>1</sup>, Adam Smith<sup>1</sup>, Noel Baluyot<sup>1</sup>**

<sup>1</sup>*Department of Chemistry and Biochemistry, California State University, Long Beach, 1250 Bellflower Blvd, Long beach, USA*

The main vitamin D source for humans is its generation by the sun's ultraviolet (UV) light. Oral administration of large vitamin D quantities can lead to an overdose, which affects negatively many regulation cycles in our body. In contrast, vitamin D overproduction due to extended sun exposure has never been observed [1]. A complex network of vitamin D photo isomers that are connected by reversible chemical and photochemical reactions in our skin prevents vitamin D overproduction. The self-regulation mechanism is still under debate [1]. An important feature is the characteristic wavelength dependent photochemistry: long-wavelength UV light induces different photo reactions than short-wavelength UV light. As a consequence, the distribution of photo isomers depends on day time and season. To understand the vitamin D photoequilibrium, we apply non-adiabatic molecular dynamics simulations [2] to study the photo dynamics of several vitamin D related reactions. Our study [3] confirms a recent hypothesis [4] that vitamin D can be formed from tachysterol at long-wavelength UV light.

- [1] MacLaughlin, J.; Anderson, R.; Holick, M. *Science* **1982**, *216*, 1001–1003; van Dijk, A.; den Outer, P.; van Kranen, H.; Slaper, H. *Photochem. Photobiol. Sci.* **2016**, *15*, 896–909.
- [2] Tapavicza, E.; Meyer, A. M.; Furche, F. *Phys. Chem. Chem. Phys.* **2011**, *13*, 20986.
- [3] Cisneros, C., Thompson, T., Baluyot, N., Smith, A. C., Tapavicza, E. *Phys. Chem. Chem. Phys.* **2017**, *19*, 5763.
- [4] Andreo, K. Generation of previtamin D3 from tachysterol3: A novel approach for producing vitamin D3 in the winter. Ph.D. thesis, Boston university, **2015**.

## Dual structure-based approach towards the design of inhibitors of the Dengue virus envelope protein

**Emilse S. Leal<sup>1,‡</sup>, M. Gabriela Aucar<sup>2,3,‡</sup>, Leopoldo G. Gebhard<sup>4</sup>, María J. Pascual<sup>5</sup>, Andrea V. Gamarnik<sup>4</sup>, Claudio N. Cavasotto<sup>2,\*</sup>, Mariela Bollini<sup>1,\*</sup>**

<sup>1</sup>Laboratory of Medicinal Chemistry, Centro de Investigaciones en Bionanociencias (CIBION)-CONICET, Godoy Cruz 2390, Ciudad de Buenos Aires, Argentina

<sup>2</sup>Laboratory of Computational Chemistry and Drug Design, Biomedicine Research Institute of Buenos Aires - CONICET - Partner Institute of the Max Planck Society, Godoy Cruz 2390, Ciudad de Buenos Aires, Argentina

<sup>3</sup>Physics Department, Natural and Exact Science Faculty, Northeastern University of Argentina and Institute of Modelling and Innovation on Technology (IMIT)-CONICET, Avenida Libertad 5460, Corrientes, Argentina

<sup>4</sup>Fundación Instituto Leloir-CONICET, Av. Patricias Argentinas 435, Ciudad de Buenos Aires, Argentina

<sup>5</sup>Instituto de Investigaciones Biotecnológicas, Universidad Nacional de San Martín, CONICET, Av. 25 de Mayo y Francia, San Martín, Prov. de Buenos Aires, Argentina

<sup>‡</sup>Equally contributed to this work; <sup>\*</sup>To whom correspondence should be addressed

Dengue is a mosquito-borne viral disease that has become a major public health concern worldwide in recent years. At present, dengue is endemic in many popular tourist destinations in Latin America, Southeast Asia and the Pacific islands.<sup>1</sup> However, no clinically approved antiviral therapy is available. The first dengue vaccine has been recently approved and licensed in six countries, but it was reported to be 60% effective and not to generate immunity against all serotypes reported. To satisfy this unmet medical need for an antiviral therapy, both industry and academia have taken multiple approaches to develop anti dengue virus agents. Entry of the dengue virus into a host cell is mediated by its major envelope protein, *E*. The crystal structure of the *E* protein reveals a hydrophobic pocket occupied by the detergent n-octyl- $\beta$ -D-glucoside ( $\beta$ -OG) lying at a hinge region between domains I and II.<sup>2</sup> Therefore, the *E* protein is an attractive target for the development of antiviral agents. We used *in silico* structure-based virtual screening and *de novo* design approaches to identify small-molecules that likely bind to the  $\beta$ -OG binding site. Twenty-three structurally different compounds were selected from docking-based virtual screening and ten compounds emerging from *de novo* design were synthesized. The antiviral activity of the compounds was evaluated using an assay based on a luciferase-expressing dengue reporter virus. Six compounds showed antiviral activity in the 3-10  $\mu$ M range and displayed a good therapeutic index. Based on their antiviral potency and selectivity, these compounds will be subject of a more detailed and elaborate virological study to gain insights into the precise molecular mechanism of action.

[1] <http://www.who.int/mediacentre/factsheets/fs117/es/>.

[2] Modis, Y.; Ogata, S.; Clements, D.; Harrison, S. C. *Proc. Natl. Acad. Sci. U. S. A.* **2003**, *100*, 6986–6991.

## Benchmark noncovalent interaction energies: balancing databases and improving dispersion damping functions

Konrad Patkowski<sup>1</sup>

<sup>1</sup>*Department of Chemistry and Biochemistry, Auburn University, 179 Chemistry Building, Auburn, AL 36849, USA*

Databases of benchmark intermolecular interaction energies have become an indispensable tool for both the assessment of existing approaches (DFT, wave function, or (semi)empirical) and the development of new approximations (parameterized density functionals, spin component scaling, ...). The “gold standard” CCSD(T) approach is the method of choice for generating accurate benchmark data, and the best strategies for obtaining basis set-converged values have been thoroughly investigated. However, the predictive power of benchmark databases depends just as much on the accuracy of individual results as on the selection of complexes and configurations making up the entire dataset. The recent development of “third-generation” benchmark databases highlights the need for including diverse interaction types (as classified by symmetry-adapted perturbation theory), diverse intermolecular separations, and diverse angular orientations (both favorable and unfavorable). In contrast, most of the existing benchmark databases are biased towards van der Waals minima and longer distances as well as towards optimal angular orientations. Trying to improve the diversity and balance of different separations, orientations, and interaction types, we arrive at a new database [1] composed of 1526 structures in the training set and 6773 more in the validation set. As the first application of this database, we revisit the problem of determining damping parameters for Grimme’s “DFT plus dispersion” (DFT-D3) variants, as these 2-3 functional-dependent coefficients were originally fitted to a highly limited set of benchmark data. Sticking to 3 damping parameters and preserving (or slightly extending) the original forms of -D3 damping functions, we were able to reduce the average DFT-D3 errors by about a quarter and to substantially alleviate (but not eliminate) the inaccuracies in the mildly repulsive region of the potential energy surfaces. However, the new database presents a particularly attractive venue for a further improvement of dispersion damping functions, going beyond the established functional forms. As a first step in this direction, we explore linear combinations of error functions as approximations to an arbitrary increasing function of interatomic distance as well as map out the optimal damping function by piecewise interpolation.

- [1] D. G. A. Smith, L. A. Burns, K. Patkowski, and C. D. Sherrill, *J. Phys. Chem. Lett.* **7**, 2197 (2016).

## Explaining the NMR spectrum of the active site of photoactive yellow protein

Phillip Taenzler<sup>1</sup>, Keyarash Sadeghian<sup>1</sup>, Christian Ochsenfeld<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of Munich (LMU) Butenandtstrasse 7,  
D-81377 Munich, Germany*

We report our theoretical findings on the NMR properties of the hydrogen bond network around the active site of photoactive yellow protein (PYP), a bacterial photoreceptor to short-wavelength light. A previously published neutron diffraction structure of PYP [1] featured an unusually short hydrogen bond between PYP's chromophore, *p*-coumaric acid, and the nearby glutamate-46, in which the proton was found at the midpoint between the donor and acceptor groups. This discovery led to both theoretical and experimental investigations into the properties of the hydrogen bond network, with particular emphasis on its NMR properties. However, theoretical and experimental results achieved little concordance. Therefore, we report our discovery of a rapid conformational exchange mechanism in the active site of PYP, which controls the NMR shifts of the participating hydrogen bonds. It is only by considering this dynamical behavior of the active site that the experimentally measured NMR shifts [2] of the hydrogen bond network can be explained [3].

- [1] S. Yamaguchi *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **106**, 440 (2009).
- [2] P. A. Sigala, M. A. Tsuchida, D. Herschlag, *Proc. Natl. Acad. Sci. U.S.A.* **106**, 9232 (2009)
- [3] P. J. Taenzler, K. Sadeghian, C. Ochsenfeld, *J. Chem. Theory. Comput.* **12**, 5170 (2016)

## Charge Transfer of a prokaryotic (6-4) Photolyase PhrB

Daniel Holub,<sup>1</sup> Tomáš Kubař,<sup>1</sup> Marcus Elstner,<sup>1</sup> Natacha Gillet<sup>1</sup>

<sup>1</sup>*Department for Theoretical Chemical Biology, Institute for Physical Chemistry,  
Karlsruhe Institute for Technology, Kaiserstr. 12, 76131, Karlsruhe, Germany*

Photolyases are light sensitive enzymes and their main task is the binding and repair of damaged DNA. This function involves several electron transfer (ET) steps, which activate a non-covalent bound FAD cofactor and carry an electron to the damage in the DNA. Quantum dynamics simulations of ET use a QM/MM approach in which the traveling charge and some selected sites e.g. amino acids are calculated with a QM-method (DFTB) and coupled to the rest of the system being propagated with MM methods.

Reaction times for several ET steps in a photolyase, PhrB of *Agrobacterium fabrum*, were calculated and compared to other proteins of this family. The same simulations were performed for mutations of PhrB to indicate the correlation between specific amino acids and the ET.

The product of these ET processes are systems with separated charges which force the protein and the environment to adapt. This leads to several processes e.g. proton transfer reactions or structural changes in the protein which will also be described and compared to experimental studies.

## Quantum Vibrational Spectroscopy of Biomolecules using *ab initio* Classical Separable Potentials

Barak Hirshberg<sup>1</sup>, R. Benny Gerber<sup>1,2</sup>

<sup>1</sup>*Institute of Chemistry and the Fritz Haber Center for Molecular Dynamics, the Hebrew University, Jerusalem, 9190401, Israel*

<sup>2</sup>*Department of Chemistry, University of California, Irvine, CA 92697, USA*

Describing the quantum dynamics of molecules that contain more than 5-6 atoms remains one of the most difficult challenges of theoretical chemistry. While treating the motion of the atoms classically is a very good approximation for heavier atoms and higher temperatures, vibrational spectroscopy is an example in which a quantum dynamical description is often essential. In addition, it is one of the strictest tests for the quality of the potential energy surface (PES). In order to calculate the vibrational spectrum of large molecules quantum mechanically, we recently developed the *ab initio* CSP (AICSP) method<sup>1,2</sup>.

The method extends the CSP method<sup>3</sup> to use *ab initio* PES for the calculation of quantum anharmonic spectra. It is a separable method, which assumes each mode evolves in time under the influence of an effective potential obtained from classical *ab initio* molecular dynamics simulations. These potentials implicitly couple each mode to all other normal modes of vibration. We test AICSP using MP2 and  $\omega$ B97X-D potentials for the vibrational spectroscopy of H-X stretching modes of amino acids (proline, alanine and glycine) as well as the guanine-cytosine base-pair, with very good agreement with experimental results. The tests suggest that the method can be applied successfully to larger biomolecules, such as peptides or small proteins. In addition, the method can be used to calculate vibrational lineshapes and linewidths as well as time-dependent spectroscopy.

[1] B. Hirshberg, L. Sagiv, and R. B. Gerber J. Chem. Theory Comput. 13 (2017) 982–991.

[2] B. Hirshberg and R.B. Gerber Advances in Quantum Chemistry, Academic Press, Volume 75, 2017, 1–26, ISSN 0065-3276, <http://doi.org/10.1016/bs.aiq.2017.01.002>.

[3] P. Jungwirth and R.B. Gerber The Journal of Chemical Physics (1995) 102, 6046.



**Studying the nature of hydride transfer and its role in the enzymatic catalysis.****R. García-Meseguer<sup>1</sup>, D. Laage<sup>2</sup>, J. T. Hynes<sup>2</sup> and I. Tuñón<sup>1</sup>**<sup>1</sup> *Departamento de Química Física, Universidad de Valencia, 46100 Burjassot, Spain.*<sup>2</sup> *Departament de Chimie, École Normale Supérieure, 75005 Paris, France.***Abstract**

Hydrogen transfer reactions are chemical processes of undeniable importance in chemistry and biology. These reactions involve the transfer of a light particle associated to charge transfer between the reacting fragments. Thus, these processes may simultaneously involve quantum tunneling and a strong coupling between the chemical system and the environment. The simulation of these reactions is challenging due to the importance of both nuclear and electronic quantum effects, as well as the effects that the environmental degrees of freedom can have in the reaction.

Formate Dehydrogenase (FDH) is an enzyme that catalyzes the oxidation of formate to carbon dioxide with the NAD<sup>+</sup> cofactor. The chemical step is the hydride transfer from formate to the cofactor. This study is based in the implementation of a new environmental coordinate for QM/MM simulations defined as the relaxed energy gap between the states resulting from the hydride transfer between the donor and acceptor atoms.

This coordinate allows the quantization of the motion not only for the transferred hydride but also of the secondary hydrogen atom bonded to the acceptor atom, which moves simultaneously with the primary hydrogen. The transition state defined according to this coordinate shows a broad distribution of donor-acceptor distances where the hydride transfer can take place in different regimes: over the barrier and through the barrier.[1] Rate constant and Kinetic Isotope Effects Have been evaluated taking into account these different regimes using an adequate expression for the transition between states. These results were compared with experimental results and with theoretical results obtained using the standard approximation.

[1] D. Borgis, J. T. Hynes *J. Phys. Chem.* **1996**, *100*, 1118-1128.

## Insights into the Photochromism of a Red/Green Cyanobacteriochrome

Christian Wiebeler, Aditya G. Rao, Igor Schapiro

*Fritz Haber Center for Molecular Dynamics Research, Institute of Chemistry, The Hebrew University of Jerusalem, Israel*

Cyanobacteriochromes (CBCRs) are promising candidates for the use as photoswitches in biotechnological applications, owing to their photochromism, compactness and spectral diversity. In case of Slr1393, one isomer absorbs red light ( $P_R$ ) and the other one green ( $P_G$ ) (Fig. 1 B). The two forms can be interconverted into each other by light illumination. Slr1393 binds phycoerythrin (PCB) as chromophore and the crystal structures of both forms have been obtained recently. Comparing PCB from both structures shows that one double bond isomerization occurs during the photoconversion (Fig. 1 A). In this contribution, results of quantum chemical and hybrid QM/MM calculations of the  $P_R$  and  $P_G$  forms of Slr1393 will be presented. In order to understand the photophysical properties, quantum chemical calculations for PCB were performed. This is extended by wave function analysis and QM/MM investigations of the protein to obtain further insights on the molecular level. In addition, the vibronic spectrum for PCB in the  $P_R$  form is presented explaining the fine structure of the measured absorption. Finally, first results regarding the photochemistry of the truncated PCB chromophore in gas phase will be shown. The study follows an approach recently used [1] and is based on Tully's Fewest Switches Surface Hopping. It demonstrates that the explicit treatment of the protein environment is needed to understand the photochemistry of Slr1393.

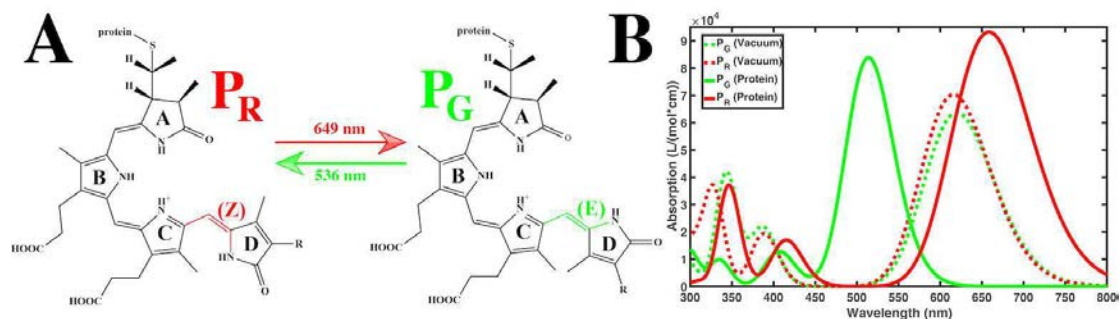


Figure 1: (A) Reaction scheme of PCB photoisomerization, the wavelengths refer to the experimental absorption maxima; (B) Calculated absorption for the  $P_R$  (red) and  $P_G$  (green) forms of PCB determined for vacuum (dotted) and protein geometry (solid).

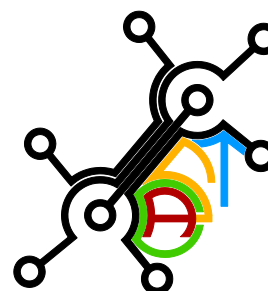
[1] C. Wiebeler *et al.*, *Phys. Chem. Chem. Phys.* **16**, 14531 (2014).

## Global optimization, analysis and simulation – the recent developments within the CAST program

**Daniel Bellinger<sup>1</sup>, Dustin Kaiser<sup>1</sup>, Susanne Sauer<sup>1</sup>, Bastian Michels<sup>1</sup>, Michael Prem<sup>1</sup>, Julian Erdmannsdörfer<sup>1</sup>, Sara Wirsing<sup>1</sup> and Bernd Engels<sup>1</sup>**

<sup>1</sup> *Institut für Phys. und Theor. Chemie, Universität Würzburg, Emil-Fischer-Straße. 42, 97074 Würzburg, Germany*

The CAST (Conformational Analysis and Search Tool)[1] contains efficient global optimization routines based on a combination of basin hopping and Tabu Search[2-3], and reaction path search approaches which combine the Nudged Elastic Band (NEB)[4] with the PathOpt[5-6] approach. It also allows MD and MC simulations, e.g. to perform free energy perturbation calculations (FEP). By its modular conception, the implemented algorithms can be easily applied employing different energy-calculating methods ranging from different force fields up to fast DFT calculations with Terachem.



The program was recently extended by the following new features: An exciton modelling approach, a new available energy interface (Gaussian09), a modified FEP routine, Principal Component Analysis (PCA)[7] and new possibilities for reaction pathway (RP) determination. The modified FEP method tries to decrease the computational effort by partitioning the system into active and inactive regions. To analyze and characterize MD or MC simulations we implemented a PCA based approach. For RP optimizations CAST now offers several additional NEB methods. In the case of exciton modelling the approach which was developed by Brückner et al.[8-9] is integrated within CAST.

[1] C. Grebner, J. Becker, D. Weber, D. Bellinger, M. Tafipolski, C. Brückner, B. Engels, *J. Comput. Chem.* **35**, 1801 (2014).

[2] C. Grebner, J. Becker, S. Stepanenko, B. Engels, *J. Comput. Chem.* **32**, 2245 (2011).

[3] C. Grebner, J. Kästner, W. Thiel, B. Engels, *J. Chem. Theo. Comp.* **9**, 814 (2013).

[4] G. Henkelman, B. P. Uberuaga, H. Jónsson, *J. Chem. Phys.* **113**, 9901 (2000).

[5] C. Grebner, L. P. Pason, B. Engels, *J. Comp. Chem.* **34**, 1810 (2013).

[6] D. Weber, D. Bellinger, B. Engels, *Methods in Enzymology* **578**, 145 (2016).

[7] A. Altis, P. H. Nguyen, R. Hegger, G. Stock, *J. Chem. Phys.* **126**, 244111 (2007)

[8] C. Brückner, F. Würthner, K. Meerholz, B. Engels, *J. Phys. Chem. C* **121**, 4 (2017).

[9] C. Brückner, F. Würthner, K. Meerholz, B. Engels, *J. Phys. Chem. C* **121**, 26 (2017)

## Dispersion-Corrected DFT Study of Enantiospecific Adsorption of Amino Acids on Hydroxylated Quartz Surfaces

Alastair Price<sup>1</sup>, and Erin R. Johnson<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Dalhousie University, 6274 Coburg Road, Halifax, Canada*

The chirality of amino acids is an important issue facing modern science with a further need to understand how controlled growth of enantiopure crystals can be achieved experimentally. <sup>[1]</sup> Hydroxylated quartz surfaces have been shown to preferentially bind specific enantiomers of amino acids, making it suitable for enantiospecific separations. <sup>[2,3]</sup> We extend the current understanding of the interaction of amino acids with these surfaces by using dispersion-corrected DFT methods, e.g., B86bPBE-XDM.<sup>[4]</sup> In addition, we contrast the use of planewave approaches and low cost methods to perform these calculations. This work can be used as a stepping stone to provide further insight into how the amino acid crystal interacts with this surface.

[1] A. J. Gellman and D. S. Sholl, *AIChE* **55**, 2484 (2009).

[2] J. W. Han and D. S. Sholl, *Langmuir* **25**, 10737 (2009).

[3] J. W. Han and D. S. Sholl, *Phys. Chem. Chem. Phys.* **12** 8024 (2010).

[4] A. Otero-de-la-Roza, and E. R. Johnson, *J. Chem. Phys.* **136**, 174109 (2012).

## Minimum Energy Path Calculations Accelerated with Gaussian Process Regression

Vilhjálmur Ásgeirsson<sup>1</sup>, Freyja B. Dagbjartsdóttir<sup>1</sup>, Olli-Pekka Koistinen<sup>1,2,3</sup>,  
Aki Vehtari<sup>2,3</sup>, Hannes Jónsson<sup>1,3</sup>

<sup>1</sup>*Science Institute and Faculty of Physical Sciences, University of Iceland, Dunhagi 3, Reykjavík, Iceland*

<sup>2</sup>*Department of Computer Science, Helsinki Institute for Information Technology, Aalto University, Espoo, Finland*

<sup>3</sup>*Department of Applied Physics, Aalto University, Finland*

The minimum energy path (MEP) connecting two local minima on a potential energy surface (PES) represents a transition path of maximal statistical weight, and the rise in energy along the path provides an estimate of the activation energy for the transition. The nudged elastic band (NEB) method[1] is a commonly used method for finding MEPs. There, paths are represented by a discrete set of system images connected by springs to control the spacing of the images. Starting with some initial path, the perpendicular component of the gradient and the parallel component of fictitious spring force are then collectively zeroed for all the intermediate images to converge on the nearest MEP. In tandem, a climbing image can be used to obtain rigorous convergence on the maximum along the path, a first order saddle point on the PES. NEB is routinely employed in combination with electronic structure methods, where a single calculation typically involves on the order of a hundred energy and gradient calculations per image to reach convergence. The calculations, therefore, require large computational resources. We have accelerated NEB calculations with Gaussian process regression (GPR)[2, 3]. An approximate energy surface (AES) is constructed locally near the path and refined iteratively by training the model with previous energy and gradient evaluations. The NEB calculations are performed on the AES and the images relaxed to new positions in each GPR iteration. Additional energy and gradient calculations are then carried out and fed to the GPR training set until convergence to the true MEP is reached. GPR is found to reduce the number of energy and gradient calculations in NEB calculations by an order of magnitude in well documented benchmark problems.[3]

- [1] G. Henkelman, B. P. Uberuaga, H. Jónsson, *J. Chem. Phys.* **13**, 9901 (2000).
- [2] O-P. Koistinen, E. Maras, A. Vehtari, H. Jónsson, *Nanosystems: Phys. Chem. Math.* **7**, 925 (2016).
- [3] O-P. Koistinen, F. B. Dagbjartsdóttir, V. Ásgeirsson, A. Vehtari, H. Jónsson, *J. Chem. Phys.* (submitted, 2017).

**Theoretical investigation into the enzymatic excision mechanism in AP endonuclease (Ape1)****Hossein Batebi, Petra Imhof.***Department Of Physics, Freie Universität Berlin, Arnimallee 14, Berlin, Germany*

There is a plethora of studies looking at DNA repair systems, base-excision repair, nucleotide-excision repair, mismatch repair and double-strand break repair. In this project, we seek greater insights into base excision repair system. We investigate the mechanism by which human AP endonuclease cleaves the DNA backbone at abasic sites, the products of base excision by DNA glycosylases. AP endonuclease requires a metal cofactor to be functional. However, the number of metal ions necessary for catalysis nor their precise role is known. In order to elucidate the enzymatic mechanism of AP endonuclease, we have performed reaction path calculations for a number of different mechanisms. In addition, molecular dynamics simulations have been successfully applied to study the role of AP-endonuclease (Ape1) active site residues in stabilization of the enzyme-DNA substrate complex.

## Steering Orbital Optimization out of Local Minima and Saddle Points Toward Lower Energy.

Alain C. Vaucher<sup>1</sup>, Markus Reiher<sup>1</sup>

<sup>1</sup>ETH Zürich, Laboratorium für Physikalische Chemie, Vladimir-Prelog-Weg 2, CH-8093 Zürich, Switzerland

In Hartree–Fock and Kohn–Sham density functional theory formalisms, the electronic density and the electronic energy of some molecular system are obtained in an iterative procedure that solves the Roothaan–Hall equations. It is often ignored that these equations can have multiple self-consistent solutions corresponding to different electronic energies. Whereas some of these solutions can be saddle points in the variational space of an electronic wave function approximation, they can also correspond to different local minima, of which only the one with the lowest energy is of interest. Converging to unwanted (i.e. high-energy) solutions delivers incorrect molecular properties, and, accordingly, a misleading description of chemical reactivity. In particular, consecutive calculations of closely related molecular structures, as in *ab initio* molecular dynamics or in interactive explorations of chemical reactivity [2, 3, 4, 5], are also affected by this problem. While stability analysis [6, 7] can detect saddle points by analyzing the local character of solutions, it cannot predict whether a solution is the global minimum or only a local minimum. Also, other methods such as electron smearing [8] can be very useful to improve convergence, but fail to reliably direct incorrect solutions to the one with the lowest energy. In order to detect and avoid convergence to incorrect electronic densities, we introduce a scheme relying on a randomized perturbation of the converged molecular orbitals, which is intended to push orbital convergence to other electronic densities (of potentially lower electronic energy) [9].

- [1] R. P. Feynman, *Phys. Rev.* **56**, 340 (1939).
- [2] K. H. Marti, M. Reiher, *J. Comput. Chem.* **30**, 2010–2020 (2009).
- [3] M. P. Haag, M. Reiher, *Int. J. Quantum Chem.* **113**, 8–20 (2013).
- [4] M. P. Haag, M. Reiher, *Faraday Discuss.* **169**, 89–118 (2014).
- [5] M. P. Haag, A. C. Vaucher, M. Bosson, S. Redon, M. Reiher, *ChemPhysChem* **15**, 3301–3319 (2014).
- [6] R. Seeger, J. A. Pople, *J. Chem. Phys.* **66**, 3045–3050 (1977).
- [7] R. Bauernschmitt, R. Ahlrichs, *J. Chem. Phys.* **104**, 9047–9052 (1996).
- [8] V. A. Basiuk, *Int. J. Quantum Chem.* **111**, 4197–4205 (2011).
- [9] A. C. Vaucher, M. Reiher, *J. Chem. Theory Comput.* **13**, 1219–1228 (2017).

## Soft Matter Morphologies with Atomistic Resolution from Coarse-Grain Solvent Evaporation Simulations

**Riccardo Alessandri<sup>1, 2</sup>, Jaakko J. Uusitalo<sup>1, 2</sup>, Alex H. de Vries<sup>1, 2</sup>, Remco W. A. Havenith<sup>1, 3, 4</sup>, Siewert J. Marrink<sup>1, 2</sup>**

<sup>1</sup>*Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*

<sup>2</sup>*Groningen Biomolecular Sciences and Biotechnology Institute, University of Groningen, Nijenborgh 7, 9747 AG Groningen, The Netherlands*

<sup>3</sup>*Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*

<sup>4</sup>*Ghent Quantum Chemistry Group, Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 (S3), B-9000 Gent, Belgium*

Control over the morphology of the active layer of bulk heterojunction (BHJ) organic solar cells is paramount to achieve high efficiency devices. However, no method currently available can predict morphologies for a novel donor:acceptor blend. An approach which allows to reach relevant length scales, retain chemical specificity, mimic experimental fabrication conditions, and which is suited for high-throughput schemes has been proven challenging to find. Here [1], we propose a multiscale method to generate atom-resolved morphologies of BHJs which conforms to these requirements. Coarse-grain (CG) molecular dynamics simulations are employed to simulate the large-scale morphological organization during solution-processing (Figure). The use of CG models which retain chemical specificity translates into a direct path to the rational design of donor and acceptor compounds which differ only slightly in chemical nature. Finally, the direct retrieval of fully atomistic detail is possible through backmapping (Figure, close up), opening the way for improved quantum mechanical calculations addressing the charge separation mechanism. The method is illustrated for the poly(3-hexyl-thiophene) (P3HT):phenyl-C61-butyric acid methyl ester (PCBM) mixture, and found to predict morphologies in agreement with experimental data. The effect of drying rate, P3HT molecular weight and thermal annealing are investigated extensively, resulting in trends mimicking experimental findings. The proposed methodology can help reduce the parameter space which has to be explored before obtaining optimal morphologies not only for BHJ solar cells but for any other solution-processed soft matter device.

- [1] R. Alessandri, J. J. Uusitalo, A. H. de Vries, Remco W. A. Havenith, Siewert J. Marrink, *J. Am. Chem. Soc.* **139**, 3697 (2017).



## Highly accurate dipole transition probabilities in molecules from finite-field relativistic multireference coupled cluster calculations.

**Ephraim Eliav<sup>1</sup>, Timur A. Isaev<sup>2</sup>, Artur Kudrin<sup>3</sup>, Alexander A. Medvedev<sup>3</sup>, Leonid V. Skripnikov<sup>2</sup>, Andrey V. Stolyarov<sup>3</sup>, and Andrei Zaitsevskii<sup>2,3</sup>**

<sup>1</sup>*School of chemistry, Tel-Aviv University, 69978 Tel-Aviv, Israel*

<sup>2</sup>*Department of Innovations, NRC KI – PNPI, 188300 Gatchina, Russia*

<sup>3</sup>*Chemistry Department, Moscow State University, 119991 Moscow, Russia*

Relativistic multireference coupled cluster (CC) methods are recognized as a robust and accurate tool for evaluating electronic transition energies in molecules containing heavy atoms. However, CC methods do not provide an explicit representation of many-electron wavefunctions, so that the direct estimate of the off-diagonal electric dipole matrix elements is not straightforward. The procedures employed to compute these entities through constructing transition density matrices are quite cumbersome and their implementation depends on the particular form of multireference CC theory. An attractive and universal alternative approach consists of evaluating transition dipoles by the finite-field technique [1], exploiting the approximate off-diagonal Hellmann-Feynman-like relations for effective operators and effective Hamiltonian eigenstates. This approach is based on the response of model space parts of many-electron wavefunctions to an external electric field. Nevertheless, the resulting transition moments incorporate implicitly the bulk of the contributions from the remainder (outer-space) part of these wavefunctions.

We report here an application of the finite-field technique in the frames of relativistic Fock-space coupled cluster methods to atoms, heavy alkali dimers, group II element halides and hydroxides, as well as to exciplexes formed by heavy alkali metal and rare gas atoms. The dependence of the resulting transition dipoles and lifetimes on the model space size is estimated and the stability of the finite-difference approximations for the derivatives with respect to the applied electric field strength is analyzed. The impact of effective spin-orbit interactions on radiative properties of the studied molecular systems is highlighted. The frontier implementation of computed transition probabilities for optimizing the laser synthesis of ultracold molecules and alkali metal - rare gas laser media is discussed.

The finite-field technique was implemented on the top of the DIRAC15 code [2].

[1] A. Zaitsevskii, A. P. Pychtchev, *Eur. Phys. J. D* **4**, 303 (1998).

[2] R. Bast, T. Saue, L. Visscher, H. J. Aa. Jensen, et al., DIRAC, a relativistic *ab initio* electronic structure program, release DIRAC15 (2015).

**Trying to unravel the mechanisms of cytotoxicity for the  
[Mo( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Br(CO)<sub>2</sub>(phen)] complex: Intercalation vs. Groove Binding**

**Adrià Gil<sup>1\*</sup>, Sawssen Elleuchi<sup>1,2</sup>, Khaled Jarraya<sup>2</sup>, Maria José Calhorda<sup>1\*</sup>**

<sup>1</sup>*Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa,  
Campo Grande 1749-016 Lisboa, Portugal*

<sup>2</sup>*Laboratory of Inorganic Chemistry UR11RS73, Faculty of Sciences of Sfax, 3000, Sfax,  
Tunisia*

**Abstract:** The interaction of the [Mo( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Br(CO)<sub>2</sub>(phen)] metal complex [1] with DNA has been studied at computational level by docking, recently developed semiempirical methods including dispersion and QM/MM methods. The [Mo( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Br(CO)<sub>2</sub>(phen)] metal complex exists as two main isomers in solution. Indeed, in one isomer phenanthroline (phen) is coordinated in the equatorial plane (Eq), whereas in the other one N of the phen is coordinated in an equatorial position and the other one in an axial position (Ax). Although the Eq structure is more stable, there is not a great difference between the energy of the isomers and we studied both systems, Eq and Ax, interacting with DNA trying to explain the experimentally found cytotoxicity.[1] We also took into account two different modes of interaction with DNA, that is, groove binding and intercalation, since such competition has been recently described in the bibliography for metal complexes with flat ligands interacting with DNA.[2-4] PM6-DH2 semiempirical method including dispersion and QM/MM methods by using M11L/6-31+G(d,p):AMBER were calibrated with the intercalated 1n37 structure of PDB and were observed to perform very well. On the other hand, for interaction of [Mo( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Br(CO)<sub>2</sub>(phen)] metal complex with the (AGACGTCT)<sub>2</sub> DNA octamer, it is observed that the [Mo( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Br(CO)<sub>2</sub>(phen)] metal complex prefers the intercalation rather than the groove binding for both isomers Eq and Ax. Moreover, also in both cases, intercalation via minor groove is more favored than through the major groove. However, it must be said that for the Ax isomer, although the most stable structure corresponds to an intercalated system through the minor groove, we found more structures intercalating via major groove in our analysis with the 100 most representative structures of the docking conformational search.

[1] D. Bandarra, M. Lopes, T. Lopes, J. Almeida, M. S. Saraiva, M. Vasconcellos-Dias, C. D. Nunes, V. Félix, P. Brandão, P. D. Vaz, M. Meireles, M. J. Calhorda, *J. Inorg. Biochem.* **104**, 1171 (2010).

[2] A. Mukherjee, R. Lavery, B. Bagchi, J. T. Hynes, *J. Am. Chem. Soc.* **130**, 9747 (2008).

[3] W. D. Sasikala and A. Mukherjee, *Phys. Chem. Chem. Phys.* **15**, 6446 (2013).

[4] D. Franco, A. V. Vargiu, A. Magistrato, *Inorg. Chem.* **53**, 7999 (2014).

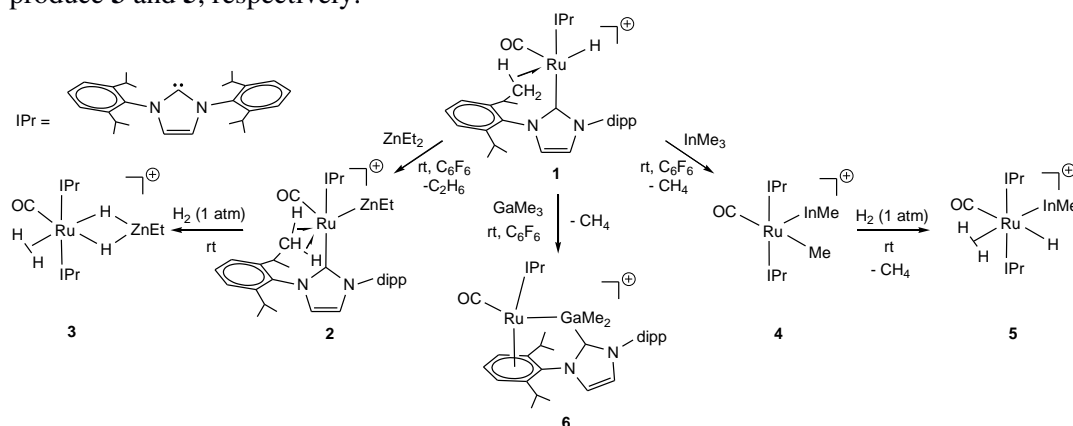
## DFT Study of Heterobimetallic Complexes Derived from the e-deficient Ru-H Complex, $[\text{Ru}(\text{IPr})_2(\text{CO})\text{H}]^+$

Nasir A. Rajabi<sup>1</sup>, Ian M. Riddlestone<sup>2</sup>, John P. Lowe<sup>2</sup>, Mary F. Mahon<sup>2</sup>,  
Stuart A. Macgregor<sup>1</sup>, Michael K. Whittlesey<sup>2</sup>

<sup>1</sup>*Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK*

<sup>2</sup>*Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, U.K*

Heterobimetallic complexes featuring transition metal (TM) and main group (MG) metals show great potential in the activation of small molecules.[1] Experimentally the cationic ruthenium hydride species **1** is a useful precursor to such species through reaction with MG-alkyls. For example, with  $\text{ZnEt}_2$  elimination of ethane produces  $\{\text{Ru}-\text{Zn}\}$  species **2**. [1b] With  $\text{InMe}_3$  methane is lost, but transfer of a second Me group to Ru also occurs to form  $\{\text{Ru}-\text{In}\}$  species **3**. With  $\text{GaMe}_3$  methane is also lost, but in this case the IPr ligand transfers from Ru to Ga to give **6**. Both **2** and **6** then undergo  $\text{H}_2$  activation reactions to produce **3** and **5**, respectively.



DFT calculations have been used to elucidate the formation mechanism of these Ru-MG heterobimetallic complexes. Our calculations show that formation of **2** and **4** involves one alkyl transfer from the MG centre to the Ru and an alkane reductive elimination step on the Ru centre to give the  $\text{Ru}^0\text{-Zn}^{\text{II}}$  and  $\text{Ru}^0\text{-In}^{\text{III}}$  species, respectively. Additionally, for the  $\text{Ru}^0\text{-In}^{\text{III}}$  species, the reductive elimination step induces a second alkyl transfer from the In centre to Ru to produce **4**. In comparison to **2** and **4**, formation of **6** occurs with initial IPr ligand transfer from Ru to Ga followed by Me transfer from the Ga to Ru. Reductive elimination of methane then forms a  $\text{Ru}^0\text{-Ga}^{\text{III}}$  intermediate from which one of the dipp rings of the IPr ligand to the Ga centre gives an  $\eta^6$  interaction with Ru to produce the half-sandwich Ru complex **6**.  $\text{H}_2$  activation across the Ru-Zn bond in **2** occurs homolytically and transfers two hydrides into the bridging position to give **3**. In contrast to **3**,  $\text{H}_2$  activation in **4** proceeds with a sigma-bond metathesis step and forms **5** and methane.

[1] a) A. Maity, T. S. Teets, *Chem. Rev.*, **116**, 8873 (2016). b) I. M. Riddlestone, N. A. Rajabi, J. P. Lowe, M. F. Mahon, S. A. Macgregor, M. K. Whittlesey, *J. Am. Chem. Soc.*, **138**, 11081 (2016).

## Central Fields from Jensen's Form

**Jan Linderberg**

*Institute of Chemistry, Aarhus University, Langelandsgade 140, Aarhus C, Denmark*

Jensen [1] formulated an energy functional for the Fermi-Thomas atom that included the Dirac exchange. A numerical procedure emanating from the finite element approach [2] is developed in order to search approximate solutions to central fields in spherical geometry.

It holds that the energy functional

$$J(q) = \int_0^{\infty} dr \left[ \left( \frac{\mu}{e} - \frac{eZ_n}{r} \right) q + \frac{q\kappa_K}{e} \left( \sqrt{\frac{q}{4\pi e r^2}} \right)^2 - \frac{q\kappa_A}{e} \sqrt{\frac{q}{4\pi e r^2}} + \frac{e^2}{2} \left( \frac{dZ_e}{dr} \right)^2 \right]$$

is stationary for a consistently determined radial charge density  $q = q(r)$  in a central field determined by an external, (nuclear), potential of the form  $eZ_n(r)/r$ . Coefficients  $\kappa_K$  and  $\kappa_A$  define the kinetic and exchange (*Austausch*) energy densities while the last term is the electron density self-interaction,  $q = q(r) = -er[d^2Z_e(r)/dr^2]$ .

A modest implementation of the finite element method represents the derivative  $dZ_e/dr$  as a piecewise linear function

$$\frac{dZ_e}{dr} = \left( \frac{r_j - r}{r_j - r_{j-1}} \right) \frac{\zeta_{j-1}}{h} + \left( \frac{r - r_{j-1}}{r_j - r_{j-1}} \right) \frac{\zeta_j}{h}; \quad r_{j-1} \leq r \leq r_j.$$

All integrals are then accessible analytically and the functional becomes a function of the amplitudes:

$$J(q) \rightarrow J(\zeta_0, \zeta_1, \zeta_2, \dots, \zeta_N).$$

Optimization of the function leads to third degree algebraic equations that provide a marching procedure on the grid of points  $\{r_j \mid j = 0, 1, 2, \dots, N\}$ . Initial and final values warrant attention.

[1] H. Jensen, *Z. Physik.* **89**, 713 (1934), *ibid.* **93**, 232, 1935.

[2] P. G. Ciarlet, *The Finite Element Method for Elliptic Problems* (North-Holland, Amsterdam, 1980)

## A Theoretical Study of CO Dissociation and C-C Bond Formation Mechanism on Fe(710)

Teng Li<sup>1,2,3</sup>, Haijun Jiao<sup>1,4</sup>

<sup>1</sup>*State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, China*

<sup>2</sup>*National Energy Center for Coal to Liquids, Synfuels China Co., Ltd., Huairou District, Beijing, 101400, China*

<sup>3</sup>*University of Chinese Academy of Sciences, No. 19A Yuquan Road, Beijing, 100049, P. R. China*

<sup>4</sup>*Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein Strasse 29a, 18059 Rostock, Germany*

**Abstract:** Pure metals are often used as the simple model to investigate the mechanisms of Fischer-Tropsch Synthesis both experimentally and theoretically. However, the perfect surfaces of Fe(110), Co(0001) and Ru(0001) are inactive for CO dissociation [1] and prefers methanol formation on Co(0001) [2]. It is necessary to take the open or stepped surfaces into consideration. Spin-polarized DFT has been used to study CO dissociation by direct or H-assisted path, CH<sub>x</sub> (x = 1, 2) self-coupling and CO insertion on Fe(710). Our computational results show that CO prefers the fourfold site above the stepped site [3] and is more likely to break C-O bond directly rather than H-assisted activation. On Fe(710), CH<sub>4</sub> formation is neither kinetically nor thermodynamically favored. Among CH<sub>x</sub> hydrogenation (CH+H → CH<sub>2</sub>, CH<sub>2</sub>+H → CH<sub>3</sub>) with self-coupling (CH+CH → C<sub>2</sub>H<sub>2</sub>, CH<sub>2</sub>+CH<sub>2</sub> → CH<sub>2</sub>CH<sub>2</sub>) and CO insertion (CH+CO → HCCO, CH<sub>2</sub>+CO → H<sub>2</sub>CCO), HC and CO coupling is most likely. Finally, CO prefers direct dissociation and insertion into surface CH group for C-C formation on Fe(710).

[1] M. R. Elahifard, M. P. Jigato, J. W. Niemantsverdriet. *ChemPhysChem*. 13, 89 (2012).

[2] S. Liu, Y. Li, J. Wang, H. Jiao. *Catal. Sci. Technol.* 6, 8336 (2016).

[3] D. C. Sorescu. *J. Phys. Chem. C*. 112, 10472 (2008).

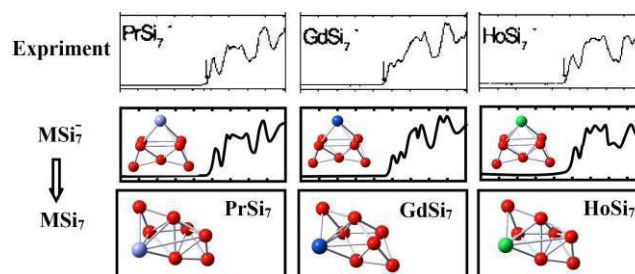
# Structural Assignment, Electronic and Magnetic Properties of $\text{Si}_7\text{M}^{0-}$ with $\text{M} = \text{Pr}, \text{Gd}, \text{Ho}$

Tran Dieu Hang, Huynh Minh Hung and Minh Tho Nguyen<sup>1</sup>

*Department of Chemistry, University of Leuven, B-3001 Leuven, Belgium*

## Abstract:

The ground state geometries of the neutral and anionic lanthanide-metal-doped silicon clusters  $\text{Si}_7\text{M}^{0-}$  with  $\text{M} = \text{Pr}, \text{Gd}, \text{Ho}$  were determined by quantum chemical computations and a detailed comparison with previous experimental photoelectron spectra. The hybrid B3LYP functional is found to be suitable for predicting the ground electronic states of lanthanide-metal-doped silicon clusters and reproducing their photoelectron spectra. All the most stable isomers are substitutive derivatives of the bicapped octahedron shape of pure  $\text{Si}_8^{0-}$  clusters. The bicapped octahedron  $\text{Si}_7\text{M}$  is generated by substituting one silicon atom on the  $D_{4h}$  planar of octahedron by one M atom. Replacement of a Si atom on the C2 axis of another bicapped octahedron a lanthanide metal atom, where two capping Si atoms are situated in front of opposite triangular face on a side of the central square, gives rise to the anionic  $\text{Si}_7\text{M}^-$ . The limited participation of f-electrons of the lanthanide metal atoms on the valence electronic structure and thereby on the bonding of  $\text{Si}_7\text{M}^{0-}$  induces high magnetic moments of the doped clusters. As a consequence, not only  $\text{Si}_7\text{M}^{0-}$  but also  $\text{Si}_n\text{Ln}^{0-}$  clusters are expected to be suitable building blocks for assembling silicon-based cluster materials with high magnetism.



[1] Hang, T. D.; Hung, H. M.; Nguyen, M. T, *Phys. Chem. Chem. Phys.* **2016**, 18 (31054).

## Modelling Photoinduced Events and Non-Linear Spectroscopy in Complex Multichromophoric Systems

**Francesco Segatta<sup>1,2,\*</sup>, L. Cupellini<sup>3</sup>, S. Jurinovich<sup>3</sup>, S. Taioli<sup>1</sup>, M. Garavelli<sup>2</sup> and B. Mennucci<sup>3</sup>**

<sup>1</sup>*European Center for Theoretical Studies in Nuclear Physics and Related Areas (ECT\*-FBK), 38123 Trento, Italy*

<sup>2</sup>*Dipartimento di Chimica Industriale "Toso Montanari", University of Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy*

<sup>3</sup>*Dipartimento di Chimica e Chimica Industriale, University of Pisa, via G. Moruzzi 13, 56124 Pisa, Italy*

*\*francesco.segatta2@unibo.it*

Light-Harvesting (LH) Pigment-Protein Complexes in plants and photosynthetic bacteria, constitute the fundamental units through which sunlight is collected. The high complexity of such systems, where multiple interacting chromophores are embedded in a fluctuating protein matrix, makes it extremely difficult to study their response to external excitations. In this respect, non-linear electronic spectroscopies, such as the Two-Dimensional Electronic Spectroscopy (2DES), represent one of the most powerful techniques available [1]: high density of information is obtained, but to accurately disentangle all the measured signals and reach a detailed and reliable map of the energy transfer (ET) routes, it is mandatory to integrate the experimental measurements with theoretical models [2].

Here we introduce a fully Quantum-Chemistry based protocol to simulate and interpret linear and non-linear spectroscopy (2DES) of complex multichromophoric architectures of known structure. The proposed scheme relies on a QM/MM multi-scale approach [3], able to link single chromophore units with the entire molecular aggregate via a so called Frenkel Exciton Hamiltonian. This includes molecular vibrations and environmental fluctuations, eventually delivering the system's manifold of states and their relaxation pathways with very high accuracy. Application to the LH2 test case, employed here as a challenging playground, gives an unprecedented insight into the interpretation of the spectral signatures of the measured 2DES signals.

[1] T. Brixner, J. Stenger, H. M. Vaswani, M. Cho, R. E. Blankenship, G. R. Fleming, *Nature* **434**, 625 (2005).

[2] F. Segatta, L. Cupellini, S. Jurinovich, S. Mukamel, M. Dapor, S. Taioli, M. Garavelli, and B. Mennucci, *J. Am. Chem. Soc.* **139**, 7558 (2017).

[3] C. Curutchet, B. Mennucci, *Chemical Reviews* **117**, 294 (2016).

## Localization errors and controllable sparsity in the coupled-cluster wave function for time-dependent response theory

**R. Glenn, Andrew M. James, T. Daniel Crawford**

*Department of Chemistry, Virginia Tech, Blacksburg, Virginia, U.S.A.*

A time-dependent framework for calculating the response of a large molecular system to an external field is motivated by the fact that the frequency-domain approach requires an efficient large-scale eigenvalue solver. Recent calculations show that the time-dependent framework provides more accurate spectra for higher energies and molecules with a large density of states [1,2]. Reduced scaling approaches to frequency-domain coupled-cluster response theory have shown localization errors and controllable sparsity in the wave function [3]. Here, we compare a time-dependent vs. frequency-dependent framework for the calculation of the linear response and examine the resulting localization errors and sparsity in the ground state wave function. Three different reduced-scaling coupled-cluster methods based upon projected atomic orbitals (PAOs), pair natural orbitals (PNOs), and orbital specific virtuals (OSVs) are employed to calculate the linear response in the time-domain. As a benchmark, we choose pseudo-linear structures such as fluoroalkane chains as well as three-dimensional structures where the localization errors are known to behave significantly differently [3].

- [1] J. J. Goings and X. Li, *J. Chem. Phys.* **44**, 234102 (2016).
- [2] D. R. Nascimento and A. E. DePrince, *J. Chem. Theory Comput.* **12**, 5834 (2016).
- [3] H. R. McAlexander and T. D. Crawford, *J. Chem. Theory Comput.* **12**, 209 (2016).



## Investigating $\pi$ -acid-base interactions of supramolecular cyclic trinuclear coinage metal complexes

Fabian Bohle<sup>1</sup>, Stefan Grimme<sup>1</sup>, Raiko Hahn<sup>2</sup>, Birgit Esser<sup>2</sup>

<sup>1</sup>Mulliken Center for Theoretical Chemistry, Institut für Physikalische und Theoretische Chemie, Universität Bonn, Beringstraße 4, D-53115 Bonn, Germany

<sup>2</sup>Institut für Organische Chemie, Albert-Ludwigs-Universität Freiburg, Albertstr. 21, D-79104 Freiburg, Germany

The detection of small, electron deficient, aromatic compounds is a task directly connected with  $\pi$ -acid-base interactions. To gain deeper understanding of these noncovalent interactions, the association free energies of electron rich cyclic trinuclear gold(I) complexes that are stacked with electron deficient systems are calculated and compared to experiment. In our quantum chemistry standard protocol [1] for calculating association free energies,  $\Delta G_a$  is obtained as the sum of the electronic association energy  $\Delta E$ , thermostistical corrections to free energy (in gas phase)  $\Delta G_{RRHO}^T$  and the solvation free energy  $\Delta \delta G_{solv}^T$ . All Geometries were preoptimized with the newly developed tight binding method GFN-xTB [2] and further refined with the global hybrid functional PBEh-3c [3]. Accurate single-point energies were obtained at the PW6B95- $D3^{ATM}$ /def2-QZVP level. Thermostistical corrections were evaluated at the same level of geometry optimization and solvation free energies were obtained with the implicit solvent model COSMO-RS.

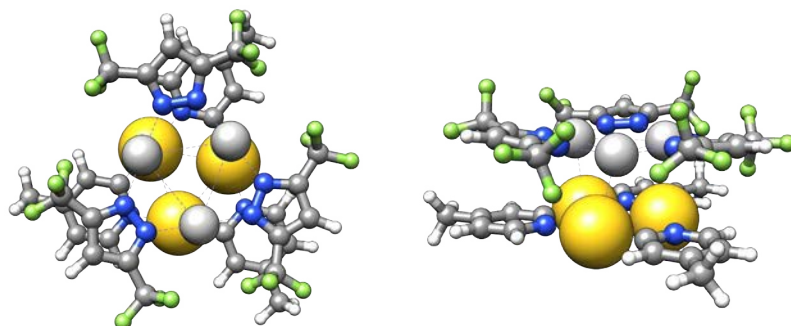


Figure 1: Complex of a pyridinate gold(I)-complex ( $\pi$ -base) stacked with a pyrazolate silver(I)-complex ( $\pi$ -acid), depicting top- and side-view.

- [1] S. Grimme, *Chem. Eur. J.* **18**, 9955-9964 (2012).
- [2] S. Grimme, C. Bannwarth, P. Shushkov, *J. Chem. Theory Comput.* **13**, 1989–2009 (2017).
- [3] S. Grimme, J. G. Brandenburg, C. Bannwarth, A. Hansen, *J. Chem. Phys.* **143**, 054107 (2015).

**Explicitly correlated electronic structure methods:  
progress towards increasing efficiency**

**Travis H. Thompson<sup>1</sup>, Christian Ochsenfeld<sup>1</sup>**

*<sup>1</sup>Department of Chemistry, University of Munich (LMU), Butenandtstr. 7,  
D-81377 Munich, Germany*

Explicitly correlated methods aim to treat the shortcomings of wave function approximations built as Fock space expansions by introducing terms that depend explicitly on interelectronic distances. Such two-electron terms are able to describe short-range correlation much more efficiently than expansions using only one-electron orbitals, leading to relaxed basis set requirements. On the other hand, they lead to more complicated molecular integrals that have only rather recently been made computationally feasible. We review some proven explicitly correlated methods already in widespread use and discuss their advantages compared to traditional methods. We also discuss some techniques recently developed for conquering the challenges that arise in explicitly correlated theories and describe our path towards further increases in efficiency.

## Understanding Chemical Bonding in Terms of Electronic Correlations

**G. Barcza<sup>1</sup>, Sz. Szalay<sup>1</sup>, Ö. Legeza<sup>1</sup>, T. Szilvási<sup>2</sup>, L. Veis<sup>3</sup>, E. Fertitta<sup>4</sup>, B. Paulus<sup>4</sup>**

<sup>1</sup>*"Lendület" Research Group, Wigner Research Centre for Physics, Budapest, Hungary*

<sup>2</sup>*Department of Chemical and Biological Engineering, University of Wisconsin-Madison, US*

<sup>3</sup>*J. Heyrovsky Institute of Physical Chemistry, Prague, Czech Republic*

<sup>4</sup>*Institut für Chemie und Biochemie, Freie Universität Berlin, Germany*

Quantum information theory (QIT) emerged in physics as standard technique to investigate effective models of interacting quantum systems. The success of the method arises the question what we can learn from QIT applying it to molecules which are inherently quantum systems as well [1]. By the rigorous analysis of the central quantities of standard QIT, which describes bonding purely in terms of two-orbital correlations, we identify covalent bond, donor-acceptor dative bond, multiple bond, charge-shift bond indicating unified picture of fundamental chemical models from ab initio [2].

In order to give a better description of more complicated multiple bonds and aromaticity, we introduce the genuine multiorbital correlation theory, consisting of a framework for handling the structure of multiorbital correlations, a toolbox of true multiorbital correlation measures, and the formulation of the multiorbital correlation clustering, together with an algorithm for obtaining that. These make it possible to quantify the correctness of the associated "naive" bonding picture. As proof of concept, we apply the theory for the investigation of the bond structures of several molecules. We show that the non-existence of well-defined multiorbital correlation clustering provides a reason for debated bonding picture of the dicarbon [3].

[1] E Fertitta, B Paulus, G Barcza, Ö Legeza *Phys. Rev. B* **90** (24), 245129 (2014)

[2] T. Szilvási, G. Barcza, Ö. Legeza *submitted to Scientific Reports* arXiv:1509.04241

[3] S. Szalay, G. Barcza, T. Szilvási, L. Veis. Ö. Legeza, *Scientific Reports* **7**, 2237 (2017).

## Proton Coupled Electron Transfer and Competing Mechanisms in Free Radical Reactions in Aqueous Solutions

Ivana Nikšić-Franjić,<sup>1</sup> Iva Džeba,<sup>2</sup> Marija Bonifačić,<sup>1</sup> Aleksandar Sabljčić,<sup>1</sup>  
Ivan Ljubić<sup>1</sup>

<sup>1</sup>Department of Physical Chemistry, Ruđer Bošković Institute, Zagreb, Croatia

<sup>2</sup>Department of Materials Chemistry, Ruđer Bošković Institute, Zagreb, Croatia

Reactions of dehalogenation of haloorganic substrates induced by small  $\alpha$ -hydroxyalkyl and  $\alpha$ -aminoalkyl alkyl free radicals in aqueous solutions are found to exhibit a rich variety of closely competing mechanisms, notably proton-coupled electron transfer (PCET), hydrogen atom transfer (HAT), free radical substitutions, abstractions and additions, etc. We present combined experimental and theoretical studies of the mechanisms and kinetics of reactions between several such free radicals derived from ethanol, 2-propanol, ethylamine, N-ethylmethylaniline, and anionic glycine, with various halogenated organics, such as alkyl-halides, haloacetates, 5-bromouracil, and iodoacetamide. The reactions are conducted in non-buffered and buffered (bicarbonate and phosphate buffer systems) aqueous solutions, in which the free radicals are generated by the process of  $\gamma$ - or pulse radiolysis. We test the predictions of a range of density functionals against the experimental product yields and reaction rate constants. The water solvent is modeled as the polarizable continuum (PCM) with the addition of one explicit water molecule at the most. These reaction systems, while being much simpler than the usual context of PCET (e.g. catalysis, biochemistry), prove to be especially suited for studying this fundamentally important mechanism because the unambiguous fingerprint of the PCET is a radical chain reaction which considerably enhances the dehalogenation yields. Also, the contribution due to the PCET can be handily controlled because it crucially depends on the proton accepting affinity of the buffer anion. Since the main thermodynamic pull for the PCET is the formation of the corresponding carbonyl or imine double bond, the choice of the alcohol (amine) precursor provides yet another means of the reaction control. The extra water molecule is seen to introduce new relevant reaction channels, such as the water assisted PCET. The kinetics of these fast reactions is difficult to model accurately because the dominant channels are typically characterized by the negative apparent activation energies. The best results for the reaction barriers and rate constants are provided by the double hybrid density functionals.

- [1] P. Neta, J. Grodkowski, A. B. Ross, *J. Phys. Chem. Ref. Data* **25**, 709 (1996).
- [2] I. Ljubić, B. Matasović, M. Bonifačić, *Phys. Chem. Chem. Phys.* **15**, 18001 (2013).
- [3] I. Ljubić, A. Sabljčić, M. Bonifačić, *J. Phys. Chem. B* **120**, 11810 (2016).

## Modelling Pt<sup>II</sup>(Ligand) – Amyloid- $\beta$ Interactions: Prediction of Ligand Effects

Matthew Turner<sup>1</sup>, Robert J. Deeth<sup>2</sup>, James A. Platts<sup>1</sup>

<sup>1</sup>*School of Chemistry, Cardiff University, Park Place, Cardiff, UK*

<sup>2</sup>*Department of Chemistry, University of Warwick, Gibbet Hill, Coventry, UK*

Alzheimer's disease (AD) is a neurodegenerative condition associated with progressive cognitive decline in patients. The causes and development of AD are poorly understood, but one hallmark of AD is the presence of amyloid plaques. The early stages of the A $\beta$  aggregation process have therefore become a target for the development of AD-therapeutics [1]. The N-terminal domain of A $\beta$  contains His-rich high-affinity metal binding sites, responsible for physiological coordination of Cu<sup>II</sup>/Zn. One route to AD-therapeutics involves disrupting coordination by using compounds that occupy these binding sites, hindering the A $\beta$  aggregation process. Recently, Barnham *et al.* showed that Pt<sup>II</sup>(phenanthroline) complexes inhibit A $\beta$  aggregation and limit its neurotoxicity *in vitro* [2].

In this work, Ligand Field Molecular Mechanics (LFMM), DFT and semi empirical methods are applied to a series of Pt<sup>II</sup>-Ligand systems binding to the N-terminal domain of the A $\beta$  peptide. Molecular dynamics (LFMM/AMBER) is used to explore the conformational freedom of the peptide fragment, and identifies favourable Pt<sup>II</sup>-binding modes and peptide conformations. Pt<sup>II</sup> coordination depends on the nature of the ligand, providing evidence that binding mode may be controlled by ligand design. Structural analysis of the sampled Pt<sup>II</sup>-A $\beta$  conformations shows that platinum coordination disrupts existing secondary structure in A $\beta$  and promotes formation of ligand-specific turn-type secondary structure. [3][4]

### References:

- [1] D. Valensin, C. Gabbiani, L. Messori, *Coord. Chem. Rev.*, **256**, 2357, (2012).
- [2] K.J. Barnham, V.B. Kenche, G.D. Ciccotosto, D.P. Smith, D.J. Tew, X. Lu, K.Perez, G.A. Cranston, T.J. Johanssen, I. Volitakis, A.I. Bush, C.L. Masters, A.R. White, J.P. Smith, R.A. Cherny, R. Cappai, *Proc. Natl. Acad. Sci. U.S.A.*, **105**, 6813, (2008).
- [3] M. Turner, J.A. Platts and R.J. Deeth, *J. Chem. Theory Comput.*, **12**, 1385, (2016).
- [4] M. Turner, R.J. Deeth and J.A. Platts, *J. Inorg. Biochem.*, **173**, 44, (2017).

## Double residues of response functions in density matrix-based response theory

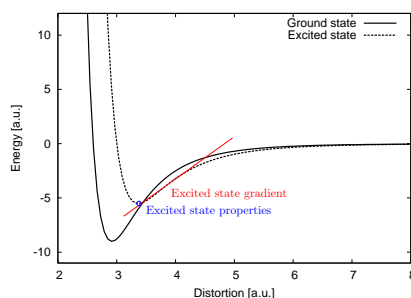
Daniel H. Frieze<sup>1</sup>, Kenneth Ruud<sup>2</sup>

<sup>1</sup>*Institut für Theoretische und Computerchemie, Heinrich-Heine-Universität Düsseldorf,  
Universitätsstraße 1, 40225 Düsseldorf, Germany*

<sup>2</sup>*Centre for Theoretical and Computational Chemistry, University of Tromsø, Hansine Hansens  
veg 18, 9037 Tromsø, Norway*

The calculation of excited state molecular properties such as gradients, dipole gradients and Hessians is a challenge for quantum chemistry due to the complexity of the fundamental expressions which increases dramatically with the property order. In recent years, the framework of density matrix-based response theory has proven to offer a very efficient tool for the calculation of higher-order molecular properties as it can be formulated in an open-ended recursive algorithm[1] which reduces programming effort for higher-order properties to a negligible level. For both response functions (ground state molecular properties)[2] and single residues (transition properties between the ground and excited states)[3, 4] this technique has allowed to study e.g. multidimensional vibrational spectroscopy, multiphoton absorption and multiphoton circular dichroism.

We will now present a first extension of this framework to double residues which will allow for calculations of both excited state molecular properties and transition moments between excited states. This approach requires some changes in the fundamental theory. The first of these will be presented for first- and second-order excited state properties.



- [1] M. Ringholm, D. Jonsson, K. Ruud, *J. Comput. Chem.* **35**, 622 (2014).
- [2] Y. Cornaton, M. Ringholm, O. Louant, K. Ruud, *Phys. Chem. Chem. Phys.* **18**, 4201 (2016).
- [3] D. H. Frieze, M. Beerepoot, M. Ringholm, K. Ruud, *J. Chem. Theo. Comput.* **11**, 1129 (2015).
- [4] D. H. Frieze, M. Ringholm, B. Gao, K. Ruud, *J. Comp. Chem.* **11**, 1184 (2015).

## Hydrogenation of Carbon Dioxide over Magnesium and Copper Alkoxide-Functionalized Metal-Organic Framework

Daniela Guzmán-Angel<sup>1</sup>, Soledad Gutiérrez-Oliva<sup>1</sup>, Alejandro Toro-Labbé<sup>1</sup>

<sup>1</sup>Laboratorio de Química Teórica Computacional (QTC), Facultad de Química, Pontificia Universidad Católica de Chile, Av. Vicuña Mackenna 4860, Macul, Santiago, Chile

In recent years, many approaches have been proposed and developed to reduce emissions [1, 2], immobilization of CO<sub>2</sub> via hydrogenation to form formic acid (HCOOH) has been revealed as one of the most promising strategies [3–5]. In addition, catalytic hydrogenation provides a variety of useful compounds for fine chemistry and industrial applications [6].

In this work, we have studied the reaction mechanism of hydrogenation of carbon dioxide catalyzed by magnesium and copper alkoxide-functionalized metal-organic framework (Mg-MOF-5 and Cu-MOF-5). The aim of this study is to compare the mechanism involved between the reaction with and without catalyst, and between both alkoxide, to understand how these influence the reaction. Both reactions, with and without catalyst, proceed via stepwise mechanism; however, a more detailed analysis of the electronic activity during the reaction shows that they are different. Transition states and energy barriers are discussed in terms of the reaction force analysis (RFA) and Marcus equation. Equilibrium and rate constants are determined and their physical nature is unveiled.

All the systems are characterized computationally using Density Functional Theory (DFT) with the methodology M06-L and the basis set 6-31G(d,p) for H, C and O, while the Mg and Zn atoms were described with the LANL2ZD pseudopotentials basis set. All calculations were performed with Gaussian 09 [7].

Acknowledgments: This work was supported by FONDECYT through project 1141098 and CONICYT-PCHA/Doctorado Nacional/2016-21161202 fellowship.

- [1] D. Aaron and C. Tsouris, *Sep. Sci. Technol.*, **40**(1-3), 321 (2005).
- [2] H. Q. Yang, Z. H. Xu, M. H. Fran, R. Gupta, R. B. Slimane, A. E. Bland and I. Wright, *J. Environ. Sci. (China)*, **20**(1), 14 (2008).
- [3] G. Férey, *Chem. Soc. Rev.*, **37**, 191 (2008).
- [4] T. Maihom, S. Wannakao, B. Boekfa and J. Limtrakul, *J. Phys. Chem. C*, **117**, 17650 (2013).
- [5] C. Federsel, R. Jackstell and M. Beller, *Angew. Chem., Int. Ed.*, **49**, 6254 (2010).
- [6] W. Wang, S. Wang, X. Ma and J. Gong, *Chem. Soc. Rev.*, **40**, 3703 (2011).
- [7] M. J. Frisch et al., *Gaussian 09*, Rev B01, Gaussian, Inc., Wallingford CT (2010).

## Efficient Implementation of the Approximate Exchange Kernel Method

Guo P. Chen, Matthew M. Agee, Filipp Furche

*Department of Chemistry, University of California, Irvine, 1102 Natural Sciences II, Irvine, USA*

The approximate exchange kernel (AXK) method is the leading correction to the random-phase approximation (RPA) for the ground-state correlation energy functional within RPA-renormalized many-body perturbation theory [1, 2]. However, the relatively high computational cost of AXK has hampered its widespread application in the past. In practice, it is important to strike a balance between favorable computational scaling with system size  $N$  and a small prefactor. Here we present two AXK algorithms with asymptotic scaling of  $O(N^4 \ln N)$  and  $O(N^5 \ln N)$ , respectively. Both algorithms take advantage of the resolution-of-the-identity (RI) approximation and imaginary frequency integration. For systems with up to approximately 100–200 atoms, applications to alkene chains illustrate that the  $O(N^5 \ln N)$  algorithm is more efficient than the integral-direct  $O(N^4 \ln N)$  algorithm. The new RI-AXK implementation in TURBOMOLE enables correlation energy calculations for molecules with well over 100 atoms on a single cluster node.

- [1] J. E. Bates, F. Furche, *J. Chem. Phys.* **139**, 171103 (2013).
- [2] G. P. Chen, V. K. Voora, M. M. Agee, S. G. Balasubramani, F. Furche, *Annu. Rev. Phys. Chem.* **68**, 421 (2017).



## Many-Fermion Tunneling Through a Barrier

Elke Fasshauer<sup>1</sup>, Axel Lode<sup>2</sup>

<sup>1</sup>*Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100  
Copenhagen, Denmark*

<sup>2</sup>*Department of Physics, University of Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland*

The tunneling of one electron through a potential is analytically solvable and a quantum mechanics textbook example. But what happens, if not only one electron is involved, but several electrons are trapped? To answer this basic question, the quantum dynamics of two electrons were studied using the Multi-Configurational Time-Dependent Hartree for Fermions (MCTDHF) method [1] implemented in the MCTDH-X program package [2]. This method allows for a numerically exact description.

We show that the fermions tunnel through the barrier individually, while they escape over the barrier collectively [3].

[1] O. E. Alon, A. I. Streltsov, L. S. Cederbaum, *J. Chem. Phys.* **127**, 154103 (2007).

[2] A. U. J. Lode, M. C. Tsatsos, E. Fasshauer, The Multiconfigurational Time- Dependent Hartree for Indistinguishable Particles X package (2015), <http://ultracold.org>.

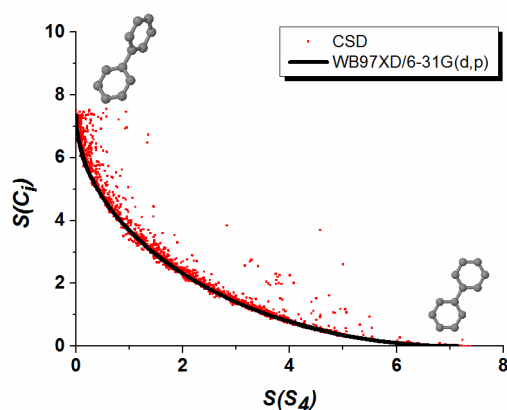
[3] E. Fasshauer, A. U. J. Lode, *J. Phys. Rev. A* **93**, 033635 (2016).

## Quantitative analysis of axial chirality in biaryl and related compounds

Inbal Tuvi-Arad

*Department of Natural Sciences, The Open University of Israel, Raanana 4353701, Israel*

Axial chirality of biaryl compounds is an important phenomenon in chemistry, particularly in the context of biological activity and catalysis. Here we apply the method of continuous symmetry and chirality measures to quantify the level of distortion of each structure and estimate the abundance of this type of chirality. For this purpose the coordinates of thousands of derivatives of biaryl compounds as well as other compounds with hindered rotation were extracted from the Cambridge crystallographic database and their distortion levels were evaluated. In addition, symmetry maps, (e.g., Figure 1 for biphenyl) were used to identify structural distortion paths. DFT calculations in the gas phase were performed in order to explore the relation between energy and chirality. Almost all molecules in our study are chiral to some degree. Additional analysis of biaryl ligands extracted from the protein data bank shows that the degree of chirality in such compounds can reach high levels, similarly, and sometimes even higher than related compounds with chiral centers. Implications of the interplay between structural flexibility and chirality are discussed.



**Figure 1.** Symmetry map based on 2345 organic derivatives of biphenyl.  $S(C_i)$  represents the distance of each structure from the planar conformer.  $S(S_4)$  represents the distance of each structure from the perpendicular conformer. Red dots - Cambridge crystallographic data. Black line - distortion along the minimum energy path in the gas phase.

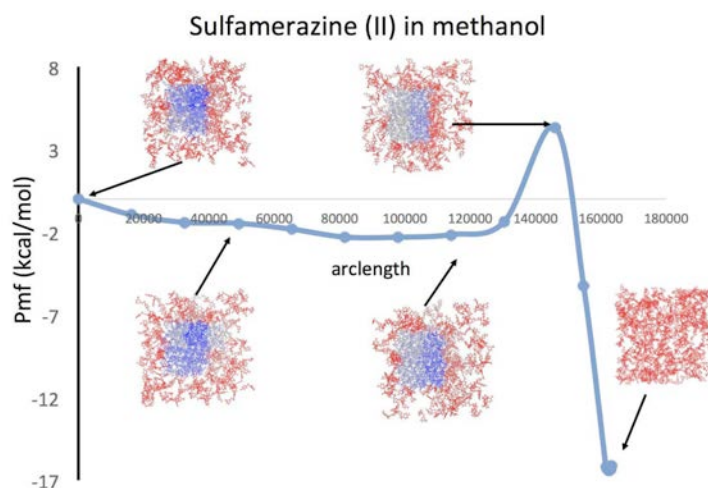
## Understanding the Crystallization Tendency of Sulfadiazine and Sulfamerazine in Different Solvents

Chenxiang Liu<sup>1</sup>, Erik E. Santiso<sup>1</sup> and Geoffrey P. F. Wood<sup>2</sup>

<sup>1</sup>*Department of Chemical & Biomolecular Engineering, North Carolina State University, Raleigh, NC, USA.*

<sup>2</sup>*Pfizer Global Research and Development, Eastern Point Road, Groton, CT, 06340, USA*

Crystallization from solution is fundamental to the pharmaceutical industry where most products consist of molecular crystals. The arrangement of molecules in the crystal lattice determines a number of key quality attributes such as solubility, bioavailability and manufacturability and so greatly influences processing and formulation of solid pharmaceutical products. However, under traditional drug discovery paradigms consideration of the molecular crystal typically comes after the chemical entity has been fixed. At times, this results in a large amount of resources being expended on candidate drug molecules with poor solid-state properties. Computational methods focused on determining the likelihood that a new chemical entity can be successfully crystallized have the potential for alleviating this burden. To this end, we seek to understand the crystallization tendency of two model drug molecules: sulfamerazine and sulfadiazine. We employ the string method in collective variables[1] along with Santiso-style crystal order parameters[2]. Using this methodology we calculate minimum free energy pathways of the nucleation process in three different solvents. Calculated barriers are compared with experiments that measure the nucleation induction times at various supersaturations. We describe the important similarities and differences between the two different systems and their interactions with the three solvent systems.



[1] L. Maragliano, A. Fischer, E. Vanden-Eijnden, G. Ciccotti, *J. Chem. Phys.*, **125**, 024106 (2006).

[2] E. E. Santiso, et al. *J. Chem. Phys.* **134**, 064109 (2011).

## Generalized coupled-cluster approaches for quantum simulation of strongly correlated system.

**Jhonathan Romero<sup>1</sup>, Hannah Sim<sup>1</sup>, Libor Veis<sup>2</sup>, Gian Giacomo Guerreschi<sup>3</sup>,  
Alán Aspuru-Guzik<sup>1</sup>**

<sup>1</sup>*Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge MA, 02138*

<sup>2</sup>*Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Dolejškova 3, 18223 Prague 8, Czech Republic*

<sup>3</sup>*Intel Labs, Santa Clara, California 95054, United States*

Quantum computers are becoming large enough to perform tasks beyond the capabilities of the biggest quantum supercomputers. The first generation of quantum machines are expected to have between 50 to 100 qubits and being able to execute thousands of quantum operations, however, they will lack error-correction. To exploit these “pre-threshold” machines as quantum simulators for chemistry, we need algorithms that are relatively robust to machine noise and can be run using fewer gates. One example of such algorithms is the variational quantum eigensolver (VQE) [1,2]. In this approach, quantum states are prepared based on a given ansatz followed by the measurement of the energy on the quantum computer. The information of the energy is then used to optimize the variational parameters associated to the ansatz using a classical optimization routine. Traditionally, single-reference unitary coupled cluster [1-4] has been used as the canonical ansatz for chemistry simulations. In this work, I present an extension of the unitarity coupled cluster approach to multireference cases. Our method is based on the preparation of an entangled initial state, obtained using classical density matrix renormalization group (DMRG) approaches, followed by the application of a generalized unitary coupled cluster implementation (GUCCI), where all the possible excitation operators are considered. We present numerical simulations of the quantum algorithm for the Hubbard model and a variety of strongly correlated molecular systems.

[1] A. Peruzzo, J.R. McClean, P. Shadbolt, M-H. Yung, X-Q. Zhou, P.J. Love, A. Aspuru-Guzik, and J.L. O'brien, "A variational eigenvalue solver on a quantum processor," *Nat. Commun.* **5**, 4213 (2014).

[2] J. R. McClean, J. Romero, R. Babbush, and A. Aspuru-Guzik, *New. J. Phys.* **18**, 023023 (2016).

[3] M-H. Yung,, J. Casanova, A. Mezzacapo, J. McClean, L. Lamata, A. Aspuru-Guzik, and E. Solano. *Sci. Rep.* **4**, 3589 (2014).

[4] J. Romero, R. Babbush, J.R. McClean, C. Hempel, P. Love, and A. Aspuru-Guzik, arXiv:1701.02691 (2017).

## A consistent molecular model to predict the behavior of early tetravalent actinides.

E. Acher<sup>1</sup>, D. Guillaumont<sup>1</sup>, M. Masella<sup>2</sup>, V. Vallet<sup>3</sup>, F. Réal<sup>3</sup>

<sup>1</sup>CEA / Nuclear Energy Division / Research Department on Mining and Fuel Recycling / SPDS / LILA, BP 17171 F-30207, Bagnols sur Cèze, France

<sup>2</sup>CEA / DRF/JOLIOT/SB2SM/LBSR, Centre CEA de Saclay, 91191, Gif sur Yvette, France

<sup>3</sup>Univ. Lille, CNRS / UMR 8523 / PhLAM - Physique des Lasers Atomes et Molecules, F-59000 Lille, France

The aim of the present study is to investigate and revisit the behavior of early tetravalent actinides, from thorium to plutonium in aqueous solution by the use of classical mechanics simulations; the latter element having not been studied by this modeling approach so far. While spectroscopy provides a good insight into the interatomic distances, the hydration structure, exchange dynamics and coordination numbers remain quite inaccurate [1]. Our objective is to probe the local structure and explore the trends along the early actinide series in the bulk conditions with molecular dynamics (MD) simulations that allows us to monitor the dynamics of a hydrated actinide in bulk conditions on a long-time scale (> 10 ns). However, the reliability of the MD results entirely depends on the quality of the force-field (FF), i.e., the description of the interaction between the solute and the solvent (An/water molecule interaction), and also on the description of the solvent properties. We propose an innovative FF model that accounts, not only for the standard electrostatic and repulsion interactions, but also for polarization and charge-transfer terms, many-body effects, and explicit hydrogen bonds in the water/water interactions.

Pursuing the efforts initiated by Réal *et al.* to simulate the Th(IV) and Cm(III) in aqueous solution [2,3,4], we present here a consistent FF model adjusted to state-of-the-art *ab initio* calculations, i.e., without using any experimental input, for the early tetravalent actinides series (Th, Pa, U, Np, Pu), and the associated results coming from bulk simulations. The average actinide/water distances almost perfectly agree with the reported EXAFS/HEXS values and our MD simulations predict that all early actinides hold 10 water molecules in their first hydration sphere. These results represent a first step towards a better description of these elements in solution or at interface.

[1] K. E. Knope, L. Soderholm, *Chem. Rev.* **113**, 944 (2013).

[2] F. Réal, V. Vallet, J. P. Flament, M. Masella, *Chem. Phys.* **16**, 139 (2013).

[3] F. Réal, M. Trumm, V. Vallet, B. Schimmelpfennig, M. Masella, J. -P. Flament, *J. Phys. Chem. B* **114**, 15913 (2010).

[4] F. Réal, M. Trumm, B. Schimmelpfennig, M. Masella, V. Vallet, *J. Comput. Chem.* **34**, 707 (2013).

## The PNO-MP2 Gradient and its Application to Molecular Geometry Optimizations

Marius S. Frank<sup>1</sup>, Gunnar Schmitz<sup>2</sup>, Christof Hättig<sup>1</sup>

<sup>1</sup>*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Universitätsstrasse 150, Bochum, Germany*

<sup>2</sup>*Department of Chemistry, Aarhus University, Aarhus C, Denmark*

Pair Natural Orbitals (PNOs) offer a systematic way to exploit the sparsity in the dynamical electron correlation by a truncation of the virtual space using a single user-defined threshold  $T_{PNO}$ . The very compact representation of the virtual space spanned by PNOs (provided a localized occupied space) enables the development of reduced scaling local counterparts to well-established canonical methods.

Due to the fact that the error of the PNO approximation in energies has already been intensively investigated, the next natural step is to determine the performance of PNOs on the determination of equilibrium geometries and molecular properties.

Here, an implementation of the PNO-MP2 gradient is presented, in which the PNOs are iteratively constructed from orbital specific virtuals (OSVs) to reduce the computational demands of the PNO construction.

The gradient is applied to geometry optimizations of a wide variety of molecules and clusters. The accuracy of PNO-MP2 in the description of bond lengths and bond angles is then investigated by carrying out a statistical analysis of the errors with respect to canonical RI-MP2.

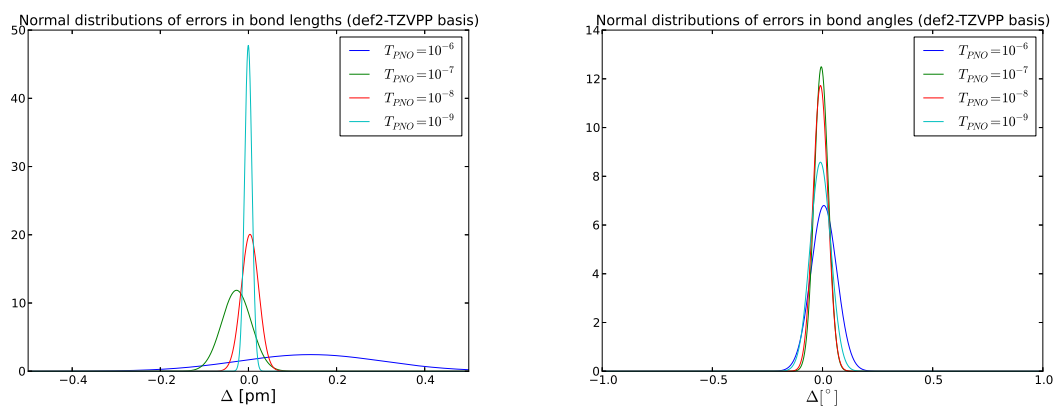


Figure 1: Normal distributions of errors in bond lengths and bond angles in Baker's test set for geometry optimizations.

## Magnetically induced currents in organic boron-nitrogen polycyclic molecules and organic ring systems containing metal ions.

Maria Dimitrova<sup>1</sup>, Heike Fliegl<sup>2</sup>, Dage Sundholm<sup>1</sup>

<sup>1</sup>Department of Chemistry, University of Helsinki, A. I. Virtasen aukio 1, 00014 Helsinki, Finland

<sup>2</sup>Centre for Theoretical and Computational Chemistry (CTCC), Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, 0315 Oslo, Norway.

The aromatic character of a molecule correlates with the current pathways induced in an external magnetic field. Calculations using the gauge-including magnetically induced currents (GIMIC) program are a reliable method to evaluate the induced current densities and compare the aromaticity in molecular rings [1]. Our recent work covers annelated-ring systems and compares the effect of boron and nitrogen on the induced current strengths. We confirm that in spite of possessing 16  $\pi$  electrons, the dibenzo[a,e]pentalene shows little resemblance to the antiaromatic pentalene core [2]. The introduction of boron and nitrogen heteroatoms further increases the aromaticity of the molecular rings. A currently ongoing research topic involves the aromaticity of dicupra[10]annulenes with 10  $\pi$  electrons. Lithium ions situated above and below each of the rings yield nearly planar rings, which makes the rings aromatic. The substitution of all hydrogen atoms of the molecular rings with trimethylsilyl and phenyl substituents distorts the rings, especially when two  $\text{Li}^+$  lie on the same side of the molecule. Very strong currents flow around the copper atoms, however, the ring current is lost.

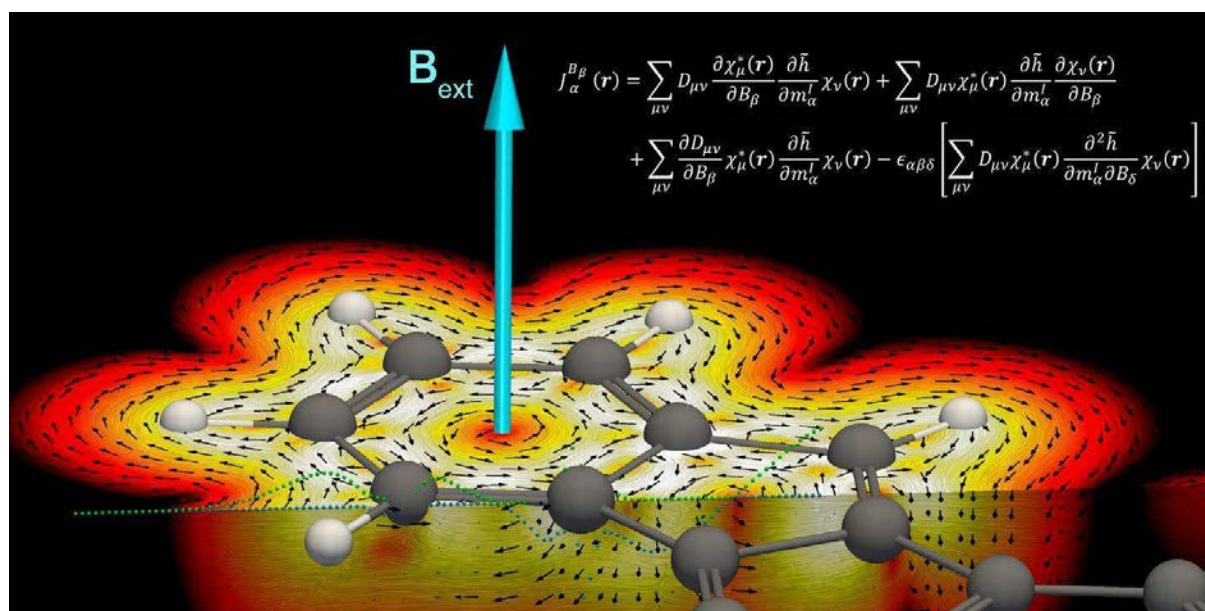


Fig. The induced current densities in the dibenzo[a,e]pentalene molecule [2]. The mathematical expression is the working equation of the GIMIC [1] program.

[1] D. Sundholm, H. Fliegl and R. J. Berger, *WIREs Comput. Mol Sci.* **639** (2016).

[2] M. Dimitrova, H. Fliegl, D. Sundholm, *PCCP* (2017) (manuscript).



## Valence bonds in elongated boron clusters

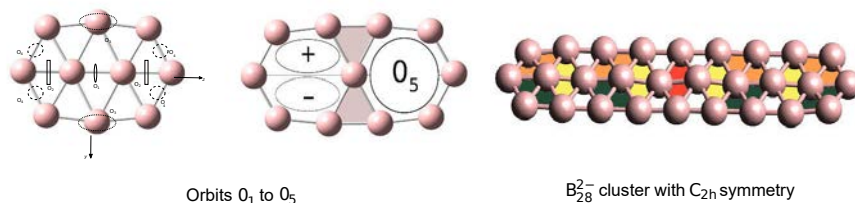
**Athanasios G. Arvanitidis<sup>1</sup>, Kie Zen Lim<sup>1,2</sup>, Remco W.A. Havenith<sup>2,3</sup>, Arnout Ceulemans<sup>1</sup>**

<sup>1</sup>*Quantum Chemistry and Physical Chemistry Section Celestijnenlaan 200f - box 2404 3001 Leuven, Theoretical Chemistry*

<sup>2</sup>*Zernike Institute for Advanced Materials and Stratingh Institute for Chemistry, University of Groningen, 9747 AG Groningen, The Netherlands*

<sup>3</sup>*Ghent Quantum Chemistry Group, Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 (S3), B-9000 Gent, Belgium*

Boron is the new carbon. As opposed to carbon, it adopts multi-center bonding patterns, thus challenging the traditional valence bond approaches. Especially planar and bowl shaped boron clusters are well documented in the literature[1]. This poster presents the comparison between valence bonds in hydrocarbons and a well-defined family of the so-called elongated boron clusters of type  $B_{7+3n}^{q-}$ . The origin of the series is the  $B_7^-$  anion, which is extended repeatedly by  $B_3$  units along a given direction up to  $B_{28}^-$ . Electron counting rules for  $\sigma$  and  $\pi$  bonding are introduced and the multi-center inner-bonding motif is explored and explained[3]. Using AdNDP[2], the inner electronic structure of these clusters is examined, rationalizing the tendency of boron to adopt delocalized 4c-2e bonds. Resonance is recognized as the key element to explain the bonding of the inner framework. To prove our hypothesis of 4c-2e bonds, the group-theoretical induction method is used. It describes the symmetries of the molecular orbitals as a binary code, which is found to be fully consistent with the ab initio results. The combination of the induction method and the 4c-2e scheme provides a clear valence bond scheme for these elongated clusters.



- [1] Alina P. Sergeeva, Ivan A. Popov, Zachary A. Piazza, Wei-Li Li, Constantin Romanescu, Lai-Sheng Wang and Alexander I. Boldyrev, *Acc.Chem.Res.*, **4**, 1349-1358 (2014)
- [2] Dmitry Yu. Zubarev and Alexander I. Boldyrev, *Phys. Chem. Chem. Phys.*, **34**, 5207-5217 (2008)
- [3] Athanasios G. Arvanitidis, Truong B. Tai, Minh Tho Nguyen and Arnout Ceulemans, *Phys.Chem.Chem.Phys.*, **34**, 18311-18318 (2014)



## Complexation of some divalent cations with morin: a spectroscopic and theoretical study

**Aurélien Moncomble, Diksha Jani Thaviligadu, Jean-Paul Cornard**

*Univ. Lille, CNRS, UMR 8516 - LASIR - Laboratoire de Spectrochimie Infrarouge et Raman, F-59000 Lille, France  
aurelien.moncomble@univ-lille1.fr*

Flavonoids are compounds that are involved in the secondary metabolism of several higher vegetables. Then their presence in the environment is very common and their interaction with others species such as cations is likely.

In previous studies, we have developed a methodology that deeply associates the electronic spectra measurements and quantum chemistry computations to determine the preferential fixation site of the cation [1,2]. In this study, we focused on the reactivity of morin, a well studied flavonoid, with zinc (II). This system had been previously studied but no consensus was obtained on the binding site. Then we applied our methodology to this system to determine more precisely the stoichiometry of the actual complex, its binding site along with the coordination sphere.

Density functional theory (DFT) based optimizations of conceivable structures, followed by time dependent computations of the electronic transitions, lead to UV-visible spectra that were compared with the experimental ones, obtained from chemometrics treatment of the experimental data.

An important aspect of these computations was the precise description of the solvent. Indeed, the solvent molecules present in the coordination sphere of the cation also act as ligands, so the description of the complex solvation needs a hybrid model associating microsolvation around the cation with an implicit model at larger distance

This methodology associating experiments and computations shed light on the morin-zinc (II) system and determined the nature of the actual complex formed in theses conditions. Following these results, the same methodology was applied to the study to manganese (II) complexation and these results will be presented.

- [1] J. P. Cornard, L. Dangleterre, C. Lapouge, *J. Phys. Chem. A* **109**, 10044 (2005).
- [2] A. Moncomble, J. P. Cornard, *RSC Adv.* **4**, 29050 (2014).

## Li<sub>2</sub>H vibrational energy levels from a new global *ab initio* potential energy surface

Michiko Ahn-Furudate<sup>1,2</sup>, Denis Hagebaum-Reignier<sup>1</sup>, Gwang-Hi Jeung<sup>1</sup>

<sup>1</sup>*Institut des Sciences Moléculaires de Marseille, Department of Chemistry, Aix-Marseille University, Marseilles, France*

<sup>2</sup>*Department of Mechatronics Engineering, Chungnam National University, Daejeon, Republic of Korea*

In this work, we built a new global potential energy surface (PES) for the ground electronic state of Li<sub>2</sub>H, based on  $\approx 20000$  *ab initio* points at the MRCI level of theory including the core-core and core-valence correlation (See Figure 1 (a) and (b)). These data were fitted using the MSA code [1], based on permutationally invariant fitting bases. The features of our surface compare very well with those of recent global PESs [2]. Accurate vibrational energy levels were then computed using the MULTIMODE software [3], which relies on a hierarchical *n*-mode representation of the potential.

We show that the bent Li<sub>2</sub>H molecule in its ground electronic state can support up to 25 vibrational levels below the barrier to linearity (Figure 1 (b)). These results could help identify spectroscopic lines in an unsolved visible spectrum [4].

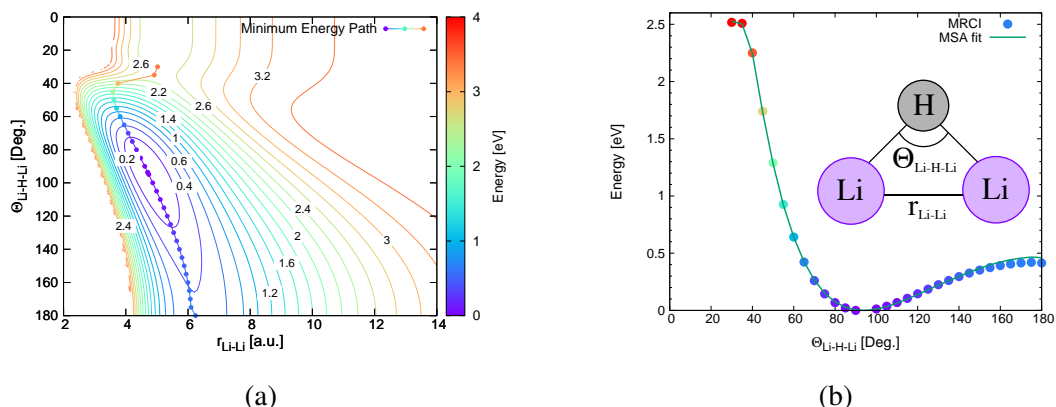


Figure 1: (a) Potential energy surface and (b) barrier to linearity of the  $\tilde{X}A_1$  state of Li<sub>2</sub>H

- [1] Z. Xie and J. M. Bowman. *Journal of Chemical Theory and Computation*, **6**, 26 (2010)
- [2] Y.-Z. Song, Y.-Q. Li, S.-B. Gao and Q.-T. Meng. *The European Physical Journal D*, **68** (2014).  
M. Yuan, W. Li and M. Chen. *International Journal of Quantum Chemistry*, **117**, e25380 (2017)
- [3] J. M. Bowman, S. Carter and X. Huang. *International Reviews in Physical Chemistry*, **22**, 533 (2003)
- [4] J. B. Crooks, K. R. Way, S.-C. Yang, C.-Y. R. Wu and W. C. Stwalley. *The Journal of Chemical Physics*, **69**, 490 (1978)

## The Catalytic Mechanism of GatA: A Molecular Dynamics and QM/MM Study

Paul Meister<sup>1</sup>, James W. Gault<sup>1</sup>,

<sup>1</sup>*Department of Chemistry and Biochemistry, University of Windsor, 401 Sunset Avenue,  
Windsor, Ontario, Canada*

Aminoacyl-tRNA synthetases (aaRSs) are an ancient family of proteins tasked with charging their cognate tRNA<sup>aa</sup> with the correct amino acid. Most organisms utilize at least 20 different aaRSs, one for each proteinogenic amino acid. Notably, in some bacteria and archaea, Asn-tRNA<sup>Asn</sup> or Gln-tRNA<sup>Gln</sup> aminoacylation occurs via initial attachment of an Asp and Glu to tRNA<sup>Asn/Gln</sup>, respectively. To maintain translational fidelity, the incorrect amino acid is typically edited through an array of editing mechanisms. However, in the case of non-discriminating (ND)-aaRSs this does not occur. Instead, Asp and Glu are converted to the correct ones through amidation by glutamine amidotransferase, GatCAB, a heterotrimeric protein. In the GatA active site, an ammonia-containing donor is deaminated to supply the GatB active site with a nitrogen source for use in converting Asp/Glu to Asn/Gln, respectively. The mechanism by which this occurs is not entirely understood. The deamination reaction is achieved through an unusual Ser-*cis*Ser-Lys catalytic triad, a feature common to amidase signature enzymes. We have used molecular dynamics (MD) and quantum mechanical/molecular mechanics (QM/MM) methods to computationally study the mechanism of ammonia cleavage from two potential ammonia donors, Asn and Gln, in *Aquifex aeolicus* GatA (PDB ID: 3H0R<sup>1</sup>). QM/MM studies were performed at the ONIOM(B3LYP-D3/6-311+G(2df,p):Amber//B3LYP-D3/6-31G(d,p):Amber) level of theory. The results of these studies provide deeper insights into the catalytic mechanism for similar amidase signature enzymes, and provide a foundation for the development of novel therapeutics.

[1] J. Wu, W. Bu, K. Sheppard, M. Kitabatake, S. T. Kwon, D. Söll, J. L. Smity, *J. Mol. Bio.* **391**, 703 (2009).

## The 340-cavity in neuraminidase provides new opportunities for influenza drug development

Nanyu Han<sup>1</sup>, Yuguang Mu<sup>2</sup>, Zunxi Huang<sup>1</sup>

<sup>1</sup>*School of Life Sciences, Yunnan Normal University, Kunming, China*

<sup>2</sup>*School of Biological Sciences, Nanyang Technological University, Singapore*

**Abstract:** Influenza neuraminidase (NA) is a pivotal target for viral infection control. However, the accumulating of mutations compromise the efficacy of NA inhibitors. Thus, it is critical to design new drugs targeted to different motifs of NA. Recently, a new motif called 340-cavity was discovered in NA subtypes close to the calcium binding site. The presence of calcium is known to influence NA activity and thermostability. Therefore, the 340-cavity is a putative ligand-binding site for affecting the normal function of NA. In this study, we performed molecular dynamics simulations of different NA subtypes to explore the mechanism of 340-loop formation. Ligand-binding site prediction and fragment library screening were also carried out to provide evidence for the 340-cavity as a druggable pocket. We found that residues G342 and P/R344 in the 340-loop determine the size of the 340-cavity, and the calcium ion plays an important role in maintaining the conformation of the 340-loop through contacts with G345 and Q347. In addition, the 340-cavity is predicted to be a ligand-binding site by metaPocket, and a sequence analysis method is proposed to predict the existence of the 340-cavity. Our study shows that the 340-cavity is not an occasional or atypical domain in NA subtypes, and it has potential to function as a new hotspot for influenza drug binding.

[1] N. Han, Y. Mu, *et al. Biochem. Biophys. Res. Commun.* **470**(1): 130-136 (2016).

## A Reliability Parameter for Frozen-Density Embedding Calculations

Alexander Zech<sup>1</sup>, Niccolo Ricardi<sup>1</sup>, Stefan Prager<sup>2</sup>, Andreas Dreuw<sup>2</sup>, Tomasz A. Wesolowski<sup>1</sup>

<sup>1</sup>*Department of Physical Chemistry, University of Geneva, Quai Ernest-Ansermet 30, 1205 Geneva, Switzerland*

<sup>2</sup>*Interdisciplinary Center for Scientific Computing, University of Heidelberg, Im Neuenheimer Feld 205, 69120 Heidelberg, Germany*

In the presence of an environment, excitation energies, properties and sometimes even reactivity of the target molecule may change drastically. Thus, including environmental effects into quantum chemical calculations either by implicit or explicit models is necessary for an adequate description of these systems. Frozen-Density Embedding Theory (FDET)[1, 2] provides a formal framework in which the whole system is described by means of two independent quantities: the embedded wavefunction (interacting or not) and the density associated with the environment. The FDET approach can conveniently be combined with perturbative wavefunction methods, e.g. the Algebraic Diagrammatic Construction (ADC) scheme for the polarization propagator[3] giving rise to FDE-ADC[4]. The current implementation of FDE-ADC uses the Linearized FDET formalism[5], which in comparison to FDET, is significantly less expensive computationally and more importantly leads to self-consistency between the energy and embedding potential preserving simultaneously the orthogonality of the embedded wave functions for each electronic state. We present a system-independent reliability parameter for FDE-ADC calculations which is computed at the beginning of each embedding calculation.

30 molecular model systems were studied using supermolecular FDE-ADC(2) and compared against their ADC(2) reference of the full system. The molecular test systems were chosen to investigate molecule - environment interactions of varying strength from dispersion interaction up to multiple hydrogen bonds. The mean absolute error of the excitation energies for each system shows linear correlation with the reliability parameter calculated with the densities  $\rho_A^{ref}(\mathbf{r})$  and  $\rho_B(\mathbf{r})$  used to construct the embedding potential. The initial results show that the reliability parameter is a promising tool to estimate the accuracy of the embedding calculation from the start and to identify problematic results.

- [1] T. A. Wesolowski, A. Warshel, *J. Phys. Chem.* **97**, 8050 (1993).
- [2] T. A. Wesolowski, *Phys. Rev. A* **77**, 012504 (2008).
- [3] J. Schirmer, *Phys. Rev. A* **26**, 2395 (1982).
- [4] S. Prager, A. Zech, F. Aquilante, A. Dreuw, T. A. Wesolowski, *J. Chem. Phys.* **144**, 204103 (2016).
- [5] A. Zech, F. Aquilante, T. A. Wesolowski, *J. Chem. Phys.* **143**, 164106 (2015).

## Computer modelling of FRET-based protein nanosensors

**Joshua A Mitchell<sup>1</sup>, Jason H. Whitfield<sup>1</sup>, Will H. Zhang<sup>1</sup>, Colin Jackson<sup>1</sup>, Megan L. O'Mara<sup>1</sup>**

*<sup>1</sup>The Australian National University, Acton, ACT, Australia*

Ratiometric fluorescent nanosensors can be engineered by combining fluorescent probes with a solute binding protein, and taking advantage of the conformational change associated with binding to alter the distance between fluorophores. The resulting change in Förster Resonance Energy Transfer (FRET) can yield a ratiometric sensor. While proteins that exhibit a conformational change upon substrate binding are available for a huge number of sensor targets, simply fusing fluorescent proteins to such a protein is often insufficient to develop a useful sensor. Unfortunately, the reasons behind this difficulty are enigmatic, and the large size and flexibility of the fusion proteins traditionally used as sensors have resisted computational modelling. We describe a combined computational and experimental technique that allows us to rapidly engineer sensors for diverse analytes with excellent sensitivity and requiring little-to-no experimental optimisation, and discuss our next steps in modelling these proteins.

## Tensor-decomposed vibrational coupled-cluster theory

Niels Kristian Madsen<sup>1</sup>, Ian H. Godtliobsen<sup>1</sup>, Ove Christiansen<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Aarhus University, Langelandsgade 140, Aarhus, Denmark*

Vibrational coupled-cluster (VCC) theory is a highly accurate method for obtaining vibrational spectra and properties of small to medium-sized molecules. Calculating the vibrational energy and wave function requires the solution of a set of non-linear equations. We have implemented an array of different non-linear equation solvers ranging from simple, diagonal quasi-Newton schemes to a full Newton-Raphson method and we find that the *conjugate residual with optimal trial vectors* (CROP) algorithm has the shortest time-to-solution as well as a small memory requirement [1]. The computational bottleneck of any VCC calculation is the calculation of the error vector from a set of trial amplitudes. For high-order VCC methods this shows steep polynomial scaling w.r.t. the size of the molecule and the number of one-mode basis functions. Both the computational cost and the memory requirements of the VCC solver can be reduced by decomposing the VCC amplitudes and error vectors to the CANDECOMP/PARAFAC (CP) tensor format. Using the CP format allows us to automatically adapt the size of the parameter space as well as the computational effort to the strength of the physical interactions in the molecule while maintaining the same accuracy as the standard VCC method. We have implemented our VCC algorithms and equation solvers such that the VCC equations can be solved without constructing any tensors in full dimension. The tensors are automatically recompressed during the summation of the many terms in the VCC equations and the accuracy is adapted in a dynamic way to the step size of the equation solver in order to save computational effort while maintaining the fast convergence rate of the CROP algorithm. Our test calculations show that the CP-VCC method allows for significant reductions of both computational cost and memory consumption compared to standard VCC calculations which paves the way for applying high-order VCC methods to larger molecules.

- [1] N. K. Madsen, I. H. Godtliobsen, O. Christiansen, *J. Chem. Phys.* **146**, 134110 (2017).

## Inhibition Mechanisms of Cathepsin B -A Theoretical Study-

**A. Heilos<sup>1</sup>, A. Geiß<sup>1</sup>, B. Engels<sup>1</sup>, P. Schmid<sup>1</sup>, W. Waigel<sup>1</sup>**

<sup>1</sup>*Department of Physical and Theoretical Chemistry, University of Würzburg, Emil-Fischer-Str. 42, Würzburg, Germany*

As a lysosomal cysteine protease Cathepsin B belongs to the so called housekeeping proteins. Hence, its natural substrates are peptide bonds of amino acid chains. Most ligands for proteases interact with their target non-covalently. Consequently the lower reactivity of such drugs prevent unintended side-reaction with DNA or other proteins. However, they have the drawback that their free energy of binding do generally not exceed 15 kcal/mol. Covalently binding inhibitors on the other hand provide higher binding affinities and therefore more efficient inhibition. We investigated carbamate-based ligands as potential covalent inhibitors. In order to avoid side reactions it is important to completely understand the inhibition mechanism of an enzyme. We calculated and compared possible reaction mechanisms using QM and QM/MM methods. Here, the focus lies on a mechanism where the active-site Cys29-anion acts as a base in the first step of the reaction instead of as a nucleophile.<sup>[1]</sup> The calculations show that water seems to play an important role in proton transfer-processes.

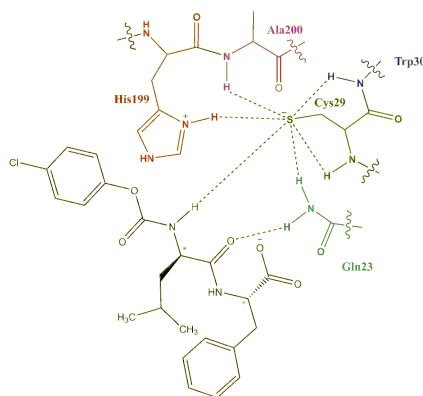


Fig1: Active site of CathB with carbamate-based inhibitor.

[1] Gütschow and Co-word, *Chem.Med.Chem.* **8**, 1330 (2014).



## Methane Activation by Titanium Neopentylidene Complexes: Modification of the ligands

**Dragan B. Ninković,<sup>1</sup> Salvador Moncho,<sup>1</sup> Predrag V. Petrović,<sup>1</sup> Snežana D. Zarić,<sup>1,2</sup> Michael B. Hall,<sup>3</sup> and Edward N. Brothers,<sup>1</sup>**

<sup>1</sup>*Science Program, Texas A&M University at Qatar, Texas A&M Engineering Building, Education City, Doha, Qatar.*

<sup>2</sup>*Department of Chemistry, University of Belgrade, 1000 Belgrade, Serbia.*

<sup>3</sup>*Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, USA.*

The conversion of natural gas to useful chemical compounds is challenging due to the carbon-hydrogen (C-H) bond being fairly inert and solution to this problem is still elusive. The titanium neopentylidene complex (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>2</sub><sup>t</sup>Bu) (PNP = N[2-P<sup>i</sup>Pr<sub>2</sub>-4-methylphenyl]<sup>2-</sup>) reported by Mindiola and coworkers is capable of activating both benzene [1] and methane [2] C-H bonds under mild conditions. They have studied the mechanism of the reaction using B3LYP method that do not included dispersion. We have revised the mechanism in our previous work [3] using ωB97XD functional to include influence of the dispersion and also to get better agreement with the experimental data. It was shown that dispersion correction is crucial to the accuracy of modeling this reaction and we found a new conformer that is both more stable and kinetically more reactive [3].

In this study we have investigated the effect of modifying the PNP and CH<sup>t</sup>Bu ligands on C-H bond activation. Additionally we have investigated tautomerization reaction of the C-H activation product to form a terminal methylidene, this reaction competes with the hydrogen abstraction reaction. Results have showed that replacing the <sup>i</sup>Pr groups in the PNP ligand with <sup>t</sup>Bu groups, both C-H activation and tautomerization reactions become more energetically favorable than in the unmodified complex, with tautomerization favored over H abstraction. Modification of the PNP ligand where N atom is replaced with P results in lower barrier for the tautomerization reaction and tautomerization product is only slightly less stable than product of C-H activation. Most of the ligand modifications do not change the barriers significantly indicating a significant resilience of this titanium complex, which could be used to enhance the practical aspects of the complex without a significant loss of its activity.

[1] B. Bailey, H. Fan, J. C. Huffman, M-H Baik, D. J. Mindiola, *J. Am.Chem. Soc.* **129**, 8781 (2007).

[2] J. A. Flores, V. N. Cavaliere, D. Buck, B. Pinter, G. Chen, M. G. Crestani, M-H. Baik, D. J. Mindiola, *Chem. Sci.* **2**, 1457 (2011).

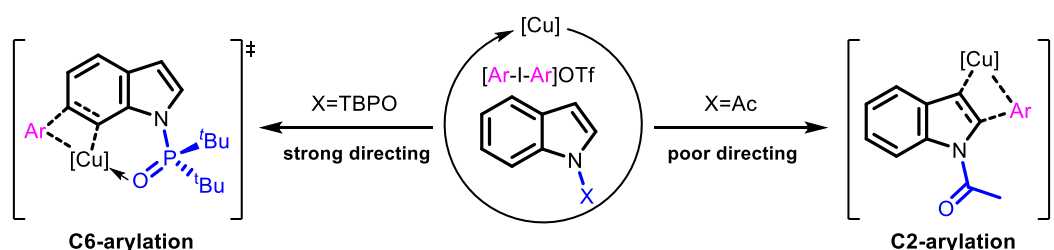
[3] D. B. Ninković, S. Moncho, P. V. Petrović, S. D. Zarić, M. B. Hall, E. N. Brothers, *J. Coord. Chem.* **69**, 1759 (2016).

## Computational Investigations for Cu-Catalyzed Site-Selective Arylation of Indoles: The Directing Group Effects

Ting Wang, Xinhao Zhang\* and Yun-Dong Wu\*

*Lab of Computational Chemistry and Drug Design, Laboratory of Chemical Genomics,  
Peking University Shenzhen Graduate School, Shenzhen 518055, China.*

Mechanistic study of the copper-catalyzed site-selective C-H arylation of indoles with diaryliodonium<sup>[1], [2]</sup> salts has been performed by density functional theory (DFT) in order to understand the origin of regioselectivity and the directing group effects. According to our studies, the reaction most likely undergoes a Heck-like four-membered-ring mechanism, which involves an aryl-Cu(III) complex.<sup>[3]</sup> In the presence of strong directing group N-P(O)<sup>t</sup>Bu<sub>2</sub> (TBPO), Cu center is located at C7 or C2-site, while the steric hindrance makes C7-position prefer over C2-position. Thus, it leads to C6-arylation product through the Heck-like four-membered-ring transition state. However, N-Ac is a poor directing group, so the electronic effect becomes dominant for selectivity. Since C3 is most electron-rich, Cu(III) center would like to coordinate with C3 carbon, and then the aryl group bonded to copper is installed to the C2-position. The computational findings are in good agreement with experimental observations and could account for the effects of directing groups.



[1] R. J. Phipps, N. P. Grimster, M. J. Gaunt, *J. Am. Chem. Soc.* **130**, 8172 (2008).

[2] B. Chen, X.-L. Hou, Y.-X. Li, Y. -D. Wu, *J. Am. Chem. Soc.* **133**, 7668 (2011).

[3] Y. Q. Yang, R. R. Li, Y. Zhao, Z. Z. Shi, *J. Am. Chem. Soc.* **138**, 8735 (2016).

## Interplay of orbital breathing and electron correlation in corner-sharing cuprates

Nikolay Bogdanov<sup>1</sup>, Giovanni Li Manni<sup>1</sup>, Sandeep Sharma<sup>1</sup>, Olle Gunnarsson<sup>1</sup>, Ali Alavi<sup>1,2</sup>

<sup>1</sup>Max Planck Institute for Solid State Research, Stuttgart, Germany

<sup>2</sup>University Chemical Laboratory, Cambridge, U.K

Electronic and magnetic properties of one- and two-dimensional cuprates have been investigated for several decades but are still not fully understood. One of the unsolved problems is the origin of the large anti-ferromagnetic (AF) exchange in cuprates with corner-sharing geometry. It is known that this large AF exchange is an important ingredient for the high-temperature superconductivity and exotic phenomena like spin-charge [1] and spin-orbital separation [2]. We study the electronic structure of two corner-sharing cuprates, one-dimensional  $\text{Sr}_2\text{CuO}_3$  with one of the largest exchange strengths and the layered  $\text{La}_2\text{CuO}_4$ , the parent compound of the high-temperature superconductors, with state-of-the-art wavefunction-based *ab initio* calculations. We find that in order to obtain reasonable agreement with the experimentally observed large magnetic exchange couplings, it is necessary to go beyond multiband models containing only Cu  $3d$  and O  $2p$  bands. To capture the competing orbital breathing and intra-site correlation effects, it is necessary to extend the model space with diffuse Cu  $4d$  and O  $3p$  orbitals. For a Cu-O-Cu unit this leads to a problem of 24 electrons in 26 orbitals that can't be solved with conventional methods. In our study we employ full configuration interaction quantum Monte Carlo (FCIQMC) [3, 4] and density matrix renormalization group (DMRG) [5] techniques. The diffuse Cu  $4d$  and O  $3p$  orbitals add new channels for superexchange and can be considered as a contemporary ingredient for effective Hamiltonian studies.

- [1] B. J. Kim, H. Koh, E. Rotenberg, S.-J. Oh, H. Eisaki, N. Motoyama, S. Uchida, T. Tohyama, S. Maekawa, Z.-X. Shen, and C. Kim, *Nat. Phys.* **2**, 397 (2006).
- [2] J. Schlappa, K. Wohlfeld, K. J. Zhou, M. Mourigal, M. W. Haverkort, V. N. Strocov, L. Hozoi, C. Monney, S. Nishimoto, S. Singh, A. Revcolevschi, J.-S. Caux, L. Patthey, H. M. Ronnow, J. van den Brink, and T. Schmitt *Nature* **485**, 82 (2012).
- [3] G. H. Booth, A. J. W. Thom, and A. Alavi, *J. Chem. Phys.* **131**, 054106 (2009).
- [4] G. Li Manni, S. D. Smart, and A. Alavi *J. Chem. Theory Comput.* **12**, 1245 (2016).
- [5] G. K.-L. Chan and S. Sharma, *Ann. Rev. Phys. Chem.* **62**, 465 (2011).

## Mono- and Di- Alkylation processes of DNA-bases by Anticancer Drug Mechlorethamine

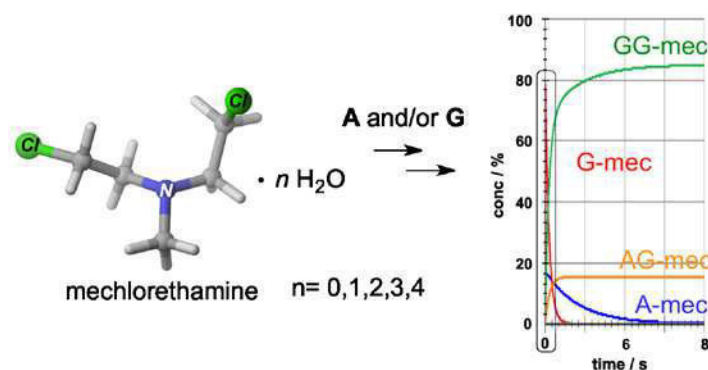
Olatz Larrañaga<sup>1</sup>, Abel de Cózar<sup>\*,1,2</sup>, and Fernando P. Cossío<sup>\*,1</sup>

<sup>1</sup>Department of Organic Chemistry I, Faculty of Chemistry, UPV/EHU and Donostia International Physics Center (DIPC) and Centro de Innovación en Química Avanzada (ORFEO-CINQA), P.K. 1072, 20018 San Sebastián, Spain.

<sup>2</sup>IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Spain.

Nitrogen mustard is the general name of bis(2-chloroethyl)amine derivatives such as mechlorethamine, chlorambucyl and mephalan and they were developed during Second World War. Although these DNA alkylating agents were synthesized to use them as chemical warfare agents, their activity was also tested in chemical trials. In particular, nitrogen mustard mechlorethamine (mec) was the first drug in being developed as an anticancer agent and nowadays it is still in use against Hodgkin's disease, chronic leukemia, breast, lung and ovarian cancer [1].

In this work, the reactivity of mec with purine bases adenine (A) or guanine (G) towards formation of mono- and dialkylated adducts has been studied using density functional theory (DFT). Our results suggest that DNA alkylation by nitrogen mustard mechlorethamine occur via aziridine intermediate instead of direct substitution. It was also found that formation of GG-mec diadduct is kinetically favored, followed by that of AG-mec.



[1] (a) A. Gilman, F. S. Philips, *Science* **103**, 409-436 (1946). (b) K. W. Khon, C. L. Spears, P. Doty, *J. Mol. Biol.* **19**, 266-288 (1966). (c) P. D. Lawley, J. H. Lethbridge, P. A. Edwards, K. V. Shooter, *J. Mol. Biol.* **39**, 181-198 (1969).

## The interaction of complex biomolecules with zeolitic layers: Ab initio and molecular dynamics study

Miroslav Rubeš<sup>1</sup>, Michal Trachta<sup>1</sup>, and Ota Bludský<sup>1</sup>

<sup>1</sup>*Institute of organic chemistry and biochemistry, AS CR, v.v.i., Flemingovo n. 2, Prague, Czech Republic*

The interaction of complex biomolecules such as proteins with inorganic supports is of growing interest in biotechnology applications.<sup>1</sup> The nature of involved interactions (e.g. dispersion, hydrogen-bonding) is well understood. For making reliable predictions of conformational changes at the protein/support interface, the accuracy of the underlying computational model is of the utmost importance. We have investigated the interaction of 19 amino acid side chains in the C<sub>β</sub>-representation with the 2D-UTL lamella (IPC-1P). The periodic DFT optimizations with two different functionals (vdW-DF2 and PBE augmented with dispersion correction) have been tested and resulting structures and interaction energies have been compared against large cluster calculations at the MP2 level of theory. The results show that the error of dispersion corrected DFT (DC-DFT) methods can reach up to 30 kJ.mol<sup>-1</sup>, which significantly impacts the dynamical behaviour of adsorbed proteins. The performance of each tested DC-DFT approach also changes with the hydrophobic and hydrophilic character of the adsorption site. Particularly, the performance of DC-DFT methods differ significantly for the silanol nest sites where a strong hydrogen bonds are formed. The implications of these findings have been addressed through re-parameterization of generic force fields using accurate DC-DFT calculations yielding system-specific (non-transferable) ab initio force fields (AIFFs). The conformational behaviour has been investigated on large oligo/poly peptide models using MD simulations with AIFFs parameterized for specific Ace-*X*-NMe/ $\alpha$ -quartz interactions (*X* stands for one of 19 amino acids). The MD simulations have enabled to evaluate the most relevant contributions to stabilizing interactions between proteins and the inorganic support.

[1] Rimola, A.; Costa, D.; Sodupe, M.; Lambert, J.; Ugliengo, P. *Chem. Rev.* **2013**, *113*, 4216–4313.

## Analytic Open-Shell Local MP2 Gradients using Intrinsic Bond Orbitals

M. Dornbach<sup>1</sup>, H.-J. Werner<sup>1</sup>

<sup>1</sup>*Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany*

Local electron correlation treatments enable the calculation of single point energies for molecules with hundreds of atoms. So far, low-order scaling analytical gradient methods only exist for closed-shell local second-order Møller-Plesset perturbation theory (LMP2) [1, 2], based on Pipek-Mezey (PM) localization [3] of the occupied orbitals and using domains of projected atomic orbitals (PAOs) for the external orbital space. In this work we have implemented analytical LMP2 energy gradients using PM localization as well as intrinsic bond orbitals (IBOs) [4, 5] for closed-shell and local restricted open-shell MP2 (LRMP2). The generation of IBOs is an alternative ansatz for occupied space localization. Contrary to PM, IBOs are faster to compute and are very insensitive to basis set variations. In particular, they avoid artifacts with diffuse basis sets. IBOs are obtained by projections of the occupied orbitals onto a minimal basis of atomic orbitals, yielding so-called intrinsic atomic orbitals (IAOs). The localization is then carried out in the basis of IAOs. The projections used in generating IBOs make it more challenging to derive the analytical gradient expressions and to implement the method efficiently. The open-shell formalism is also more involved than the corresponding closed-shell theory, but the computational effort is similar as in the closed-shell case. Both, an integral-direct and a density fitting implementation are available, and we will present benchmarks with these methods for closed-shell and open-shell systems.

- [1] ElAzhary, A., Rauhut, G., Pulay, P., and Werner, H.-J. *J. Chem. Phys.*, **1998**, *108*, 5185.
- [2] Schütz, M., Werner, H.-J., Lindh, R., and Manby, F. R. *J. Chem. Phys.*, **2004**, *121*, 737.
- [3] Pipek, J. and Mezey, P. G. *J. Chem. Phys.* **1989**, *90*, 4916.
- [4] Knizia, G. *J. Chem. Theory Comput.*, **2013**, *9*, 4834.
- [5] Janowski, T. *J. Chem. Theory Comput.* **2014**, *10*, 3085.

## The Zwitterionic Nature of the Tetrasilatetramide $\text{Si}_4\{\text{N}(\text{SiMe}_3)\text{Dipp}\}_4$ - Quantum Chemical Characterization of a Small Silicon Cluster

Christian Mück-Lichtenfeld<sup>1</sup>, Felicitas Lips<sup>2</sup>

<sup>1</sup>*Organisch-Chemisches Institut and Center for Multiscale Theory and Computation, Westfälische Wilhelms-Universität, Corrensstraße 40, 48163 Münster, Germany*

<sup>2</sup>*Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität, Corrensstraße 28/30, 48163 Münster, Germany*

Tetrasilatetramide **1** has been synthesized and characterized spectroscopically. The observed closed shell character of **1** and the chemical bonding in the  $\text{Si}_4$  core has been investigated with quantum chemical methods.[1] The butterfly shape of **1** can be shown to be a consequence of larger aryl groups destabilizing the chair conformation, which is preferred by the model  $\text{Si}_4\{\text{NMe}_2\}_4$  (**2**). The closed shell character of **2** can be proven with CASSCF calculations.

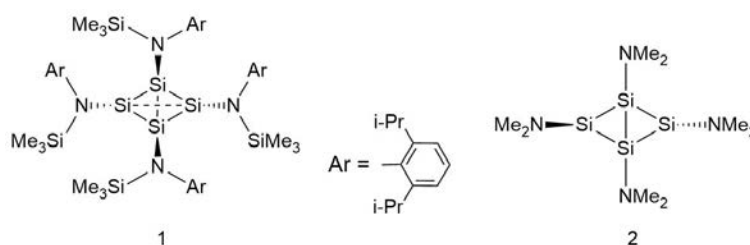


Figure 1: Tetrasilatetramides **1** and **2** (Model)

The two trivalent Si atoms in **1** have different contributions to the HOMO and LUMO (Figure 2) and notably different partial charges. This leads to zwitterionic character of the central ring and non-symmetric out-of-plane bending of the amido substituents. DFT-analysis of the potential energy and MD simulations show that the bending angles are correlated and interchange fast.

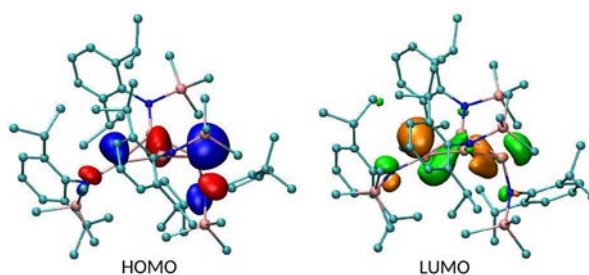


Figure 2: Frontier Orbitals of **1**

[1] J. Keuter, K. Schwedtmann, O. Janka, C. Doerenkamp, H. Eckert, C. Mück-Lichtenfeld, F. Lips, *submitted*

## Empirical Charge Scheme for Transition Metals and Lanthanoids: Development and Applications

**Bodo Martin<sup>1</sup>, Peter Comba<sup>1</sup>**

<sup>1</sup>*Inorganic Chemistry, Heidelberg University, Im Neuenheimer Feld 270, Heidelberg,  
Germany*

Molecular surface polarities are important descriptors for QSAR models for e.g. predicting hydrophobicities or biodistributions. While the derivation of “atomic charges” for organic compounds is well established, this is not yet the case for complexes containing transition metals or lanthanoids. Based on previous results [1-2] we present an MM-based model for geometry optimization, atomic charge parameterization via a Qeq-based approach and logD predictions for complexes containing In<sup>III</sup>, Ga<sup>III</sup>, La<sup>III</sup>, Lu<sup>III</sup> and Tb<sup>III</sup>, which are of particular interest as possible radiopharmaceuticals for multimodal imaging as PET or SPECT centers.

[1] P. Comba; B. Martin; A. Sanyal, *J. Comput. Chem.* **34**, 1598 (2013).

[2] P. Comba; B. Martin; A. Sanyal; H. Stephan, *Dalton Trans.* **42**, 11066 (2013).



## Explicit-Implicit Embedding Strategy to calculate Raman and Raman Optical Activity Spectra of Solvated Systems

**Tommaso Giovannini<sup>a</sup>, Marta Olszówka<sup>a</sup>, Franco Egidi<sup>a</sup>, James R. Cheeseman<sup>b</sup>, Giovanni Scalmani<sup>b</sup>, Chiara Cappelli<sup>a</sup>**

<sup>a</sup> *Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy*

<sup>b</sup> *Gaussian Inc. 340 Quinnipiac St Bldg 40, Wallingford, CT 06492, USA*  
[tommaso.giovannini@sns.it](mailto:tommaso.giovannini@sns.it)

The increasing availability of QM strategies for the calculation of the molecular response to an external electric field has allowed the study of a great number of spectroscopic properties for isolated molecules. However, most experimental data are measured in solution. Computational strategies to include environmental effects are nowadays valuable tools used to bridge the gap between theory and experiment [1,2]. Here, we rely on a mixed explicit/implicit description of the environment based on a multiscale approach [3].

More in detail, in this work we extend the fully polarizable QM/MM/PCM model based on fluctuating charges (FQ) [4-8] (QM/FQ/PCM) to analytical third derivatives with respect to electric/magnetic field and nuclear coordinates, which are used to calculate Raman and Raman Optical Activity (ROA) spectra. In this model, the solvent molecules are explicitly described in terms of the FQs, i.e point charges that can vary in agreement with the Electronegativity Equalization Principle (EEP) [9]. A third layer is also considered and described by means of the Polarizable Continuum Model (PCM). [10]

To test our implementation, we apply the method to the Raman and ROA spectra of (R)-Methyloxirane and (S)-methyl lactate in aqueous solution [11], for which our approach has already been proven to reliably reproduce other optical properties [12,13].

- [1] F. Egidi, C. Cappelli. *Elsevier Reference Module in Chemistry, Molecular Sciences and Chemical Engineering* 2015.
- [2] H.M. Senn, W. Thiel. *Angew. Chem. Int. Ed.* **48**, 1198-1229 (2009).
- [3] A. Warshel, M. Levitt. *J. Mol. Biol.* **103**, 227-249 (1976).
- [4] C. Cappelli, *Int. J. Quantum Chem.* **116**, 1532–1542 (2016).
- [5] Lipparini, F., Barone, V. *J. Chem. Theory Comput.* **7**, 3711 (2011).
- [6] Lipparini, F., Cappelli, C., Barone, V. *J. Chem. Theory Comput.* **8**, 4153 (2012).
- [7] Lipparini, F., Cappelli, C., Scalmani, G., De Mitri, N., Barone, V. *J. Chem. Theory Comput.* **8**, 4270 (2012).
- [8] Lipparini, F., Cappelli, C., Barone, V. *J. Chem. Phys.* **138**, 234108 (2013).
- [9] R.T. Sanderson. *Science* **114**, 670-672 (1951).
- [10] Tomasi, J., Mennucci, B., Cammi, R. *Chem. Rev.*, **105**, 2999-3094 (2005).
- [11] T. Giovannini, M. Olszówka, F. Egidi, J. R. Cheeseman, G. Scalmani, C. Cappelli *submitted*.
- [12] F. Lipparini, F. Egidi, C. Cappelli, V. Barone. *J. Chem. Theory Comput.* **9**, 1880-1884 (2013).
- [13] T. Giovannini, M. Olszówka, C. Cappelli, *J. Chem. Theory Comput.* **12**, 5483-5492 (2016).

## An Accurate Force Field for Both Folded and Disordered States of Peptides and Proteins

Hao-Nan Wu<sup>1</sup>, Fan Jiang<sup>1</sup>, Yun-Dong Wu<sup>1,2</sup>

<sup>1</sup>Laboratory of Computational Chemistry and Drug Design, Laboratory of Chemical Genomics, Peking University Shenzhen Graduate School, Shenzhen, China

<sup>2</sup>College of Chemistry and Molecular Engineering, Peking University, Beijing, China

E-mails: wuhn@pku.edu.cn, jiangfan@pku.edu.cn, wuyd@pkusz.edu.cn

Although force fields that can well describe the folded or unfolded structures of peptides and proteins have been developed separately, the physical model that accurately describe both folded and disordered systems is still an unsolved challenge. Recently, a new water model TIP4P-D<sup>[1]</sup> has been proposed to correct the significantly underestimated radius of gyration ( $R_g$ ) of unfolded (disordered) peptides and proteins in previous simulations, but it cannot stabilize the native structures of  $\alpha$ -helical and  $\beta$ -hairpin systems when used with popular force fields. Here, we found that our recently developed residue-specific force fields (RSFF1 and RSFF2)<sup>[2,3]</sup> can successfully fold these model systems with the TIP4P-D. Especially, when extra Lennard-Jones potentials between all backbone  $O_i$  and  $H_{i+4}$  atoms were added to mimic the special cooperativity in  $\alpha$ -helix formation, the modified RSFF2+ force field with the TIP4P-D water can excellently reproduce experimental melting curves of both  $\alpha$ -helical and  $\beta$ -hairpin systems at the full temperature range, and produces more expanded unfolded structures in better agreement with experiments at the same time.<sup>[4]</sup> The new RSFF2+/TIP4P-D method can also stabilize the native structures of well folded globular proteins and reproduce their NMR order parameters very well. It may pave the way for more harmonious descriptions of the systems including both folded and disordered states in solution, such as marginally stable proteins, structured proteins with disordered loops.

### Reference:

- [1] S. Piana, A. G. Donchev, P. Robustelli, D. E. Shaw, *J. Phys. Chem. B* **119**, 5113 (2015)
- [2] F. Jiang, C.-Y. Zhou, Y.-D. Wu, *J. Phys. Chem. B* **118**, 6983 (2014)
- [3] C.-Y. Zhou, F. Jiang, Y.-D. Wu, *J. Phys. Chem. B* **119**, 1035 (2015)
- [4] H.-N. Wu, F. Jiang, Y.-D. Wu, *J. Phys. Chem. Lett.* in revision.

## Rotational Constants and Vibrational Spectra of Acenaphthene Water Complexes.

Jens Antony<sup>1</sup>, Stefan Grimme<sup>1</sup>, Melanie Schnell<sup>2</sup>

<sup>1</sup>Mulliken Center for Theoretical Chemistry, Institute of Physical and Theoretical Chemistry, University Bonn, Beringstraße 4, D-53115 Bonn, Germany

<sup>2</sup>Max-Planck-Institut für Struktur und Dynamik der Materie, Luruper Chaussee 149, D-22761 Hamburg, Germany

The noncovalent complexes of acenaphthene and one, two or three water molecules are characterized theoretically in the course of a joint theoretical-experimental project within the DFG priority program "Control of London dispersion interactions in molecular chemistry" (SPP 1807). Microwave spectroscopy experiments were performed by the group of M.S., infrared spectra have been recorded by A. Rijs and A.K. Lemmens at the FELIX free electron laser laboratory. Molecular parameters determined by rotational spectroscopy are computed using a previously described protocol.[1] The experimental  $B_0$  values are back-corrected to equilibrium rotational constants ( $B_e$ ) by computation of the vibrational corrections  $\Delta B_{vib}$  using perturbation theory. Employing a new, well-performing spin-component scaled MP2 variant,[2] computed  $B_e$  values deviate from experimental back-corrected ones by less than one percent, thus allowing unambiguous structural assignments.

Theoretical reproduction of vibrational spectra in the far infrared region appears challenging due to strong anharmonic effects of intramolecular motions in the water cluster requiring a treatment beyond vibrational perturbation theory. Here we address this issue by performing quantum mechanical calculations of stationary states in one dimensional potentials obtained by deforming the complex out of its equilibrium structure along normal modes, an approach that has been applied to another hydrogen bonded system earlier.[3] With classical dynamics simulation in full dimensionality on the same (or eventually on a different) potential energy surface remaining anharmonic effects are approximated.[4, 5] Beyond qualitative insight into the nature of the anharmonic motions the applied procedure promises also a quantitative reproduction of the measured spectra when a sufficiently high level of electronic structure theory is used.

- [1] S. Grimme, M. Steinmetz, *Phys. Chem. Chem. Phys.* **15**, 16031-16042 (2013).
- [2] T. Risthaus, M. Steinmetz, S. Grimme, *J. Comput. Chem.* **35**, 1509-1516 (2014).
- [3] J. Antony, G. v. Helden, G. Meijer, B. Schmidt, *J. Chem. Phys.* **123**, 014305 (2005).
- [4] M. Brehm, B. Kirchner, *J. Chem. Inf. Model.* **51**, 2007-2023 (2011).
- [5] M. Thomas, M. Brehm, R. Fligg, P. Vöhringer, B. Kirchner, *Phys. Chem. Chem. Phys.* **15**, 6608-6622 (2013).

## A Scalable and Efficient Approach to Polarizable Force Fields in Molecular Dynamics Simulations

Jonathan P. Coles<sup>1</sup>

*Physik-Department, Technische Universität München, James-Franck-Str. 1, 85748 Garching, Germany*

Standard biophysical molecular dynamics simulations use complex, fixed-charge force field models to capture the atomic interactions of solvated proteins and other organic molecules. These force fields are typically parameterized to reproduce experimental results and are often very specific to the system being simulated. More flexible models that capture induced polarization and dynamically account for the changing electrostatic environment around proteins and DNA are increasingly recognized as a critical step towards more accurate and predictive simulations. However, such models are generally much more computationally expensive, which has limited their adoption. In this talk, I will present a sophisticated, polarizable force field model [1] that can be evaluated with an efficient  $O(N)$  implementation of the Fast Multipole Method [2]. Together, the cost overhead of using a polarizable force field has been significantly reduced, allowing simulations of large molecules to be achieved. Recent work involving a highly scalable and parallel version of FMM will be presented along with an application to large biomolecules.

### References

- [1] F. Réal, V. Vallet, J.-P. Flament, M. Masella, *J. Chem. Phys.* **Sept. 2013**, 139.
- [2] J. P. Coles, M. Masella, *J. Chem. Phys.* **Jan. 2015**, 142.

## Properties of Molecular Magnets

**Andreas Nyvang<sup>1</sup>, Maja Thomsen<sup>1</sup>, Jacob Overgaard<sup>1</sup>, Jeppe Olsen<sup>1</sup>, James P. S. Walsh<sup>2</sup>, Jeffrey R. Long<sup>3</sup>, Phil Bunting<sup>3</sup>, Michael Atanasov<sup>4</sup>**

<sup>1</sup>*Kemisk Institut, Aarhus Universitet, Langelandsgade 140, 8000 Aarhus C, Denmark*

<sup>2</sup>*Northwestern University, Evanston, IL 60208, USA*

<sup>3</sup>*Department of Chemistry, University of California, Berkeley, California 94720-1460, USA*

<sup>4</sup>*Max Planck Institute for Chemical Energy Conversion, 45470 Mülheim an der Ruhr, Germany*

Starting with the observation that a  $\text{Mn}_{12}$  molecule showed molecular magnetism [1], the field of single molecule magnets has developed rapidly.

For such complexes, Density Functional Theory calculations is often not sufficient, and instead multi-configurational wavefunction methods are necessary.

Recently, there has been an interest in semi-linear organometallic complexes. The idea is that by having a semi-linear complex, the oxidation state of the metal center can have a very low oxidation state, and additionally there will be near-degenerate states leading to a highly anisotropic magnetic moment due to the influence of ligands and spin-orbit coupling. In particular, pseudolinear complexes with iron in oxidation states I and II have shown promising results [2].

The poster will show examples of this for an iron(I) and an iron(II) complex, both with a structure similar to the one shown in figure 1. This will include energies of spin-orbit coupled states as well as magnetic properties, such as the  $\mathbf{g}$  tensor and magnetic susceptibility using the program MOLCAS [3].



Figure 1: Pseudolinear iron(II) complex.

- [1] Sessoli, R. and Gatteschi, D. and Caneschi, A. and Novak, M. A. *Nature* **365**, 141 (1993).
- [2] Zazrozny, J. M. *Nat. Chem.* **5**, 577 (2013).
- [3] Aquilante, F. et al *J. Comput. Chem.* **37**, 506 (2015).

**Solvent Dynamics Controls the Schlenk Equilibrium of Grignard Reagents:  
Computational Study of CH<sub>3</sub>MgCl in Tetrahydrofuran.**

**Raphael M. Peltzer,<sup>a,b</sup> Odile Eisenstein,<sup>b,c</sup> Ainara Nova,<sup>\*,a,b</sup> Michele Cascella<sup>\*,a,b</sup>**

*a Department of Chemistry, University of Oslo, Sem Sælands vei 26, 0371 Oslo, Norway*

*b Centre for Theoretical and Computational Chemistry (CTCC), University of Oslo, Sem Sælands vei 26, 0371 Oslo, Norway*

*c Institut Charles Gerhardt, UMR 5253 CNRS-Université de Montpellier, cc 1501, Place E. Bataillon, Université de Montpellier 34095 Montpellier, France.*

*\* email to: [ainara.nova@kjemi.uio.no](mailto:ainara.nova@kjemi.uio.no), [michele.cascella@kjemi.uio.no](mailto:michele.cascella@kjemi.uio.no)*

The Schlenk equilibrium [1] is a complex reaction governing the presence of multiple chemical species in solution of Grignard reagents. [2] A full characterization at the molecular level of the transformation of CH<sub>3</sub>MgCl into MgCl<sub>2</sub> and Mg(CH<sub>3</sub>)<sub>2</sub> in tetrahydrofuran (THF) by means of ab initio molecular dynamics simulations with enhanced-sampling metadynamics was carried out. The reaction occurs via formation of dinuclear species bridged by chlorine atoms. At room temperature, the different chemical species involved in the reaction accept multiple solvation structures, with two to four THF molecules that can coordinate the Mg atoms. The energy difference between all dinuclear solvated structures is lower than 5 kcal mol<sup>-1</sup>. The solvent is shown to be a direct key player driving the Schlenk mechanism. In particular, our study illustrates how the most stable symmetrically solvated dinuclear species, (THF)CH<sub>3</sub>Mg(μ-Cl)<sub>2</sub>MgCH<sub>3</sub>(THF) and (THF)CH<sub>3</sub>Mg(μ-Cl)(μ-CH<sub>3</sub>)MgCl(THF), need to evolve to *less* stable asymmetrically solvated species, (THF)CH<sub>3</sub>Mg(μ-Cl)<sub>2</sub>MgCH<sub>3</sub>(THF)<sub>2</sub> and (THF)CH<sub>3</sub>Mg(μ-Cl)(μ-CH<sub>3</sub>)MgCl(THF)<sub>2</sub>, in order to yield ligand exchange or product dissociation. In addition, the transferred ligands are always departing from an axial position of a pentacoordinated Mg atom. Thus, solvent dynamics is key to successive Mg–Cl and Mg–CH<sub>3</sub> bond cleavages because bond breaking occurs at the most solvated Mg atom and the formation of bonds takes place at the least solvated one. The dynamics of the solvent also contributes to keep relatively flat the free energy profile of the Schlenk equilibrium.

[1] Schlenk, W.; Schlenk, W., *Ber. dtsch. Chem. Ges. A/B* **1929**, 62, 920-924.

[2] V. Grignard, *C. r. d. l'Acad. des Sciences* **1900**, 130, 1322-1324.

## A rational look at fluorescent proteins through excited state reaction path calculations

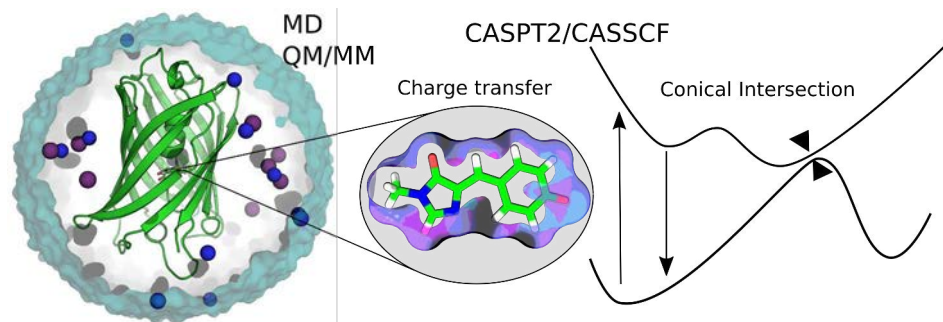
Daryna Smyrnova<sup>1</sup>, María del Carmen Marín<sup>2,3</sup>, Massimo Olivucci<sup>2,3</sup>, Arnout Ceulemans<sup>1</sup>

<sup>1</sup>*Quantum Chemistry and Physical Chemistry Division, Department of Chemistry, KU Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium*

<sup>2</sup>*Department of Biotechnology, Chemistry e Pharmacy, Università di Siena, via A. Moro 2, I-53100 Siena, Italy*

<sup>3</sup>*Department of Chemistry, Bowling Green State University, Bowling Green, OH 43403, USA*

One reversibly-switchable fluorescent protein (RSFP) Dronpa[1] and four of its closest mutants (rsFastLime, rsKame, Padron (anionic form) and bsDronpa) spread over 40 nm in absorption maxima and only 18 nm in emission. They carry exactly the same chromophore and differ just in a few mutations thus providing an ideal set for mechanistic investigations. Using input from MD simulations and QM/MM calculations[2] we assess major reasons controlling the spectral tuning and photophysical properties on the basis of a consistent model set. On the basis of the RSFPs models, which are based on a CASPT2//CASSCF level of QM theory we reproduce an experimental absorption/emission trend with only 1.5 kcal/mol blue-shift. Then we analyse the chromophore's charge-transfer patterns during the absorption and emission, which in turn trigger a cascade of a hydrogen-bond-network rearrangements indicating preparation to isomerization. Also we show how contribution of an individual aminoacids correlates with spectral tuning of the absorption and emission. Furthermore, we identify how the conical intersection topography correlates with protein's photophysical properties. Thus we establish a detailed mechanistic explanation of a higher absorption sensitivity in comparison to emission as well as provide a consistent protocol for a high-throughput study of spectral tuning in RSFPs.



[1] Stiel et al, *Biochem. J.* **402**, 35 (2007)

[2] Smyrnova et al, *J. Phys. Chem. B* **120**, 12820 – 12825 (2016)

## Controlling electron transfer through selective vibrational excitation.

Theo Keane<sup>1</sup>, Milan Delor<sup>2</sup>, Julia A. Weinstein<sup>1</sup>, Anthony J. H. M. Meijer<sup>1</sup>

<sup>1</sup>Department of Chemistry, University of Sheffield, Brook Hill, Sheffield, United Kingdom

<sup>2</sup>Department of Chemistry, University of California, Berkeley, California, United States

Electron transfer is a fundamental physical process and underpins various phenomena, including photosynthesis. Over the past decade, there has been increasing interest in the manipulation of electron transfer pathways through selective vibrational excitation, from both theoretical[1] and experimental[2] perspectives.

Recently, we have investigated a series of Pt(II) acetylide complexes in which electronic transfer can be manipulated,[3, 4] as illustrated in Figure 1.

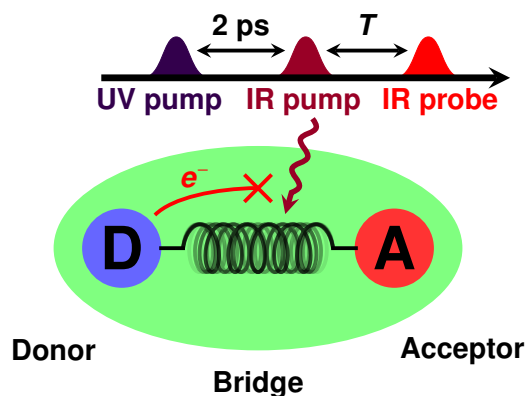


Figure 1: Illustration of the vibrational control phenomenon

In this contribution, we will outline the advances made in the efforts to understand the vibrational control phenomenon.

- [1] D. Xiao, S. S. Skourtis, I. V. Rubstov, D. N. Beratan, *Nano Lett.*, **9**, 1818 (2009).
- [2] Z. Lin, C. M. Lawrence, D. Xiao, V. V. Kireev, S. S. Skourtis, J. L. Sessler, D. N. Beratan, I. V. Rubstov, *J. Am. Chem. Soc.*, **131**, 18060 (2009).
- [3] M. Delor, P. A. Scattergood, I. V. Sazanovich, A. W. Parker, G. M. Greetham, A. J. H. M. Meijer, M. Towrie, J. A. Weinstein, *Science*, **346**, 1492 (2014).
- [4] M. Delor, T. Keane, P. A. Scattergood, I. V. Sazanovich, G. M. Greetham, M. Towrie, A. J. H. M. Meijer, J. A. Weinstein, *Nature Chem.*, **7**, 689 (2015).



## **Improving AMBER non-bond parameters for inorganic and alkyl oxoanions, when experimental data is not available**

**Sadra Kashef Ol Gheta<sup>1</sup>, Ana Vila Verde<sup>1</sup>**

*<sup>1</sup>Department of Theory & Bio-systems, Max Planck Institute of Colloids and Interfaces,  
Am Mühlenberg 1, 14476 Potsdam, Germany*

Organic and inorganic oxoanions are abundant in biological systems and play a significant role in many physiological processes. The molecular scale behavior of these ions towards proteins and other biomolecules are not completely understood, partly due to the absence of reliable model parameters. A good parameter should be able to capture both ion-water and ion-ion interactions simultaneously, and reproduce the corresponding thermodynamics properties. However, for many ions, reliable thermodynamic data are not necessarily available in the literature, restraining us from developing proper parameters for the ions of our interest. Here, we propose an approach that combines the ab initio calculations with the empirical optimization, to develop non-bond parameters for ions in aqueous solutions. We developed parameters for the interaction of HSO<sub>4</sub><sup>-</sup>, RSO<sub>4</sub><sup>-</sup>, RSO<sub>3</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, R<sub>2</sub>PO<sub>4</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HPO<sub>4</sub><sup>2-</sup> and RPO<sub>4</sub><sup>2-</sup> with TIP3P water, as well as with Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup> and RNH<sub>3</sub><sup>+</sup> (R=alkyl groups), using our approach. The approach yields an internally consistent parameter set for the ion-water and ion-ion interactions, for the ions above.

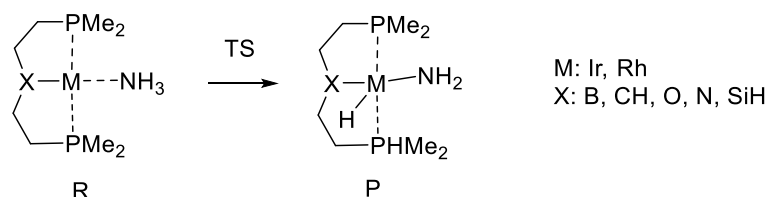
## Computationally Guided Design of Transition Metal PXP Pincer Complexes for NH<sub>3</sub> Fixation

Julen Munarriz<sup>1</sup>, Victor Polo<sup>1</sup>

<sup>1</sup>*Departamento de Química Física and Instituto de Biocomputación y Física de los Sistemas Complejos (BIFI), Universidad de Zaragoza. Pl. S. Francisco S/N 50009, Zaragoza, Spain*

Ammonia fixation is one of the most challenging chemical reactions as it would open new synthetic routes for hydroamination processes as well as contribute to remove ammonium-derived byproducts that are harmful for the environment. One promising way of achieving this is through N-H oxidative addition by transition metal complexes and under mild conditions. However, although some paradigmatic examples have been reported, this kind of processes are rare as the metal-amido parent species tend not to be thermodynamically favorable. [1][2]

The electronic features that govern this processes have not been fully characterized. In order to shed light, a comprehensive analysis of the factors determining energy cost and activation barrier for the oxidative addition of ammonia to the metal center (Ir and Rh) of some paradigmatic and promising PXP complexes (X = B, Si, C, O, N) is presented.



Electron localization function analysis provided an understanding of the sequence of bond formation and cleavage, allowing to understand the changes on electron pairing along reaction path. This way, it was possible to reveal that the metal oxidation from M(I) to M(III) takes place at the transition state, having an important effect in the activation energy. On the contrary, electrostatic interactions between the metal and the atom situated in *trans* position to ammonia (X) (which were revealed using Interacting Quantum Atoms, IQA, approach) were found to be crucial for the energy variation of the whole oxidative addition process. It is also remarkable to notice that the formed metal-amido product presents a significant double bond character, as shown by Natural Bond Orbital (NBO) analysis.

[1] J. Zhao, A. S. Golman, J. F. Hartwig, *Science* **307**, 1080 (2005).

[2] E. Morgan, D. F. MacLean, R. McDonald, L. Turculet, *J. Am. Chem. Soc.* **131**, 14234 (2009).

## How reliable is density functional theory to describe uranium-based molecular compounds?

**Daniel Reta,<sup>1</sup> Fabrizio Ortu,<sup>1</sup> Simon Randall,<sup>1</sup> David P. Mills,<sup>1</sup> Nicholas F. Chilton,<sup>1</sup> Richard E. P. Winpenny,<sup>1</sup> Louise Natrajan,<sup>1</sup> Bryan Edwards<sup>2</sup> and Nikolas Kaltsoyannis<sup>1</sup>**

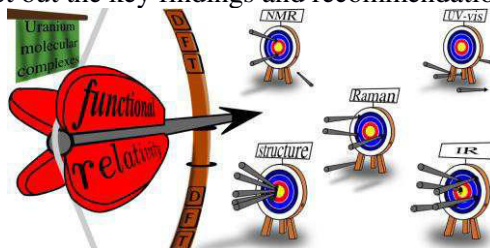
<sup>1</sup>*School of Chemistry, The University of Manchester, Oxford Road, Manchester M13 9PL, UK*

<sup>2</sup>*Science and Technology Facilities Council, Rutherford Appleton Laboratory, Harwell Oxford, Didcot OX11 0QX, UK*

Molecular uranium complexes are the most widely studied in actinide chemistry, and make a significant and growing contribution to inorganic and organometallic chemistry. However, reliable computational procedures to accurately describe the properties of such systems are not yet available. In this contribution, 18 experimentally characterized molecular uranium compounds, in oxidation states ranging from III to VI and with a variety of ligand environments, are studied computationally using density functional theory (DFT). For all investigated compounds, X-ray crystallographic, infra-red and Raman spectroscopic data are compared to the computed geometries and vibrational frequencies; for a selection of closed-shell U(VI) compounds, NMR parameters and UV-Vis spectra are compared to <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts, spin-spin couplings and electronic absorption spectra, to establish which computational approach yields the closest agreement with experiment.

For each of the mentioned experimental observables, the impact of the chosen functional is addressed by investigating different representative functionals belonging to the main families in DFT, i.e., generalized gradient approximation (GGA), *meta*-GGA, hybrid and range-corrected approaches. The description of relativistic effects on the uranium centers was performed via a relativistic pseudopotential and associated valence basis set, or with an all-electron basis set with the ZORA Hamiltonian. The effect of the nature and type of the employed basis set, together with the inclusion of dispersion corrections was also investigated.

Our results clearly identify which theoretical and computational procedure is best suited for the description of a given experimental observable, and permits us to rationalize the situations in which DFT performs erratically in a systematic manner. We believe that suggestions derived from our study on how to computationally describe uranium-based molecular compounds will prove valuable for the community of actinide chemists, and in my presentation I will set out the key findings and recommendations from our work.



## Prediction of DFT-derived point-charges using a Machine Learning Model

P. Bleiziffer<sup>1</sup>, S. Riniker<sup>1</sup>

<sup>1</sup>Laboratory of Physical Chemistry, ETH Zurich, Vladimir-Prelog-Weg 2, 8093 Zurich, Switzerland

The parametrisation of classical bimolecular force fields, that are applied to systems like proteins, DNA, lipids and sugars is relatively straight-forward. Since only a few number of building blocks is required for parametrization and validation, fitting the parameters to experimental or *ab initio* values is feasible. For small organic molecules on the other hand, the situation is different. The size and diversity of just the drug-like chemical space is vast, making it difficult to construct building blocks and thus requiring an individual parametrisation of each ligand. The general approach is thereby either to inherit the parameters of the bonded and van der Waals (Lennard-Jones) parameters from a protein force field, or to parametrise them in a similar way based on experimental data and higher level calculations of a set of organic liquids. For a new molecule, partial charges are usually obtained *ad hoc* from semi-empirical or *ab initio* calculations of questionable accuracy. Examples of such force fields for organic molecules are the general Amber force field (GAFF) [1], or the OPLS all-atom force field (OPLS-AA) [2]. The quality of the net atomic charges (NACs) of small organic molecules generated in this fashion depends on the level of the quantum-chemical calculation as well as on the fitting procedure that is used to derive the NACs. The extraction of NACs from *ab initio* data is a long-standing problem, which has no unique solution. Here we present a machine-learning (ML) based approach for predicting NACs extracted from density function theory (DFT) electron densities via the DDEC6-scheme [3]. The training-set for the ML-model was chosen with the goal to cover the chemical space of drug-like molecules as far as possible. In addition to an instantaneous computation of the NACs, the charges are also less dependent on the molecular conformation than the ones obtained by fitting to the electrostatic potential (ESP). To assess the quality and compatibility with standard force fields like OPLS-AA and GAFF, we performed benchmark calculations for the free energy of hydration and liquid properties.

- [1] M. J. Wang, *J. Comput. Chem.* **25**, 1157– 1174 (2005).
- [2] W. L. Jorgensen, D. S. Maxwell, and J. Tirado-Rives, *J. Am. Chem. Soc.* **118**, 11225–11236 (1996).
- [3] T. A. Manz and N. G. Limas, *RSC Adv.* **6**, 47771-47801 (2016).

## **Description and Modelling of Spectra, Structure and Function of Histidin Kinase Rhodopsin (HKR).**

**Franziska E. Beyle<sup>1</sup>, Marcus Elstner<sup>1</sup>, Igor Schapiro<sup>2</sup>**

<sup>1</sup>*Department of Theoretical Chemical Biology, Institute of Physical Chemistry, KIT,  
Kaiserstrasse 12, 76131 Karlsruhe, Germany*

<sup>2</sup>*Fritz Haber Center for Molecular Dynamics Research, Institute of Chemistry, The  
Hebrew University of Jerusalem, 9190401 Jerusalem*

Rhodopsins are light-sensitive receptor proteins, they respond to light and enable the signal pathways of the cells. The discovery of the Channelrhodopsins in the last decade paved the way for a new technology in the field of neuroscience. These light-gated ion channels enable neuroscientists to selectively activate nerve cells in tissues with short laser pulses. This technique is called Optogenetics and is a milestone for the investigation of neural networks. However, the inactivation of the nerve cells is not yet possible, especially by moderate light intensities. One solution might be provided by the recent discovery of the bimodal switching Histidin Kinase Rhodopsin (HKR) [1]. In detail, irradiating the protein with two different wavelengths makes it switch between two stable states [2][3]. The mechanism has to be understood and clarified in order to adapt this unique feature on other rhodopsins. Thereby rhodopsins with new features can be developed for applications in the Optogenetic field. In this project, several structure models (homology models) are built and simulated on the molecular and quantum mechanic level in order to gain an equilibrium state and validate them by calculating the spectroscopic characteristics and compare them to experimental spectra. On the received structures, calculations in the excited state are performed and give an insight into the reactions which take place in the excited state. This information is important to get an idea about the lifetime and transition probability between the two stable states of the protein. Relax scans in the excited state are calculated in order to characterize the photochemical reaction path ways in Histidin Kinase Rhodopsins by using the quantum mechanical method CASSCF (Complete Active Space Self-Consistent Field) and molecular dynamic simulations in the excited state. Based on the data, we get an insight in the photochemical process in the HKR.

[1] M. Luck et al., *J. Biol. Chem.*, **287**, 40083 (2012).

[2] M. Luck, et al., *FEBS Lett.*, **589**, 1067 (2015).

[3] A. Penzkofer, et al., *Photoche Photobiol.*, **90**, 773 (2014).

## Characterization of the intermediate states of transport cycle of sodium symporters via transition-path sampling methods

Ina Bisha<sup>1,2</sup>, Alessandra Magistrato<sup>3</sup>, Alessandro Laio<sup>4</sup>, Iris Antes<sup>2</sup>, Ville R. I. Kaila<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Technical University of Munich, Lichtenbergstr. 4, 85747 Garching, Germany*

<sup>2</sup>*Protein Modelling Group, Technical University of Munich, Emil-Erlenmeyer-Forum 8, 85354, Freising, Germany*

<sup>3</sup>*CNR-IOM-Democritos National Simulation Center, SISSA, Trieste, Italy*

<sup>4</sup>*SISSA, Via Bonomea 265, 34165 Trieste, Italy*

Sodium symporters are membrane proteins that use Na<sup>+</sup> ions to co-transport a variety of substrates such as sugars, amino acids, neurotransmitters, across cellular membranes against their chemical concentration gradient [1-2]. This process is of fundamental biological importance, and therefore these proteins represent an important target for many diseases. Despite belonging to different gene families these symporters share a common structural core of 10 trans-membrane helices composed of two five-helix inverted repeat motifs, known as ‘LeuT-fold’ [3]. In order to explore the *alternating access mechanism* of sodium symporters, we investigate here the dynamics of these proteins in different conformational states, where substrate accessibility changes from one side to the other of the cellular membrane. To this end, we combine several computational techniques from advanced free energy sampling techniques to hybrid quantum mechanics/classical mechanics (QM/MM) calculations in order to quantitatively describe the transport mechanism, and to investigate how binding of ligands in intermediate states along the transport cycle is coupled to the global conformational protein changes.

[1] H. Krishnamurthy, C. L. Piscitelli, and E. Gouaux, *Nature*, **459**, 347-355 (2009).

[2] O. Jardetzky, *Nature*, **211**, 969–970 (1966).

[3] I. Bisha, A. Magistrato, *RSC Advances*, **6**(12), 9522-9540 (2016).

## Implications of Axial Coordination on the Redox Behavior and H-Atom-Abstraction Reactivity of Compound I Analogues.

Mauricio Maldonado-Domínguez<sup>1</sup>, Martin Srnec<sup>1</sup>

<sup>1</sup>*Department of Theoretical Chemistry, J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Dolejškova 2155/3, Prague 8-Libeň, Czech Republic.*

**Abstract:** Iron-oxo complexes are crucial for the function of many enzymes carrying out chemical transformations that are key to sustain life. In this work, we seek to correlate the redox properties and reactivity of iron systems with their electronic structure, applying theoretical methods calibrated with available electrochemical and spectroscopic data [1,2]. Our study is focused on porphyrin-based complexes where axial coordination tunes reactivity at the central iron-oxo moiety towards H-atom abstraction, aiming to shed light on the role of redox potential in the control of reactivity and selectivity towards activation of C-H and O-H bonds. With these results we strive to generalize the electronic and structural factors controlling reactivity in H-atom abstraction, as carried out by natural systems such as cytochrome P450, providing guidelines to foster the design of biomimetic catalysts to achieve difficult chemical transformations such as direct and selective hydrocarbon functionalization, of current interest to pharmaceutical and fuel industries.

[1] A. Takahishi, D. Yamaki, K. Ikemura, T. Kurahashi, T. Ogura, M. Hada, H. Fujii, *Inorg. Chem.* **51**, 678, (2012).

[2] C. V. Sastri, J. Lee, K. Oh, Y. J. Lee, J. Lee, T. A. Jackson, K. Ray, H. Hirao, W. Shin, J. A. Halfen, J. Kim, L. Que Jr., S. Shaik, W. Nam, *Proc. Natl. Acad. Sci. U.S.A.*, **104**, 19181, (2007).

## Shedding UV-light on the Origins of RNA Nucleotides

Rafał Szabla<sup>1, 2</sup>, Jiri Šponer<sup>2</sup>, Robert W. Góra<sup>3</sup>

<sup>1</sup>*Institute of Physics, Polish Academy of Sciences, Warsaw*

<sup>2</sup>*Institute of Biophysics, Academy of Sciences of the Czech Republic, Brno*

<sup>3</sup>*Department of Physical and Quantum Chemistry, Wrocław University of Technology*

Identification of prebiotically plausible pathways that could lead to RNA nucleotides has been one of the greatest challenges in the studies of the origins of life on Earth. Despite numerous efforts during the past 50 years, the first clean and highly efficient synthesis yielding  $\beta$ -ribocytidine and  $\beta$ -ribouridine nucleotides was published recently.[1] However, many related problems, e.g. the formation purine nucleosides, remain largely unsolved. Since UV irradiation played a central role in these syntheses, thorough understanding of the underlying photochemical reaction mechanisms might be crucial in putting the remaining elements of the puzzle together.

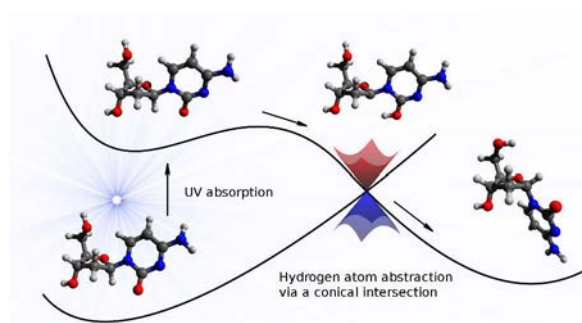


Figure 1: UV-induced C1'–H atom abstraction of 2'-dC, which explains its photoanomerisation.

Recent joint experimental and theoretical efforts provided important mechanistic insights into the photochemical processes governing the UV-assisted formation of pyrimidine nucleotides and the photodestruction of biologically irrelevant by-products. This was achieved by the detailed NMR analysis of the composition of product mixtures and state-of-the-art quantum chemical calculations employing multiconfigurational methods.[2, 3] With this knowledge we aim to address the remaining questions in the field in order to propose pathways that could have lead to the complete set of RNA building blocks on the Archean Earth.

[1] J.D. Sutherland, *Angew. Chem. Int. Ed.* **55**, (2016).

[2] R. Szabla, J. Campos, J.E. Šponer, J. Šponer, R.W. Góra, J.D. Sutherland, *Chem. Sci.* **6**, (2015).

[3] J. Xu, M. Tsanakopoulou, C.J. Magnani, R. Szabla, J.E. Šponer, J. Šponer, R.W. Góra, J.D. Sutherland, *Nature Chem.* **9**, (2017).



## Domain-based Local Pair Natural Variant of Mukherjee's Multireference Coupled Cluster Method

Jiří Brabec<sup>1</sup>, Masaaki Saitow<sup>2</sup>, Jiří Pittner<sup>1</sup>, Frank Neese<sup>2</sup>, Ondřej Demel<sup>1</sup>

<sup>1</sup>J. Heyrovský Institute of Physical Chemistry, AS CR, Dolejškova 3, Prague, Czech Republic

<sup>2</sup>Max Planck Institute of Chemical Energy Conversion, Stiftstrasse 2-4, Mülheim an der Ruhr, Germany

Multireference coupled cluster methods are an accurate approach for systems with quasidegeneracies. However, the applicability of these methods is limited due to the steep  $O(n^6)$  scaling. This poster reports development of a local variant of Mukherjee's state specific multireference coupled cluster method [1] based on the domain based pair natural orbital approach (DLPNO) [2]. A common set of pair natural orbitals is constructed by the diagonalization of the density matrix, obtained at the DLPNO NEVPT2 level, for the each pair of internal and / or active orbitals. The active orbitals are kept unchanged. The current implementation in ORCA package is restricted to single and double excitations and mutually up to biexcited references. The resulting method has a near linear scaling, which is a significant improvement compared to previously reported LPNO MkCC method [3].

The performance of the DLPNO MkCC methods has been benchmarked on tetramethyleneethane, naphthynes, and  $\beta$ -carotene.

[1] U. S. Mahapatra, B. Datta, and D. Mukherjee, *J. Phys. Chem.* **110**, 6171 (1999).

[2] C. Riplinger and F. Neese, *J. Phys. Chem.* **138**, 034106 (2013).

[3] O. Demel, J. Pittner, and F. Neese, *J. Chem. Theory Comput.* **11**, 3104 (2015).

## Modeling and NMR calculations of Oximes in Water and Ionic Liquids: Solvation Shell Structure implications

Faria, J. A.<sup>1</sup>, de Castro, A. A.<sup>1</sup>, Assis, L. C.<sup>1</sup>, Mancini, D. T.<sup>1</sup>, Costa, L. T.<sup>2</sup>, da Cunha, E. F. F.<sup>1</sup>, Ramalho, T. C.<sup>1</sup>

<sup>1</sup>Department of Chemistry, Federal University of Lavras, University Campus, PO Box 3037, CEP 37200-000, Lavras/MG, Brazil. <sup>2</sup>Department of Chemistry, Fluminense Federal University, Miguel de Frias's Street, 9, Icaraí, CEP 24220-900, Niterói/RJ, Brazil

Organophosphorus compounds (OP) have been employed in the agricultural activity for several decades and have neurotoxic effects on the central nervous system, and their toxicity is due to the irreversible inhibition of the acetylcholinesterase (AChE) enzyme. An antidote commonly employed to reactivate AChE is the so-called oxime. These compounds perform a nucleophilic attack on the phosphorus center of the OP reactivating the enzyme [1, 2]. Generally, the detection of OP is performed by employing expensive techniques such as GC and HPLC, but new techniques to detect them have been researched [3]. The use of Ionic Liquid as support for sensors, biosensors and as electrolyte is still little explored, but it is very promising [4]. This work aims to employ molecular dynamics and NMR calculations to investigate the solvent and thermal effects on NMR parameters of oximes in two different solvents, water and 1-Butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF<sub>4</sub>). By using the OPLS force field in the GROMACS 4.6.5 program, classical molecular dynamics simulations were performed for the oxime 3-fluoro-4-[(hydroxyimino)methyl]-1-methyl-pyridinium (3-Fluoro-4-PAM) in both solvents, at times of 1ns and 10ns, respectively. Due to the large number of conformations generated, quantum dynamics calculations were performed to obtain 1000 points using ADMP and B3LYP/6-31G at 310K temperature, starting from the last frame. For NMR calculations, the GIAO method was performed for both the dynamics and static systems, which were obtained through systems optimized at B3LYP/6-31G by using the Gaussian 09 program. The methods were tested for the vacuum optimized oxime on the dynamic and thermal effects employed, without the presence of the solvent, and with the use of explicit and implicit solvent (PCM). Calculations using the 4-PAM oxime were employed to validate the methodology, and with the theoretical NMR results, it was possible to notice that the <sup>13</sup>C chemical shift values were very close to those reported experimentally [5], being the best results from the employment of dynamic, thermal and solvent effects. The same was observed for the 3-Fluoro-4-PAM oxime that presented the best results in the presence of the solvent, with the thermal and dynamic effects. When the solvent is BMIM-BF<sub>4</sub>, the <sup>19</sup>F chemical shift values were about 6 units lower than when water is used, which shows that the OP poisoning detection is best observed when there is an ionic solvent used. According to those data, the use of fluorinated oximes assists in the detection process; this is related to their smaller chemical shift when exposed to solvents.

- [1] K. Kuca, D. Jun, K. Musilek, *Mini. Rev. Med. Chem.* **6**, 269-277 (2006).
- [2] F. P. Carvalho, *Environ. Sci. Policy.* **9**, 685-692 (2006).
- [3] A. Beyer, M. Biziuk, *Food. Chem.* **108**, 669-680 (2008).
- [4] L.-G. Zamfir, L. Rotariu, C. Bala, *Biosens. Bioelectron.* **46**, 61-67 (2013).
- [5] D. Waysbort, D. Balderman, G. Amitai, *Org. Magn. Resonance.* **16**, 7-10 (1981).

## Mechanistic insights into the selective hydrolysis of Asp-X peptide bonds in proteins by Zr(IV)-substituted polyoxometalates

**Tzvetan T. Mihaylov, Hong Giang T. Ly, Tatjana N. Parac-Vogt, Kristine Pierloot**

*Department of Chemistry, KU Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium*

Several recent investigations have shown that metal-substituted polyoxometalates (MSPs) consisting of highly Lewis acidic metal ions, such as Zr(IV) and Ce(IV), embedded into W(VI)-oxygen frameworks induce hydrolytic cleavage of proteins in a regioselective manner [1-2]. A common feature of the MSP-promoted hydrolysis of proteins is that the hydrolytic cleavage occurs exclusively at peptide bonds located at (or in the vicinity of) positively charged patches of the protein surface, regardless of the size, three dimensional folding and surface charge density of the protein. In addition, the MSPs tend to cleave preferentially peptide bonds linking amino acids with carboxylate groups in their side chains (Asp and Glu). A remarkable selectivity has been observed for the hydrolysis of horse heart myoglobin (HHM) catalyzed by a series of Zr(IV)-substituted polyoxometalates (POMs). Although this protein contains also 13 Glu residues a hydrolytic cleavage was observed exclusively at Asp-X type peptide bonds [3].

Here, we report on another example of highly selective protein cleavage by MSPs. In the presence of Zr(IV)- and Ce(IV)-substituted POMs bovine hemoglobin (Hb) was selectively cleaved under mild conditions. Eleven cleavage sites were identified as in all of them the hydrolysis occurs next to Asp residues (Asp-X) located in the vicinity of positively charged patches of the protein surface. This high specific selectivity seems does not depend on the nature of the X amino acid residue, as the latter can be either aliphatic, positively charged or negatively charged, and cannot be explained in terms of non-bonding MSP-protein interactions alone. In order to provide an explanation for the observed selectivity at atomistic level DFT calculations were performed on a model system. Based on this we propose a mechanism of MSP-promoted hydrolysis which may explain why Asp-X type peptide bonds are exclusively cleaved while Gly-X, X-Asp and X-Glu type peptide bonds remain intact.

[1] K. Stroobants, G. Absillis, E. Moelants, P. Proost, T. N. Parac-Vogt, *Chem. Eur. J.* **20**, 3894 (2014).

[2] K. Stroobants, E. Moelants, H. G. T. Ly, P. Proost, K. Bartik, T. N. Parac-Vogt, *Chem. Eur. J.* **19**, 2848 (2013).

[3] H. G. T. Ly, G. Absillis, R. Janssens, P. Proost, T. N. Parac-Vogt, *Angew. Chem. Int. Ed.* **54**, 7391 (2015).

## Excitons and charge transfer states in light-harvesting antenna complexes

**Lorenzo Cupellini<sup>1</sup>, Sandro Jurinovich<sup>1</sup>, Stefano Caprasecca<sup>1</sup>, Ciro A. Guido<sup>2</sup>,  
Marco Campetella<sup>3</sup>, Thomas Renger<sup>4</sup>, Benedetta Mennucci<sup>1</sup>**

<sup>1</sup>*Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Moruzzi 13, Pisa, Italy*

<sup>2</sup>*CEISAM, UMR CNRS 6230, Université de Nantes, 2 rue de la Houssinière, Nantes, France*

<sup>3</sup>*MSC, ENSCP - Chimie ParisTech, 11 rue Pierre et Marie Curie, Paris, France*

<sup>4</sup>*Institute of Theoretical Physics, Johannes Kepler University Linz, Linz, Austria*

Antenna complexes of photosynthetic organisms are pigment-protein aggregates, whose spectroscopic and photophysical properties are determined by the interaction between the pigments and the protein matrix, as well as the interactions among the pigments themselves. The complexity of the interactions and the dimension of such systems hamper the application of standard electronic structure methods. Instead, their properties can be described through an excitonic approximation, in which the properties of single pigments and the couplings among pigments are joined to describe the full system. Nevertheless, a faithful description of the properties and couplings needs to account for the presence of the protein matrix surrounding the pigments.[1] Recently, two-dimensional electronic spectroscopy has revealed that charge-transfer states have a role in the excited-state dynamics of the LH2 antenna complex, by mixing into the bright locally excited states.[2] However, a complete theoretical modelling of such states in the antenna complexes is still a challenge.

Starting from our previous description of the excitonic states in LH2,[3, 4] we present an exciton model that includes charge-transfer states to describe the exciton structure of the LH2 antenna complex. The charge-transfer couplings are obtained along a molecular dynamics simulation employing the Fragment Charge Difference diabatization scheme in its multistate formulation.[5] We show that the mixing to charge-transfer states significantly red-shifts the lowest bright exciton states of the antenna complex. Moreover, the disorder in the energies and couplings of charge-transfer states causes inhomogeneous broadening of the lowest exciton absorption band.

- [1] C. Curutchet, B. Mennucci, *Chem Rev.* **2017**, *117*, 294–343.
- [2] M. Ferretti, R. Hendrikx, E. Romero, J. Southall, R. J. Cogdell, V. I. Novoderezhkin, G. D. Scholes, R. van Grondelle, *Sci. Rep.* **2016**, *6*, 20834.
- [3] L. Cupellini, S. Jurinovich, M. Campetella, S. Caprasecca, C. A. Guido, S. M. Kelly, A. T. Gardiner, R. Cogdell, B. Mennucci, *J. Phys. Chem. B* **2016**, *120*, 11348–11359.
- [4] F. Segatta, L. Cupellini, S. Jurinovich, S. Mukamel, M. Dapor, S. Taioli, M. Garavelli, B. Mennucci, *Journal of the American Chemical Society* **2017**, *139*, 7558–7567.
- [5] C.-H. Yang, C.-P. Hsu, *The Journal of chemical physics* **2013**, *139*, 154104.

## $O(n)$ Concentric Atomic Density Fitting for Hartree-Fock Exchange

Cannada Lewis<sup>1</sup>, Edward Valeev<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Virginia Tech, Blacksburg, Virginia, USA*

Concentric Atomic Density Fitting[1] (CADF), also known as Pair Atomic Resolution of the Identity[2] (PARI), yields a drastic approximation of the two-electron four-center integrals, that allows for  $O(n)$  storage of the density fitting coefficients. Even though the approximate of the electron repulsion integrals is poor, CADF can be safely used to compute the exchange contribution to the Fock matrix with acceptable errors in  $O(n^3)$  operations.[3] To reduce the operation complexity we explore a novel screening method that skips small contributions to the exchange (K) matrix by exploiting the sparsity of both the CADF coefficients and localized molecular orbitals. In doing so we can readily achieve  $O(n)$  operation complexity while having a smaller prefactor than the traditional  $O(n)$  algorithm for exchange LinK.[4] Our approximations greatly improve the performance of CADF exchange (CADF-K) while introducing new errors much smaller than the error already present in the CADF-K approach.

Furthermore we show how the Clustered Low-Rank (CLR) tensor framework[5] can be used to massively reduce the storage required for the three-center two-electron integrals, allowing us to avoid their direct computation further reducing the prefactor associated with CADF-K. Our new screening approximation coupled with the use of the CLR framework yields a highly performant Hartree-Fock exchange algorithm with acceptable accuracy, requiring relatively small amounts of memory and only  $O(n)$  operations within each iteration of the SCF algorithm.

Finally, these algorithms were implemented in the TILEDARRAY framework, a distributed memory massively parallel tensor contraction library, allowing them to scale to thousands of cores. We show the parallel scaling of traditional CADF-K along with our  $O(n)$  implementation across multiple nodes and hundreds of processors.

- [1] D. S. Hollman, H. F. Schaefer, and E. F. Valeev, *J. Chem. Phys.* **140**, 064109 (2014).
- [2] P. Merlot, T. Kjergaard, T. Helgaker, R. Lindh, F. Aquilante, S. Reine, and T. B. Pedersen, *J. Comput. Chem.* **34**, 1486 (2013).
- [3] S. F. Manzer, E. Epifanovsky, and M. Head-Gordon, *J. Chem. Theory Comput.* **11**, 518 (2015).
- [4] C. Ochsenfeld, C. A. White, and M. Head-Gordon, *J. Chem. Phys.* **109**, 1663 (1998).
- [5] C. A. Lewis, J. A. Calvin, and E. F. Valeev, *J. Chem. Theory Comput.* **12**, 5868 (2016).

## The intricate case of tetramethyleneethane

**Libor Veis<sup>1</sup>, Andrej Antalík<sup>1</sup>, Ali Alavi<sup>2, 3</sup>, Örs Legeza<sup>4</sup>, Jiří Pittner<sup>1</sup>**

<sup>1</sup>*J. Heyrovský Institute of Physical Chemistry, ASCR, 18223 Prague, Czech Republic*

<sup>2</sup>*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom*

<sup>3</sup>*Max Planck Institute for Solid State Research, Heisenbergstrasse 1, 70569 Stuttgart, Germany*

<sup>4</sup>*Strongly Correlated Systems “Lendület” Research group, Wigner Research Centre for Physics, H-1525, Budapest, Hungary*

Tetramethyleneethane (TME) represents the simplest disjoint non-Kekulé diradical structure. Although the system might seem simple at the first sight, correct calculation of its electronic structure poses a very challenging problem, indeed. It has been shown that the accurate description of its potential energy surface with respect to rotation around the central carbon-carbon bond requires well-balanced treatment of both, static and dynamic correlation, as well as a large-enough basis set [1].

In this study, we follow the work of Pozun *et al.* [1] and provide new benchmark data calculated by the full configuration interaction quantum Monte Carlo (FCIQMC) method using the active space of 60 molecular orbitals. Our FCIQMC results, which agree well with the available experimental data, are then used for testing of the accuracy of state-of-the-art multireference coupled cluster methods, namely the Mukherjee’s multireference coupled clusters (MR CC) [2] and the coupled clusters with singles and doubles tailored by the density matrix renormalization group method (DMRG-TCCSD).

[1] Z. D. Pozun, X. Su, K. D. Jordan, *J. Am. Chem. Soc.* **135**, 13862 (2013).

[2] D. I. Lyakh, M. Musial, V. F. Lotrich, R. J. Bartlett, *Chem. Rev.* **112**, 182 (2012).

[3] L. Veis, A. Antalík, J. Brabec, F. Neese, Ö. Legeza, J. Pittner, *J. Phys. Chem. Lett.* **7**, 4072 (2016).

## DFT investigation on the *trans*–*cis* C–Pd–C rearrangement in heteroleptic Pd-hemichelates

**S. Dohm<sup>1</sup>, C. Werlé<sup>2</sup>, A. Hansen<sup>1</sup>, S. Grimme<sup>1\*</sup> and J. P. Djukic<sup>2</sup>**

*1. Mulliken Center for Theoretical Chemistry, Institut für Physikalische und Theoretische Chemie, Universität Bonn, Beringstraße 4, D-53115 Bonn, Germany*

*2. Institut de Chimie de Strasbourg, UMR 7177 CNRS, Université de Strasbourg, 4 rue Blaise Pascal, 67000 Strasbourg Cedex 08, France*

Hemichelation is understood as a mode of metal chelation with a heteroditopic ligand where a covalent coordinative bond is supplemented with a predominantly non-covalent stabilizing delocalized interaction of the metal with another metal centered moiety. The ready *trans*-to-*cis* isomerization of such a hemichelate was investigated by dispersion corrected density functional theory. Variable temperature NMR experiments reveal, that the isomerization process requires a rather low activation barrier and that the two systems follow a first-order kinetic law. DFT-D calculations confirm that, in spite of the more important contribution of covalence to the Pd···Cr(CO)<sub>3</sub> in the *trans*-complex, the latter is metastable and converts readily into the *cis* isomer in a single elementary reaction step.

It can be shown, that this isomerization is facilitated dynamically because hemichelation by an arenetricarbonylchromium-ligand dynamically offers in the transition state of the *trans* → *cis* isomerization process alternative coordination positions to the Pd center, which preserves its square planar coordination and keeps the energetic barrier payload low. Instead, in the isomerization of conventional homoleptic *trans*-bispalladacycles involves partial chelate decoordination and an unfavorable high-lying Y-shaped-Pd(II) transition state.

We demonstrate the application of a multilevel composite scheme of decent methods applicable to a wide range of compounds, to obtain reasonable free energies within feasible times. A new tight-binding semiempirical method[1] is used to locate stationary points including transition states. Geometries are refined with the fast, yet accurate PBEh-3c[2] composite method. Solvation contributions are obtained with the COSMO-RS[3] continuum solvent model. The presented scheme allows the calculation of such reactions with reasonable errors of ≈3 kcal/mol within several days even on regular desktop computers.

[1] S. Grimme, C. Bannwarth, P. Shushkov, J. Chem. Theory Comput. (2017), **13**, 1989-2009.

[2] S. Grimme, J. G. Brandenburg, C. Bannwarth, A. Hansen, J. Chem. Phys. (2015), **143**, 054107

[3] A. Klamt, J. Chem. Phys. 1995, **99**, 2224–2235

## Coarse Grained Cross-scale Expression of Complex Combustion Reaction Mechanism Based on Master Equation

Lin Ji, An Ning

*Department of Chemistry, Capital Normal University, Beijing 100048, China*

Combustion chemistry is a special branch of chemistry that aims at getting stable effective combustion condition as the target. Therefore, the key task of combustion chemistry mechanism investigation is to effectively represent the detail combustion mechanism as simplified phenomenological mechanism. Common mechanism reduction method usually “select” the important reactions from the detailed reaction network, trying to improve the simulation efficiency by at the cost of least information lost. Based on the “coarse grained” idea, we propose to develop a three-level coarse grain ansatz, including the statistic of “microscopic state” clustering, the “fluctuationize” expression of multi-channel reaction in mesoscopic level, and extraction of feedback loop in the macroscopic level. Master equation is the expression of law of mass conservation in the Markov stochastic processes. Depending on the definition of “state” at different scale, master equation have different name and form in different area, such as Energy Grained Master Equation[1] in RRKM/ME theory, Markov State Model[2] in protein dynamics and Chemical Master Equation[3] in stochastic reaction dynamics. Altogether, we would develop a set of “information loss free” multiscale coarse grained combustion reaction mechanism expression method, so that we can effectively “simplify” the reaction mechanism model and connect the elementary reaction mechanism investigation with those of fluid dynamics in turbulence combustion research

[1] JA Miller, SJ Klippenstein; *J. Chem. Phys.* **110**:1052.(2006)

[2] CR Schwantes, RT McGibbon, VS Pande; *J. Chem. Phys.* **141**:090901 (2014)

[3] DT Gillespie; *Annu. Rev. Phys. Chem.* **58**: 35 (2007)



## Soft X-ray Spectroscopy of Transition Metal Compounds: A Theoretical Perspective

Sergey I. Bokarev<sup>1</sup>

<sup>1</sup>*Institute of Physics, Rostock University, Albert-Einstein-Str. 23-24, Rostock, Germany*

To date, X-ray spectroscopy has become a routine tool that can reveal highly local and element-specific information on the electronic structure of atoms in complex environments. Here, we aim at the development of an efficient and versatile theoretical methodology for the treatment of soft X-ray spectra of transition metal compounds mainly based on the multi-configurational self-consistent field electronic structure theory combined with a perturbative LS-coupling scheme for spin-orbit coupling [1]. A special focus is put on the L-edge photon-in/photon-out and photon-in/electron-out processes, i.e. X-ray absorption, resonant inelastic scattering, partial fluorescence yield, photoelectron and Auger spectroscopy treated on the same theoretical footing [2-4]. We address the application of the X-ray metal L-edge and ligand K-edge spectroscopy to unraveling electronic structure and nature of chemical bonds [5-7], oxidation and spin-states [4], the interplay of radiative and non-radiative decay channels [3], fingerprints of nuclear dynamics [8,9] as well as ultrafast electron dynamics triggered by X-ray light [10,11]. The investigated systems range from the small prototypical coordination compounds and catalysts [1-7] to the aggregates of biomolecules [12].

- [1] S.I. Bokarev et al. *Phys. Rev. Lett.*, **111**, 083002 (2013).
- [2] G. Grell et al. *J. Chem. Phys.* **143**, 074104 (2015).
- [3] R. Golnak et al. *Sci. Rep.*, **6**, 24659 (2016).
- [4] S.I. Bokarev *J. Phys. Chem. C*, **119**, 19192 (2015).
- [5] E. Suljoti et al. *Angew. Chem. Int. Ed.*, **52**, 9841 (2013).
- [6] N. Engel et al. *J. Phys. Chem. B*, **118**, 1555 (2014).
- [7] K. Atak et al. *J. Phys. Chem. B*, **117**, 12613 (2013).
- [8] S. Karsten et al. *J. Phys. Chem. Lett.* **8**, 992 (2017).
- [9] S. Karsten et al. *J. Chem. Phys.* **146**, 224203 (2017).
- [10] H. Wang et al. *Phys. Rev. Lett.* **118**, 023001 (2017).
- [11] H. Wang et al. *Mol. Phys.* doi:10.1080/00268976.2017.1294267 (2017).
- [12] M. Preuße et al. *Struct. Dynamics* **3**, 062601 (2016).

## Elucidating the structure of merocyanine dyes with the ASEC-FEG method

**Leandro R. Franco, Idney Brandão, Tertius L. Fonseca, Marcos A. Castro,  
Herbert C. Georg**

*Instituto de Física, Universidade Federal de Goiás, Campus Samambaia, 74690-900,  
Goiânia, GO, Brazil*

Merocyanine dyes form an interesting class of materials with many applications. They are used as indicators of polarity, acidity and other properties, as fluorescent probes of macromolecules, as biomarkers, etc. They have also been investigated as possible sensitizers for photodynamic therapy and for solar cells.

Due to their importance in several applications, it is relevant to investigate how the environment affects the structure of merocyanine dyes. However, because of the extended  $\pi$ -electron system connecting the electron donor and acceptor groups, these molecules have sensitive electronic and conformational structure, making the modeling of such systems in medium a difficult task.

In the present work we have applied the ASEC-FEG method (which combines the sequential QM/MM method [1] with the Free Energy Gradient method [2]) to elucidate the structure of Phenol Blue, a typical merocyanine dye, in several solvents, both protic and aprotic, covering a wide range of dielectric constant [3]. The structure of this molecule has been object of some debate in the literature. Some authors suggest that the molecule is mostly in the neutral state whereas other authors point that it is mostly in the zwitterionic state, in solutions of different polarities.

Our results show that the molecule is mostly in the neutral state in aprotic solvents and is displaced to a cyanine-like structure in polar protic solvents. The results also illustrate the important role played by the hydrogen bonds in the conformation of merocyanine dyes.

Acknowledgements: The authors gratefully acknowledge the financial support given by the brazilian agencies CAPES, CNPq and FAPEG.

### References:

- [1] K. Coutinho, S. Canuto, *J. Chem. Phys.* **113**, **9132** (2000).
- [2] N. Okuyama-Yoshida, K. Kataoka, M. Nagaoka, T. Yamabe, *J. Chem. Phys.* **113**, 3519 (2000).
- [3] L. R. Franco, I. Brandão, T. L. Fonseca, H. C. Georg, *J. Chem. Phys.* **145**, 194301 (2016); I. Brandão, L. R. Franco, T. L. Fonseca, M. A. Castro, H. C. Georg, *J. Chem. Phys.* in press (2017).

## Accelerating equilibrium isotope effect calculations by stochastic change of mass

Konstantin Karandashev<sup>1</sup>, Jiří Vaníček<sup>1</sup>

<sup>1</sup>*Laboratory of Theoretical Physical Chemistry, Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015, Lausanne, Switzerland*

Accurate path integral Monte Carlo or molecular dynamics calculations of isotope effects have until recently been expensive because of the necessity to reduce three types of errors present in such calculations: statistical errors due to sampling, path integral discretization errors, and thermodynamic integration errors. While the statistical errors can be reduced with virial estimators and path integral discretization errors with high-order factorization of the Boltzmann operator, here we propose a method for accelerating isotope effect calculations by eliminating the integration error [1]. In particular, we show that the error of thermodynamic integration [2, 3] can be removed entirely by changing particle masses stochastically during the calculation (a trick closely related to lambda-dynamics [4, 5]) and by using a piecewise linear umbrella biasing potential. Moreover, we demonstrate numerically that this approach does not increase the statistical error. An alternative approach to remove the integration error is based on so-called direct estimators [6]. We demonstrate that combining the stochastic change of mass with the direct estimators results in a method with a lower statistical error, and therefore, in more efficient simulations [7]. The resulting acceleration of isotope effect calculations is demonstrated on a model harmonic system and on deuterated species of methane.

- [1] K. Karandashev, J. Vaníček, *J. Chem. Phys.* **146**, 184102 (2017).
- [2] J. Vaníček, W. H. Miller, J. F. Castillo, F. J. Aoiz, *J. Chem. Phys.* **123**, 054108 (2005); T. Zimmermann, J. Vaníček, *J. Chem. Phys.* **131**, 024111 (2009); M. Buchowiecki, J. Vaníček, *Chem. Phys. Lett.* **588**, 11 (2013).
- [3] O. Marsalek, P.-Y. Chen, R. Dupuis, M. Benoit, M. Méheut, Z. Bačić, M. E. Tuckerman, *J. Chem. Theory Comput.* **10**, 1440 (2014); M. Ceriotti, T. E. Markland, *J. Chem. Phys.* **138**, 014112 (2013).
- [4] Z. Liu, B. J. Berne, *J. Chem. Phys.* **99**, 6071 (1993).
- [5] A. Pérez, O. A. von Lilienfeld, *J. Chem. Theory Comput.* **7**, 2358 (2011).
- [6] B. Cheng, M. Ceriotti, *J. Chem. Phys.* **141**, 244112 (2015).
- [7] K. Karandashev, J. Vaníček, in preparation.

## Describing Chemical Reactions in Explicit Solvent Using Adaptive QM/MM Models

**J.M. Boereboom<sup>1</sup>, P. Fleurat-Lessard<sup>2</sup>, R.E. Bulo<sup>1</sup>**

<sup>1</sup>*Inorganic Chemistry and Catalysis group, Debye Institute for Nanomaterials Science,  
Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands*

<sup>2</sup>*Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB), 9 avenue Alain  
Savary, 21078 Dijon Cedex, France*

Solvation plays an important role in chemical reactivity: Changing the solvent can drastically change the mechanism of a reaction. This is especially true for polar protic solvents that can strongly interact with charged intermediates. Taking these effects into account accurately requires an explicit description of the solvent molecules. To obtain reliable insights into the thermodynamics and kinetics of bond formation in the presence of (explicit) solvent, very long and computationally intensive simulations are required. This is only feasible if a multi-scale description of the solvent is adopted. The presented work is two-fold: We compare and test recent multi-scale explicit solvation models [1-3], and present new insights into the role of solvent in an illustrative bond-breaking reaction. The reaction features the solvated  $\text{Me}_2\text{N}-(\text{CH}_2)_3-\text{CH}=\text{O}$  molecule. In its closed form, this molecule contains a five-membered ring with a short  $\text{N}|\cdots\text{C}=\text{O}$  bond. The molecule was selected for this unusual  $\text{N}|\cdots\text{C}=\text{O}$  bond that mimics the transition states of nucleophilic additions onto a carbonyl moiety [4]. The multi-scale models all define two spherical domains in which the solvent molecules are described at the quantum mechanical level. One such domain is centered on the oxygen atom while the second one is centered on the nitrogen.

The accuracy of the models is benchmarked against a reference simulation describing the structural features of the solvated  $\text{Me}_2\text{N}-(\text{CH}_2)_3-\text{CH}=\text{O}$  molecule in its closed form. We show that the closed state is best described by multi-scale solvation models that change smoothly between the QM and MM description. Surprisingly, a micro-solvation model can describe the structure of the closed  $\text{N}|\cdots\text{C}$  state with similar accuracy. Using the best adaptive QM/MM model, we then obtain the first reliable energy for the  $\text{N}|\cdots\text{C}$  bond breaking reaction. This binding energy is around 6.0 kcal/mol, which is stronger than an average hydrogen bond. The micro-solvation model fails to describe this bond formation process. Indeed, only an explicit dual-sphere approach can accurately account for the long-range solvation changes along the reaction path.

- [1] R.E. Bulo, B. Ensing, J. Sikkema, L. Visscher. *J. Chem. Theory Comput.* **5**, 2212 (2009)
- [2] N. Bernstein, C. Varnai, I. Solt, S.A. Winfield, M.C. Payne, I. Simon, M. Fuxreiter, G. Csanyi. *Phys. Chem. Chem. Phys.* **14**, 646 (2012)
- [3] C.N. Rowley, B. Roux, *J. Chem. Theory Comput.* **8**, 3526 (2012)
- [4] J. Pilmé, H. Berthoumieux, V. Robert, P. Fleurat-Lessard. *Chem. Eur. J.* **13**, 5388 (2007)

**Time-resolved X-ray scattering by non-stationary states in atoms and molecules**

**Mats Simmermacher<sup>1</sup>, Andrés M. Carrascosa<sup>2</sup>, Adam Kirrander<sup>2</sup>, Niels E. Henriksen<sup>1</sup>, Klaus B. Møller<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, Technical University of Denmark, Kemitorvet 207, 2800 Kongens Lyngby, Denmark*

<sup>2</sup>*School of Chemistry, University of Edinburgh, David Brewster Road, Edinburgh EH9 3FJ, Scotland*

Modern pulsed X-ray sources permit time-dependent measurements of dynamical changes in atoms and molecules via non-resonant scattering. The planning, analysis, and interpretation of such experiments, however, require a firm and elaborated theoretical framework. Appropriate expressions for the X-ray scattering signal have previously been derived by use of first-order perturbation theory and a quantized description of the electromagnetic radiation [1–3]. In the present work, this approach is applied to non-stationary electronic wave packets in atoms [4] as well as to molecules that undergo rapid dynamics subsequent to excitation. It is demonstrated how the time-resolved X-ray scattering signal can be described and understood in terms of electronic scattering matrix elements, which are Fourier transformed expectation values of the one-electron density operator. Since these elements are obtainable from multi-configurational electronic wave functions in a Gaussian-type orbital basis [5], the scattering signal can be simulated by integration of available electronic structure and quantum dynamics codes into the framework of an appropriate program. Furthermore, a general analytic solution to the scattering signal by electronic wave packets in the hydrogen atom is derived [4]. This establishes an accurate benchmark for numerical calculations and permits further insights into the physics of time-resolved X-ray scattering.

- [1] N. E. Henriksen, K. B. Møller, *J. Phys. Chem. B* **112**, 558 (2008).
- [2] U. Lorenz, K. B. Møller, N. E. Henriksen, *Phys. Rev. A* **81**, 023422 (2010).
- [3] G. Dixit, O. Vendrell, R. Santra, *Proc. Natl. Acad. Sci. U.S.A.* **109**, 11636 (2012).
- [4] M. Simmermacher, N. E. Henriksen, K. B. Møller, *Phys. Chem. Chem. Phys.*, DOI: 10.1039/C7CP01831B (2017).
- [5] A. M. Carrascosa, A. Kirrander, *Phys. Chem. Chem. Phys.*, DOI: 10.1039/C7CP02054F (2017).

## Towards highly accurate correlation energies for molecular systems

**Jian-Hao Li<sup>1</sup>, Clémence Corminboeuf<sup>1</sup>**

*<sup>1</sup>Institute des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland*

Novel ab initio approaches based on the GW approximation are proposed and validated for improving the correlation energies of molecular systems. GW-based methods have been implemented for solid state computations but have become increasingly popular for the description of molecules [1-3]. In the language of diagrammatic many-body perturbation theory, these methods take into account bubble diagrams to all orders via a screened Coulomb interaction. Here, we combine traditional quantum chemistry and GW, with the goal of achieving robust and cost-effective methods that go beyond conventional quantum chemistry for computing the energies of molecules in both the ground and excited state.

- [1] D. Jacquemin, I. Duchemin, X. Blase, *J. Chem. Theory. Comput.* **11**, 3290-3304 (2015).
- [2] F. Caruso, M. Dauth, M. J. van Setten, P. Rinke, *J. Chem. Theory. Comput.* **12**, 5076-5087 (2016).
- [3] F. Bruneval, T. Rangel, S. M. Hamed, M. Shao, C. Yang, J. B. Neaton, *Comput. Phys. Commun.* **208**, 149-161 (2016).

## Mechanistic investigation of solvent-controlled CO<sub>2</sub> reduction by triphos-iron-hydride complex

**Abhishek Khedkar<sup>1, 2</sup>, Anette Petuker<sup>3</sup>, Linda Iffland<sup>3</sup>, Maurice Van Gastel<sup>4</sup>, Michael Roemelt<sup>\* 1, 2</sup>, Ulf-Peter Apfel<sup>\* 3</sup>**

<sup>1</sup>*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany*

<sup>2</sup>*Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany*

<sup>3</sup>*Fakultät für Chemie und Biochemie, Anorganische Chemie I, Ruhr-Universität Bochum, 44780 Bochum, Germany*

<sup>4</sup>*Max-Planck-Institut für Chemische Energiekonversion, Mülheim an der Ruhr, Germany*

There has been increasing interest for converting the greenhouse gas CO<sub>2</sub> into valuable fuels and small organics. The selective reduction of CO<sub>2</sub> is of high value towards a future application as a C1-building block. Existing catalysts used to overcome the low reactivity of CO<sub>2</sub> reduction are mainly based on noble transition metals like ruthenium, rhodium and iridium. First-row transition metals, however, provide the advantage of being less expensive, more abundant and less toxic. As a consequence, the replacement of noble metals with nonprecious metals such as iron, as catalysts for CO<sub>2</sub> reduction is an important target. Recently, we found that a triphos-based iron-hydride complex that is capable of performing solvent-controlled reduction of CO<sub>2</sub>. In THF, the complex reduces CO<sub>2</sub> to CO selectively whereas in acetonitrile, the reduction reactions exclusively afford formate, HCOO<sup>-</sup>. Here we present the results of a theoretical investigation based on density functional theory (DFT) and coupled cluster (CC) calculations that was aimed at elucidating reaction mechanisms of the selective reduction. Importantly, the theoretical studies demonstrate the crucial role of the applied solvent in altering the course of the reaction.

[1] A. Khedkar, A. Petuker, L. Iffland, M. V. Gastel, M. Roemelt and U. Apfel *manuscript in preparation* (2017)

## Detailed Mechanistic Studies on Palladium/Norbornene Catalyzed C-H Amination of Aryl Halide

Ping Chen, Xinhao Zhang\* and Yun-Dong Wu \*

*Lab of Computational Chemistry and Drug Design, Peking University Shenzhen Graduate School, Shenzhen, China*

C-H functionalization of aryl halides have had an important impact on modern organic chemistry<sup>[1]</sup>. Different types of bonds can be constructed through Pd/NBE co-catalyzed C-H activation of aryl halide, but the mechanism is still unclear. A catalytic cycle involving three different oxidation states of palladium ( $\text{Pd}^0/\text{II}/\text{IV}$ ) was proposed<sup>[2]</sup>. Inspired by Catellani reaction, Dong and coworkers developed a novel ortho C-H amination reaction<sup>[3]</sup>. In the reaction, two oxidants, i.e. aryl iodide and  $\text{BzO-NR}_2$ , are involved. Aryl iodide is preferred in the oxidative addition of  $\text{Pd}^0$ , while  $\text{BzO-NR}_2$  is favored in the oxidative addition of  $\text{Pd}^{\text{II}}$  intermediate **C**. In mass spectrometric experiment, a  $\text{Pd}^{\text{IV}}$  intermediate containing Cs atom was observed. Therefore, a Cs model that  $\text{Cs}_2\text{CO}_3$  assist oxidative addition to  $\text{Pd}^{\text{II}}$  intermediate was proposed. The computational results show that  $\text{Pd}^{\text{II}}$  intermediate selectively react with benzoxyl morpholine, which is consistent with experimental results. Distortion-interaction analysis show that the reduction of the distortion energy of benzoxyl morpholine in Cs model is the key factor for the change of the substrate selectivity.

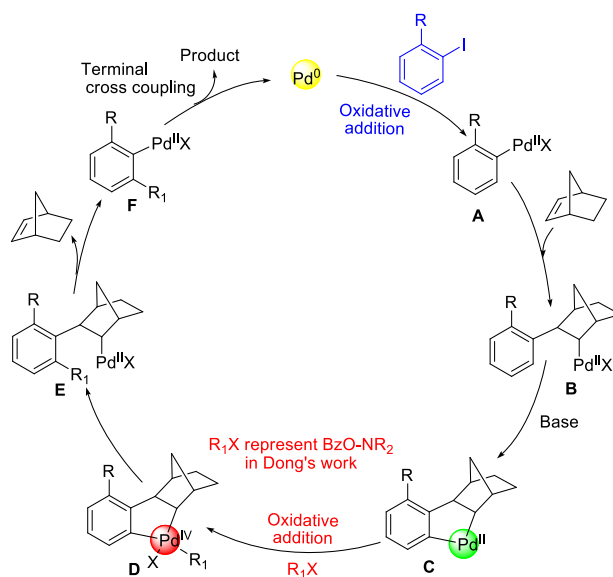


Figure 1. Proposed mechanism of Catellani reaction.

[1] J. Ye, M. Lautens, *Nat. Chem.* **7**, 863-870 (2015).

[2] M. Catellani, F. Frignani, A. Rangoni, *Angew. Chem. Int. Ed.* **36**, 119-122 (1997).

[3] Z. Dong, G. Dong, *J. Am. Chem. Soc.* **135**, 18350-18353 (2013).



## Enhancing fluctuations in chemical reactions

GiovanniMaria Piccini<sup>1</sup>, Michele Parrinello<sup>1</sup>

<sup>1</sup>Department of Chemistry and Applied Biosciences, ETH Zurich, c/o USI Campus, Via Giuseppe Buffi 13, CH-6900, Lugano, Ticino, Switzerland

Molecular dynamics is a powerful tool to study the evolution of complex chemical systems. However, reactant and product states are often separated by very large activation energy barriers. Because of this fact, the typical time scales of a chemical transition cannot be reached in a standard simulation. This limitation can be overcome by applying a bias potential to the underlying potential energy surface, thus enhancing the fluctuations between reactants and product states.

Here we show how two different enhanced sampling methods, namely variationally enhanced sampling<sup>1</sup> (VES) and Metadynamics, can be used to study chemical reactions characterized by large energy barriers and involving rather complex degrees of freedom. We studied the asymmetric  $\text{CH}_3\text{F} + \text{Cl}^- \leftrightarrow \text{CH}_3\text{Cl} + \text{F}^-$   $S_N2$  reaction using VES to obtain the Free-energy profile (see Fig. 1a) and calculate the rates.<sup>2</sup> We then studied the cyclization reaction of deprotonated 4-chloro-1-butanethiol to tetrahydrothiophene (see Fig. 1b) using metadynamics. Within this framework we applied the variational approach for conformation dynamics (VAC) to identify the best combination of variables allowing a proper Free-energy sampling.

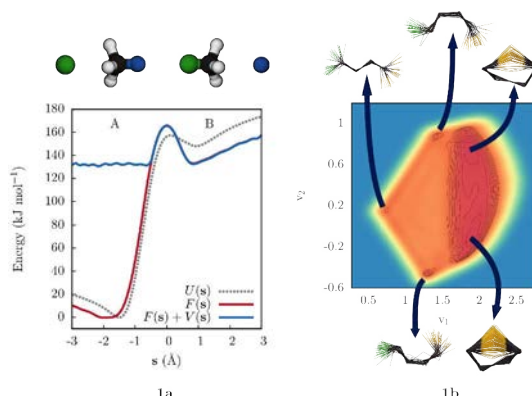


Figure 1: a), Flooded Free-energy profile for the  $\text{CH}_3\text{F} + \text{Cl}^- \leftrightarrow \text{CH}_3\text{Cl}$ , b), FES of the tetrahydrothiophene cyclization reaction showing the different conformers of reactants and products.

[1] O. Valsson, M. Parrinello, *Phys. Rev. Lett.* **2014**, 113, 90601.

[2] G. Piccini, J. J. McCarty, O. Valsson, M. Parrinello, *J. Phys. Chem. Lett.* **2017**, 8, 580–583.

## Ultrafast spin-flip dynamics in transition metal complexes triggered by soft X-ray light

Huihui Wang<sup>1</sup>, Sergey I. Bokarev<sup>1</sup>, Saadullah G. Aziz<sup>2</sup>, Oliver Kühn<sup>1</sup>

<sup>1</sup>*Institute of Physics, Rostock University, Albert-Einstein-Str. 23-24, Rostock, Germany*

<sup>2</sup>*Chemistry Department, Faculty of Science, King Abdulaziz University, 21589 Jeddah, Saudi Arabia*

Recent advances in attosecond spectroscopy open the door to understanding the correlated motion of valence and core electrons on their intrinsic timescales. For valence excitations, processes related to the electron spin are usually driven by nuclear motion. When going, however, to the core-excited states where the core hole has a nonzero angular momentum, a strong spin-orbit coupling starts to play a role [1-3]. In this work, we present a theoretical simulation of an ultrafast spin-flip dynamics driven solely by spin-orbit coupling and electron correlation in the L-edge (2p→3d) excited states of a prototypical Fe(II) complex, which occurs faster than the core hole lifetime (about 4 fs) [4,5]. The non-equilibrium electron dynamics is studied by means of time-dependent restricted active space configuration interaction recast in the form of reduced density matrix propagation. The spin-orbit coupling between electronic states of different multiplicity is considered within the LS-coupling limit employing atomic mean-field integral approximation. Dissipative effects of electronic and vibrational origin are considered as well. A detailed analysis of such phenomena will help to gain a fundamental understanding of spin-crossover processes and build up the basis for their control by light.

[1] S.I. Bokarev, M. Dantz, E. Suljoti, O. Kühn, E.F. Aziz *Phys. Rev. Lett.* **111**, 083002 (2013).

[2] S.I. Bokarev, M. Khan, M.K. Abdel-Latif, J. Xiao, R. Hilal, S.G. Aziz, E.F. Aziz, O. Kühn *J. Phys. Chem. C* **119**, 19192 (2015).

[3] R. Golnak, S.I. Bokarev, R. Seidel, J. Xiao, G. Grell, K. Atak, I. Unger, S. Thürmer, S.G. Aziz, O. Kühn, B. Winter, E.F. Aziz *Sci. Rep.* **6**, 24659 (2016).

[4] H. Wang, S.I. Bokarev, S.G. Aziz *Phys. Rev. Lett.* **118**, 023001 (2017).

[5] H. Wang, S.I. Bokarev, S.G. Aziz *Mol. Phys.* doi: 10.1080/00268976.2017.1294267 (2017).

## Theoretical Investigations of Sigma-Hole Interaction in Condensed Halogen Systems

Carsten Müller<sup>1</sup>

<sup>1</sup>*Theoretical Chemistry, Institute for Chemistry and Biochemistry, Freie Universität Berlin,  
Takustr. 3, 14195 Berlin, Germany*

Sigma-hole interaction determines the crystal structures of Cl<sub>2</sub>, Br<sub>2</sub> and I<sub>2</sub> and of many polyhalogen compounds. Here we investigate more recently explored polyhalogen crystals of chlorine [1-2], bromine [3] and iodine monobromide [4]. By means of theoretical periodic density functional theory calculations, we not only confirm experimental X-Ray structures and vibrational spectra but also interpret the bonding pattern in the polyhalogen network and explore the influence of different cations.

In the two modifications of solid F<sub>2</sub> – on the other hand – sigma hole interaction does not appear to be important and solids based on polyfluorine networks seem not to exist due to the less developed sigma hole in F<sub>2</sub>. Here we investigate  $\alpha$ - [5] and  $\beta$ -F<sub>2</sub> [6] at coupled cluster level applying an incremental scheme to understand why F<sub>2</sub> behaves differently in solids than other halogens and to confirm experimentally observed X-Ray structures from literature.

[1] R. Brückner, H. Haller, S. Steinhauer, C. Müller, S. Riedel, *Ang. Chem. Int. Ed.* **54**, 15570 (2015).

[2] R. Brückner, P. Pröhm, A. Wiesner, S. Steinhauer, C. Müller, S. Riedel, *Ang. Chem. Int. Ed.* **55**, 10904 (2016).

[3] K. Sonnenberg, P. Bröhm, S. Steinhauer, A. Wiesner, C. Müller, S. Riedel, *Z. Anorg. Chem.* **643**, 101 (2017).

[4] L. Mann, P. Voßnacker, C. Müller, S. Riedel, *Chem. Eur. J.* **23**, 244 (2017).

[5] S. Mattsson, B. Paulus, C. Müller, *in preparation*.

[6] C. Müller, *in preparation*.

## Theory of Strong-Field Effects in Femtosecond Electronic Two-Dimensional Spectroscopy

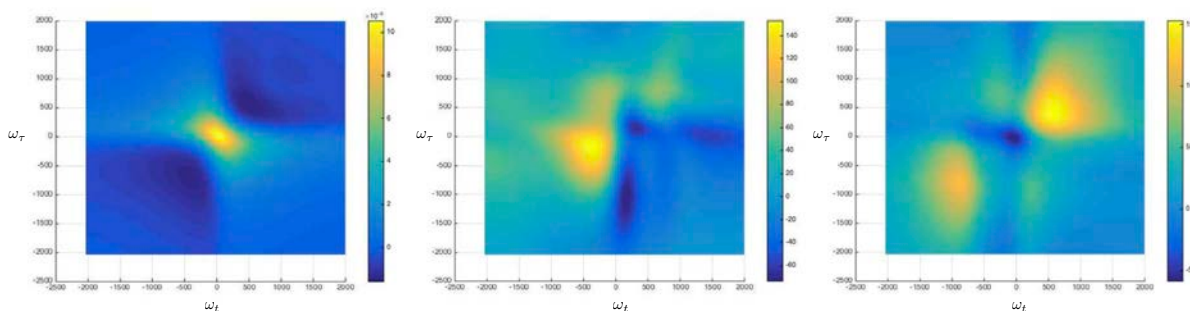
Elisa Palacino-González\*, Lipeng Chen, Maxim F. Gelin and Wolfgang Domcke  
Department of Chemistry, Technical University of Munich, D-85747 Garching, Germany

\*Corresponding author: [elisa.palacino@ch.tum.de](mailto:elisa.palacino@ch.tum.de)

Usually, femtosecond spectroscopic experiments are performed in the regime of weak coupling between the chromophore and the applied laser fields. The goal of femtosecond time-resolved spectroscopy is to obtain information on the photoinduced dynamics of the molecule under study rather than to manipulate its dynamics. Nevertheless, a growing number of experimental and theoretical studies reveal that the signals induced by suitably chosen comparatively strong laser fields may provide more information on the photoinduced dynamics than weak-field signals. For example, it was demonstrated that strong pump and probe pulses in femtosecond pump-probe spectroscopy can significantly enhance weak transitions which cannot be detected with pump-probe spectroscopy in the weak-field regime [1].

Electronic two-dimensional (2D) spectroscopy is currently one of the most popular techniques in coherent femtosecond spectroscopy. In the present work, we theoretically investigate the application of this technique beyond the weak-field limit. We consider a model consisting two electronic states which are linearly coupled to a single vibrational mode, assuming that the displacement of the potential-energy function of the excited electronic state relative to the electronic ground state is relatively small. This situation is typical, for example, for porphyrins and related molecules.

Strong matter-field coupling causes a breakdown of theories which are based on perturbation theory in the matter-field coupling. We therefore evaluate the nonlinear polarization in the rephasing and non-rephasing phase matching directions in a nonperturbative manner, solving the relevant driven master equations numerically. In the limit of weak matter-field coupling, the polarization obtained in this way reduces to the third-order polarization. For intermediate and strong matter-field coupling, on the other hand, the thus-obtained polarization contains all relevant higher-order contributions beyond the weak-field limit.



Typical computed non-rephasing 2D spectra for a two-state one-mode model are presented in the figure. The left panel shows the weak-field signal which is indistinguishable from that of the electronic two-level system without electron-vibration coupling. Stronger pulses enhance the effective electron-vibration coupling of the system, revealing vibrational transitions in the 2D spectra (middle and right panels). Our analysis shows that the strength of the laser field at the peak of the pulses and the duration of the pulses can be fine-tuned to enhance the information content of the 2D spectra.

### References

- [1] Gelin, M. F., Belyaev, A. K. and Domcke, W. Pump-probe spectroscopy with strong pulses as a tool to enhance weak electronic transitions, *Phys. Rev. A* **87**, 063416 (2013).

**Virtual screening through molecular fingerprinting of existing antipsychotic drugs.****Ashish Radadiya<sup>1b</sup>, Harshika Patel<sup>3</sup>, Payal Bhalodia<sup>3</sup>, Hardevsinh Vala<sup>2</sup>, Anamik Shah<sup>2\*</sup> and Nigel Richards<sup>1</sup>**<sup>1</sup>*School of Chemistry, Cardiff University, Cardiff, UK*<sup>2</sup>*National Facility for Drug Discovery Centre, Department of Chemistry, Saurashtra University, Rajkot-360005, Gujarat, India*<sup>3</sup>*Department of Pharmacology, R. K. College of Pharmacy, Rajkot, Gujarat, India.****E-mail:*** *anamik\_shah@hotmail.com*

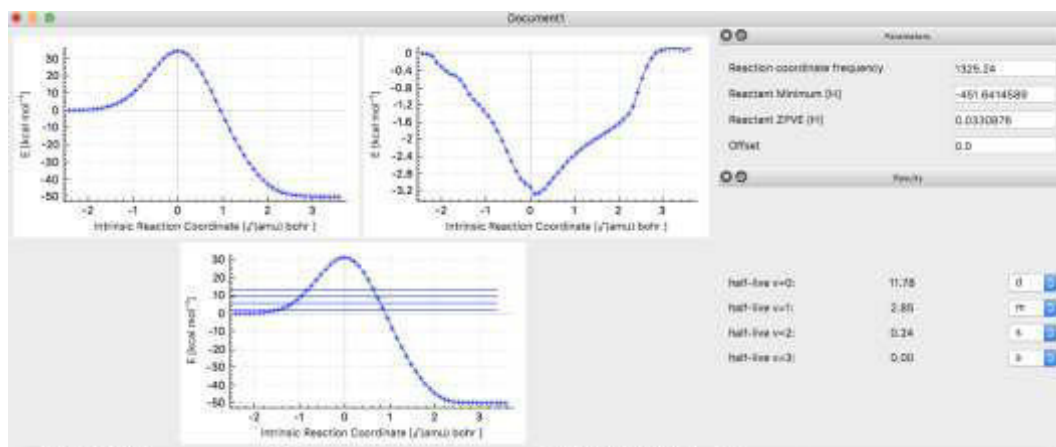
**Abstract:** Use of molecular fingerprinting in virtual screening is easier and faster but yet powerful technique in medicinal chemistry research for initial hit identification. Here, an attempt has been made for finding similar compounds from the FPMD library (an in-house collection of 7000 small organic molecules) based on approved antipsychotic drugs targeting D2 receptors, serotonin receptors and 5-HT<sub>2A</sub>. Different molecular fingerprints like FCFP, ECFP, ECFC were used for comparative studies of Drug database. Top 20 ranked molecules were identified and among them HKV-54, 68, 71, 86, 102 and 115 were screened for their in vivo antipsychotic activity against rat model of 48 mice. The study includes Catalepsy, Inhibition of Apomorphine induced stereotypic reaction, Pole climbing avoidance and sedative effect. Results obtained were comparable with existing antipsychotic drugs available in market.

## Tunnex: A user-friendly program to compute tunneling kinetics

Henrik Quanz<sup>1</sup> and Peter R. Schreiner<sup>1</sup>

<sup>1</sup>*Institute of Organic Chemistry, Justus-Liebig University, Heinrich-Buff-Ring 17, 35392 Gießen, Germany*

Since the discovery of *tunneling control* in our group [1], demands for computing tunneling kinetics have increased significantly.[2-4] Tunnex is a cross-platform free open-source program under development to estimate reaction rates from electronic structure packages (ESPs). Transition state theory (TST), Variational TST (VTST), tunneling corrections, including the Wigner, Eckart as well as the Wentzel, Kramers and Brillouin (WKB) approximations, will be included in the final version. The program consists of two parts: a graphical user interface (GUI) to visualize and compute the results and a command line tool to collect the data from ESPs. Currently, only Gaussian is supported, but the interface will be made extendable by script languages through plugins. Tunnex offers customizable 2d plots and the data are accessible in tables; data export is also supported. The goal is to combine the GUI and the command line tool to one final program including project management and server support.



- [1] P. R. Schreiner, H. P. Reisenauer, D. Ley, D. Gerbig, C.-H. Wu and W. D. Allen, *Science* **332**, 1300 (2011)
- [2] M. Schäfer, K. Peckelsen, M. Paul, J. Martens, J. Oomens, G. Berden, A. Berkessel and A. J. Meijer, *J. Am. Chem. Soc.* (2017)
- [3] S. Karmakar and A. Datta, *J. Org. Chem.* **82**, 1558 (2017)
- [4] C. M. Nunes, S. N. Knezz, I. Reva, R. Fausto and R. J. McMahon, *J. Am. Chem. Soc.* **138**, 15287 (2016)

## Activation of the GTP Hydrolysis by the Switch I region in the Elongation Factor EF-Tu

**Gülşah Çifci<sup>1</sup>, Şeref Gül<sup>2</sup>, Mehtap Işık<sup>3</sup>, Selami Ercan<sup>4</sup>, Viktorya Aviyente<sup>1</sup>, Neş'e Bilgin<sup>5</sup>, Bülent Balta<sup>6</sup>**

<sup>1</sup>Bogazici University, Department of Chemistry, 34342 Bebek, Istanbul

<sup>2</sup>Koç University, Department of Chemical and Biological Engineering, 34450 Sariyer, Istanbul

<sup>3</sup>Tri-Institutional PhD Program in Chemical Biology, Weill Cornell Graduate School of Medical Sciences, 1300 York Ave, New York, NY 10065

<sup>4</sup>Batman University, School of Health, 72060 Batman

<sup>5</sup>Boğaziçi University, Department of Molecular Biology and Genetics, 34342 Bebek, Istanbul

<sup>6</sup>Istanbul Technical University, Department of Molecular Biology and Genetics, 34469 Maslak, Istanbul

Elongation factor Tu (EF-Tu) is responsible of the delivery of the aminoacyl-tRNA to the ribosome. EF-Tu is a G-protein with a low intrinsic GTPase activity, but this activity can be accelerated by  $\approx 6 - 7$  orders of magnitude by programmed ribosomes. The stimulation of the GTP hydrolysis is thought to be triggered by a conformational rearrangement of EF-Tu, which is in turn caused by a conformational rearrangement of the ribosome and tRNA.

Molecular dynamics simulations, 200-300 ns long, have been carried out on the wild type and mutant EF-Tu·GTP complexes from *T. aquaticus* and *E. coli*. The Amber ff03 force field has been used, together with a periodic box of TIP3P water molecules.

In *T. aquaticus*, the Switch I region has been found to be very mobile and R57 of Switch I enters the active site like the catalytic arginine in other G-proteins. While in the wild type *E. coli* EF-Tu, the corresponding K56 has remained out of the active site, in the simulations at a higher temperature or using the K56R mutant, this residue has come close to GTP.

pK<sub>a</sub> calculations via thermodynamic integration simulations show that an important fraction of H85, a residue known to mediate the stimulatory effect of the ribosome, is doubly protonated. When doubly protonated, H85 spends a considerable time in the active site even in the absence of ribosomes.

We also show that the T62- $\gamma$ -phosphate and T62-Mg<sup>2+</sup> interactions are necessary to maintain the GTP bound conformation of Switch I, whereas D51 is not crucial.

## Q-Chem 5: Facilitating Worldwide Scientific Breakthroughs

Evgeny Epifanovsky<sup>1</sup>

<sup>1</sup>*Q-Chem, Inc. 6601 Owens Drive, Suite 105, Pleasanton, California 94588, USA*

Founded in 1993, Q-Chem strives to bring its customers state-of-the-art methods and algorithms for performing quantum chemistry calculations. Cutting-edge innovation, performance, and robustness are Q-Chem's distinguishing features. Q-Chem is an open-teamware project, and the latest release includes contributions from more than 100 developers in 9 countries.

This poster presents methodological advances and algorithmic improvements contained in the new release of our software, Q-Chem 5:

- Quantum chemistry's broadest range of density functionals. Over 200 functionals!
- New parallel capabilities. The new occ-RI-K method significantly speeds up hybrid DFT calculations of the energy and gradient in large basis sets. OpenMP parallel DFT frequency is available. Improved parallel RI-MP2 and coupled cluster gradients.
- All-new effective core potential library. Vital for heavy elements, it provides higher angular momentum capabilities for energies, analytical gradients and analytical frequencies. Also improved precision and support for OpenMP parallel evaluation.
- New solvation and QM/MM capabilities. The CMIRS solvation method is available. New capabilities to model solvation effects on excited states and NMR are included.
- New energy decomposition analysis (EDA) methods. The DFT-based second generation ALMO-EDA with stable basis set limits is implemented, and its single bond extension is available. The adiabatic EDA and MP2 ALMO-EDA are included.
- New anharmonic methods. The uncoupled mode model is available for more accurate anharmonic thermochemistry than harmonic analysis. A new anharmonic vibrations module is included for accurate spectroscopic prediction.
- New electron correlation methods. For strongly correlated molecules, unique new methods, include NOCI-MP2, spin-flip extensions, CCVB for open shells, CCVB-SD energies and gradients for closed shells. Traditional CASSCF is now available.
- General improvements. Greatly expanded basis set library. New visualization capabilities in IQmol front end.



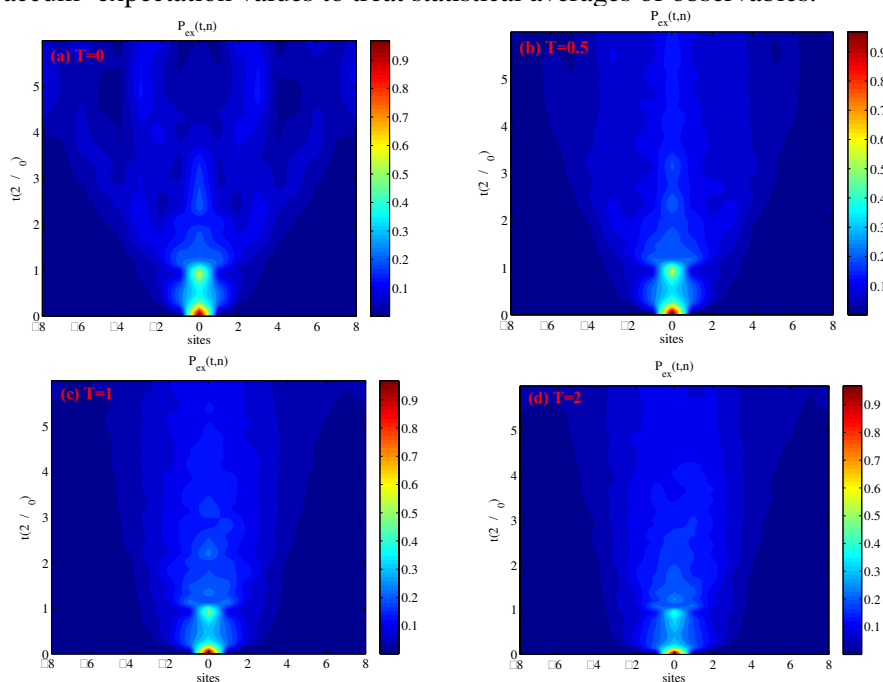
## Finite temperature dynamics of a Holstein polaron: Thermo Field dynamics approach

Lipeng Chen

*Department of Chemistry, Technische Universität München, D-85747 Garching, Germany*

Organic solar cells (OSCs) offer the advantage of wide-ranging chemical functionalities which render tunable their optical, electrical, electrochemical, and morphological properties. However, OSCs have yet to possess the photocurrent efficiencies of their inorganic counterparts, thereby limiting their large-scale commercial applications. It is thus imperative that uncovering the mechanisms of charge transport will immensely facilitate the design of solar-to-electronic energy conversion devices with high efficiency and robustness. Despite many intriguing facets of charge transport uncovered in recent years, a consensus has yet to emerge on fundamental mechanisms of charge transport in organic semiconductors.

Theoretical study of charge transport in organic molecular crystals has a long and rich history dating back to as early as 1950s when Holstein pioneered the concept of small-polaron movement. A large body of literature exists on the study of the conventional form of Holstein Hamiltonian with the diagonal coupling only. However simultaneous presence of diagonal and off-diagonal electron-phonon coupling seems crucial to characterize the charge carriers transport behavior in organic semiconductors. Previously, we have proposed a multitude of the Davydov trial states, i.e., a superposition of the  $D_1$  or the  $D_2$  Ansatz, referred to the ‘multi- $D_1$ ’ or ‘multi- $D_2$ ’ Ansatz to systematically study the dynamics of a one dimensional Holstein polaron in the presence of simultaneous diagonal and off-diagonal exciton-phonon coupling at zero temperature. Here, we extend polaron dynamics described by multiple Davydov ansatz to finite temperature by seamlessly integrating the multi- $D_2$  ansatz into the thermo field dynamics (TFD) framework, a finite temperature representation of quantum mechanics employing temperature dependent ‘vacuum’ expectation values to treat statistical averages of observables.



The time evolution of the exciton probability at different temperatures  $T=0, 0.5, 1, 2$  are displayed in Figure above. We have found that the increase of temperature inhibits polaron mobility for weak to moderate diagonal coupling, while off-diagonal coupling induce phonon-assisted transport which dominates at high temperature. It is also demonstrated that band-like transport features dominate the diagonal coupling case, and there exists a crossover from band-like to hopping transport with increasing temperature when including off-diagonal coupling.

## Applicability of the Effective Oxidation State analysis

**Verònica Postils, Carlos Delgado-Alonso, Josep M. Luis, Pedro Salvador\***

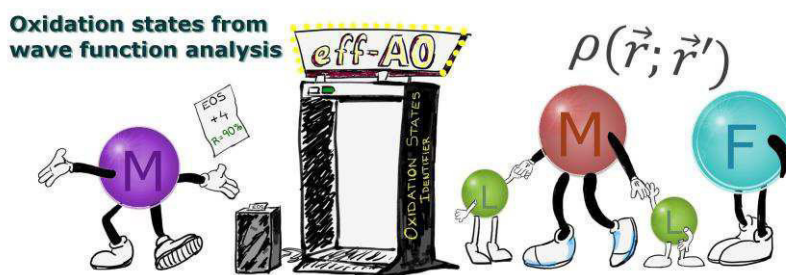
*Institut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona, Maria Aurèlia Capmany 69, 17003, Girona, Spain.  
email: vpostils@gmail.com*

Oxidation State (OS) is a relevant and worldwide-used concept in Chemistry defined as the charge an atom has (*might be imagined to have*) after applying an agreed-upon rules. However, conceptually, the OS is a property intrinsically related to the distribution of electrons around the atom. Thus, the electronic wave function of the system should contain this type of information if a proper partition and scheme is devised. In 2015, we introduced a general scheme to measure the OS from wave function analysis, the so-called effective oxidation state (EOS) analysis [1].

Here we present a systematic EOS analysis [2] taking into account, among others, the compounds described in the recent Karen's IUPAC Report on the revision of the OS concept [3]. Remarkably, the results of our quantum mechanical approach can be reconciled with the empirical rules given by Karen to calculate OSs in most cases and, in some difficult or unclear situations where Karen used special provisions to reproduce the expected OS, our approach is free of such considerations. For instance, when the more electronegative atom is bonded as a Lewis acid or when the molecule cannot be described by a single Lewis structure.

The determination of the OS in carbene structures represents another limitation of the *new* empirical rules reported in the IUPAC's report. Mainly, they cannot retrieve the different splitting of the carbene double bond and the different OSs Fischer- and Schrock-like carbenes have due to differences in their electronic structure and bonding. The empirical rules given by Karen, unlike EOS analysis, cannot describe the homolytic double bond cleavage is expected by Fischer-like carbenes.

Finally, the results obtained from EOS analysis on a large set of  $\pi$ -haptocomplexes will be presented, where a broader rule to determine the OS for these compounds can be devised: the  $\pi$ -haptoligand in the complex presents the OS that corresponds to an aromatic structure, according to Huckel's and Baird's aromaticity rules.



- [1] E. Ramos-Cordoba, V. Postis, P. Salvador, *J. Chem. Theory Comput.* **11**, 1501 (2015).
- [2] V. Postils, C. Delgado-Alonso, J. M. Luis, P. Salvador, *in preparation*.
- [3] P. Karen, P. McArdle, J. Takats, *Pure Appl. Chem.* **86**, 1017 (2014). P. Karen, *Angew. Chem. Int. Ed.* **54**, 2 (2015).

## Spectroscopy of Cooperative Laser Electron- $\gamma$ -Nuclear Processes in Molecules and Clusters: New Effects in Cryogenic Molecules

**A.V. Glushkov<sup>1,2</sup>, A.A. Kuznetsova<sup>2</sup>, O.Yu. Khetselius<sup>1,2</sup>**

<sup>1</sup>*Department of Applied Mathematics and Quantum Optics, Odessa State University – OSENU, Lvovskaya str.,15, Odessa, 65016, Ukraine*

<sup>2</sup>*International Centre of Quantum Chemistry, Odessa State University – OSENU, Lvovskaya str.,15, Odessa, 65016, Ukraine*

In the modern molecular spectroscopy a great interest attracts studying a new class of phenomena, connected with modelling the cooperative laser-electron- $\gamma$ -nuclear processes. It includes calculation of the probabilities of the mixed  $\gamma$ -optical transitions in molecules, intensities of the complicated  $\gamma$ -transitions due to the changing of the molecular excited state population due to a laser field effect. The first qualitative estimates of the cooperative effects parameters were earlier presented (e.g. [1] and refs. therein). We develop an advanced computational approach to calculation of laser-electron- $\gamma$ -transition spectra (electron-vibrational-rotational satellites) of nucleus in diatomic and multiatomic molecules, based on density functional (one version) and model potential (second version) methods and energy approach [2].

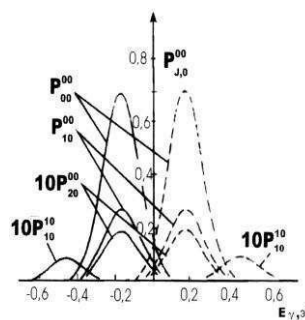


Fig.1 Emission and absorption spectrum of  $^{127}\text{I}$  in  $\text{H}^{127}\text{I}$  ( $\nu_a=0, J_a=0$ )

Decay and excitation probability are linked with imaginary part of the molecule - field system. New data on the electron-nuclear  $\gamma$ -transition spectra of a nucleus in some molecules are presented, namely, for diatomics, 3-atomic  $\text{XY}_2$  ( $\text{D}_{\infty h}$ ), 5-atomic  $\text{XY}_4$  ( $\text{T}_d$ ), 7-atomic  $\text{XY}_6$  ( $\text{O}_h$ ) ones ( $\text{HI}$ ,  $\text{HBr}$ ,  $\text{OsO}_4$ ,  $\text{UF}_6$ , alkali dimers). As example, in fig.1 the theoretical emission (solid curve) and absorption spectrum of nucleus  $^{127}\text{I}$  in  $\text{H}^{127}\text{I}$  is presented. It is shown that studying cooperative electron-gamma-nuclear processes in cryogenic Rydberg molecules (such as  $^{133}\text{Cs}$  nucleus;  $E_{\gamma}^{(0)}=81$  keB;  $^{85}\text{Rb}^{133}\text{Cs}$ ) allows to discover the cooperative effects experimentally for the first time.

- [1] V. Letokhov, C. Moore, *Chemical and Biochemical Applications of Lasers*, Acad. Press, N-Y, 1979; V. Letokhov, V. Minogin, *JETP.Sov.Phys.* **70**, 794 (1976); L. Ivanov, V. Letokhov, *JETP.Sov.Phys.* **93**, 396 (1987); A. Glushkov, L. Ivanov, V. Letokhov, Preprint ISAN N-AS4, Moscow-Troitsk, 1992; *Phys.Lett.A.* **170**, 33 (1992).  
 [2] A. Glushkov, O. Khetselius, S. Malinovskaya, *Molec. Phys.* **160**, 1257 (2008); *Frontiers in Quantum Systems in Chemistry and Physics, Ser.: Progress in Theor.Chem. and Phys.* Ed. S. Wilson, P. Grout, J. Maruani, G. Delgado-Barrio, P. Piecuch (Springer) **18**, 523 (2008).

## A Detailed View into Structural and Functional Mechanism of the First Intermediate State of Channelrhodopsin-2

**Beatrix M. Bold<sup>1</sup>, Yanan Guo<sup>1</sup>, Franziska E. Beyle<sup>1</sup>, Peter Hegemann<sup>2</sup>, Marco Marazzi<sup>1,3</sup> and Marcus Elstner<sup>1</sup>**

<sup>1</sup>*Department of Theoretical Chemical Biology, Institute of Physical Chemistry, KIT, Kaiserstrasse 12, 76131 Karlsruhe, Germany*

<sup>2</sup>*Experimental Biophysics, Institute of Biology, Humboldt-Universität, Invalidenstrasse 42, 10115 Berlin, Germany*

<sup>3</sup>*Université de Lorraine-Nancy & CNRS, SRSMC, Vandoeuvre-lès-Nancy, France*

Channelrhodopsins (ChRs) are light-gated ion channels and widely used in the field of optogenetics, because of their easy expressibility in various host cells and their ability to generate photo currents in a very controlled fashion.

They consists of the light-isomerizable chromophore retinal. Light absorption of the dark-state of ChR causes the isomerization of retinal from all-*trans* to 13-*cis*. The isomerization triggers a cyclic reaction, where a sequence of different reactions like opening or closing of the channel take place. It is called photocycle and consists of several intermediate states, which are spectroscopically identified.

A QM/MM study of the dark state of ChR2 Wild-Type give already an insight into the active site [1]. A detailed atomistic knowledge of the active site is needed for further studies of the several intermediate states. The first intermediate state of ChR2 is called P1. Spectroscopic results give an insight of changes happen in P1. However, a detailed atomistic description of P1 still lacks, which is important to understand the complete photocycle.

Several techniques are used to characterize the atomistic and functional mechanism of this first intermediate state. QM/MM and MM simulations were performed to study the P1 state. Calculation of excitation energies and vibrational frequencies are used to compare with spectroscopic data and to characterize changes in the active site and in the protein environment of the chromophore retinal in P1.

[1] Y. Guo, *Chemical Science* 7, 3879 (2016).

## Spectroscopy Interatomic Potentials, Collisional Spectral Line Shift and Broadening for molecular pairs “heavy atom- noble gas atom”

**O.Yu. Khetselius<sup>1,2</sup>, A.A. Kuznetsova<sup>2</sup>, V. F. Mansarliysky<sup>2</sup>**

<sup>1</sup>*Department of Applied Mathematics and Quantum Optics, Odessa State University – OSENU, Lvovskaya str.,15, Odessa, 65016, Ukraine*

<sup>2</sup>*International Centre of Quantum Chemistry, Odessa State University – OSENU, Lvovskaya str.,15, Odessa, 65016, Ukraine*

We present new advance computational approach and new data for interatomic potentials and collisional spectral lines shifts and broadening for molecular systems, which include heavy elements atoms (alkali, alkali-earth, lanthanides and others) in an atmosphere of the noble gas atoms. Besides, computing the spectral line (including the hyperfine structure) shift allows to determine a quality of the electron wave functions and study a contribution of the relativistic and correlation effects. In order to calculate, for example, the hyperfine spectral lines collision shift one should use the expression from kinetical theory of the spectral lines and computational code [1]:

$$f_p = \frac{D}{p} = \frac{4\pi w_0}{kT} \int_0^\infty d\omega(R) \exp(-U(R)/kT) R^2 dR$$

where  $U(R)$  is an effective potential of the inter atomic interaction, which has a central symmetry in a case of the pairs A-B;  $T$  is temperature,  $w_0$  is a frequency of the hyperfine transition in the isolated active atom;  $d\omega(R) = Dw(R)/w_0$  is the relative local shift of the hyperfine lines, which is due to the disposition of atoms of the A and B on a distance  $R$ . The relativistic many-body perturbation theory [2] is used to determine the relativistic Dirac functions for studied atoms. We present new data on the interatomic potentials, local and observed collisional  $f_p$  shifts and widths for pairs: A-B (A=Rb,Cs,Tl,Yb; B=He,Ar, Kr,Xe) in dependence on temperature  $T$ . Our results are compared with the available experimental data and other theoretical results (see Refs. in [2]), which are obtained within a perturbation theory with the Hartree-Fock or Dirac-Fock zeroth approximation.

[1] A. Glushkov, O. Khetselius et al, Theory and Applications of Comput. Chem. (AIP) **1102**, 172 (2009); *Int. J. Quant. Chem.* **109**, 3325 (2009). .

[2] O. Khetselius, *Frontiers in Quantum Methods and Applications in Chem. and Phys., Ser.: Progress in Theor. Chem. and Phys.*, ed. M.Nascimento, J.Maruardi, E.Brändas, G.Delgado-Barrio (Springer).**29**, 54 (2015).

## Exploring the Structure of Dialkyl and Diallyl Magnesium Clusters by Means of Global Search Algorithm

S. Bouaouli<sup>1</sup>, L. Perrin<sup>1</sup>, P. Carbonnière<sup>2</sup>

<sup>1</sup>ICBMS UMR 5246, Université de Lyon, Bat Curien, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne cedex, France

<sup>2</sup>IPREM/ECP UMR CNRS 5254, Université de Pau et des Pays de l'Adour, 2 Avenue du Président Pierre Angot, F-64000 Pau, France

Organomagnesium reagents occupy a central position in organometallic chemistry, not only in organic synthesis but also in coordinative chain transfer polymerization, in which they are used, in combination with a catalyst, as a chain transfer agent [1]. Formally, the chain exchange reaction relies on a associative / dissociative mechanism that involves hetero-polymetallic complexes, either as transition states or reaction intermediates [2].

The modeling of this type of reaction, that is formally a transmétallation, is critical in order to depict and understand the mechanism of polymerizations that are carried out under chain transfer condition. Currently no mechanistic study provides a rational basis for the research and development of catalytic chain transfer polymerization systems, and especially the match or mismatch between the active catalyst and the chain transfer agent [3]. This most probably originates from (i) the lack of information on the nature and structure of the homo- and heteropolymetallic systems involved in the polymerization, (ii) the conformational heterogeneity of such systems.

In order to raise information on the clusters involved in alkene and conjugated diene polymerization, a global search algorithm of minima (GSAM) [4] has been used in order to identify the most stable clusters and to assess their conformational heterogeneity. This method, which is based on the sampling of the topological form generated on the basis of a set of molecular fragments, allows an efficient exploration of the most stable polymetallic clusters.

In this communication we present an unprecedented exhaustive sampling of two organomagnesium systems:  $[\text{Mg}(\text{Allyl})_2]_n$  and  $[\text{Mg}(\text{Bu})_2]_n$ ,  $n$  varying from 1 to 6. In addition to the structural information collected from this sampling, the stability of the  $n$ -mers is discussed and the most relevant structures isolable in solution are proposed. Based on this sampling, precise energy profiles for ethylene and butadiene polymerization, under chain exchange conditions can be computed and will be presented.

- [1] A. Valente, A. Mortreux, M. Visseaux, P. Zinck, *Chem. Rev.* **113**, 3836 (2013).
- [2] R. Ribeiro, R. Ruivo, H. Nsiri, S. Norsic, F. D'Agosto, L. Perrin, C. Boisson, *ACS Catal.* **6**, 851 (2016).
- [3] G. J. P. Britovsek, S. A. Cohen, V. C. Gibson, M. van Meurs, *J. AM. CHEM. SOC.* **126**, 10701 (2004).
- [4] R. Marchal, P. Carbonnière, C. Pouchan, *Int. J. Quantum Chem.* **110**, 2256 (2010).



## New Electron- $\beta$ -Nuclear Spectroscopy of Molecules and Chemical Bond Effect on The $\beta$ -Decay Parameters

**V.V. Buyadzh**<sup>1,2</sup>, **A.V. Glushkov**<sup>1,2</sup>, **Y.V. Dubrovskaya**<sup>1,2</sup>, **O.Yu. Khetselius**<sup>1,2</sup>

<sup>1</sup>*Department of Applied Mathematics and Quantum Optics, Odessa State University –  
OSEN, Lvovskaya str., 15, Odessa, 65016, Ukraine*

<sup>2</sup>*International Centre of Quantum Chemistry, Odessa State University – OSEN,  
Lvovskaya str., 15, Odessa, 65016, Ukraine*

We present the theoretical fundamentals of electron-beta-nuclear computational spectroscopy of molecules and discuss the cooperative electron  $\beta$ -nuclear processes in molecules, including the excitation, ionization, electronic rearrangement, induced by the nuclear reactions and  $\beta$ -decay [1]. The many-body perturbation theory (PT) with the optimized Kohn-Sham zeroth approximation [1] is used to calculate the  $\beta$ -decay parameters for a number of allowed (superallowed) transitions ( $^{33}\text{P}$ - $^{33}\text{S}$ ,  $^{241}\text{Pu}$ - $^{241}\text{Am}$  etc) and study a chemical bond effect on  $\beta$ -decay parameters. There are taken into account the following effects: i) Changing the electron wave functions because of the changing molecular electric field; changing the valence shell occupation numbers in different chemical substances; ii) The integration limits (calculating the Fermi integral function) changing due to different chemical substances; iii) additional channel, when  $\beta$ -electron occupies a free state in the bound molecular spectrum and other decay channels. We calculated the final-state probability distribution for excitations to the electronic continuum of  $^3\text{HeT}^+$  resulting from the  $\beta$ -decay of  $\text{T}_2$ . We studied the electronic rearrangement induced by nuclear transmutation in the  $\beta$ -decay  $^6_2\text{He}_4 \rightarrow (^6_3\text{Li}_3)^+ + e^- + \bar{\nu}_e$ . The half-life period  $T_{1/2}$  for  $\beta$ -decay of tritium atom (molecule) has been estimated while taking into account the bound  $\beta$ -decay channel and some other accompanying effects. The estimated values of  $T_{1/2}$  for the tritium  $\beta$ -decay and free triton decay are:  $(T_{1/2})_a = 12.26$  years (correction due to the electron-atomic-molecular effects  $(\Delta T_{1/2}/T_{1/2})_a = 0.8\%$ ) for the tritium atom and  $(T_{1/2})_t = 12.36$  years for the triton decay. We firstly present the value  $T_{1/2}$  in a case of the  $\beta$ -decay in the halogen-containing molecular tritium ( $^3\text{HCl}$ ):  $(T_{1/2})_m = 12.28$  years ( $^3\text{HCl}$ ); the correction due to the chemical bond effect is  $(\Delta T_{1/2})_{am} = 0.024$  (i.e. 0.20%).

[1] A. Glushkov, O. Khetselius, L. Lovett, *Advances in the Theory of Atomic and Molecular Systems: Dynamics, Spectroscopy, Clusters, and Nanostructures. Series: Progr. in Theor. Chem. and Phys*, Eds. P. Piecuch, J. Maruani, G. Delgado-Barrio, S. Wilson (Springer). **20**, 125 (2009).

## A Theoretical Study of the Interaction of Calcite with Amino Acids

**Robert Stepić<sup>1, 2</sup>, Zlatko Brkljača<sup>1, 2, 3\*</sup>, Ana-Sunčana Smith<sup>1, 2, 3</sup>, David M. Smith<sup>2, 3</sup>**

<sup>1</sup>*PULS Group, Institute for Theoretical Physics I, FAU, NögelsbachstraÙe 49b, Erlangen, Germany*

<sup>2</sup>*Cluster of Excellence: Engineering of Advanced Materials, NögelsbachstraÙe 49b, Erlangen, Germany*

<sup>3</sup>*CLS Group, Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia*

Calcite is one of the most widespread minerals on earth which interacts favourably with a variety of biomolecules. This interaction can mediate the growth of calcite resulting in formation of biominerals with remarkable mechanical properties useful in a number of applications [1]. In this work we utilize a bottom-up approach and study the interaction of protein building blocks, amino acids, with the stable (104) surface of calcite. We also probe the interactions with different morphologies deriving from (104) surface which incorporate kinks and edges. Amino acids are studied in their native zwitterionic and protected forms. Our method of choice for this study encompasses fully atomistic molecular dynamics simulations using two different state of the art force fields for these types of systems [2, 3]. We employ enhanced sampling techniques with biasing potentials to obtain free energy profiles for binding of amino acids to the surface. This enables us to estimate the free energies of binding of amino acids to the calcite as well as the molecular details of the interaction. Importance of polar groups for binding to the stable (104) surface is illustrated. These results provide a force field benchmark and reference data on binding energies and conformations of specific amino acids which could help interpret the experimental data on peptide and protein mediated calcite functionalization and growth.

[1] J. H. Harding, D. M. Duffy, M. L. Sushko, P.M. Rodger, D. Quigley, J. A. Elliot, *Chem. Rev.* **108**, 4823 (2008).

[2] C. L. Freeman, J. H. Harding, D. J. Cooke, J.A. Elliot, J. S. Lardge, D. M. Duffy, *J. Phys. Chem. C* **111**, 11943 (2007).

[3] P. Raiteri, J. D. Gale, D. Quigley, P.M. Rodger, *J. Phys. Chem. C* **114**, 5997 (2010).

---

\*currently at Faculty of Science, Department of Physical Chemistry, Zagreb, Croatia



## Solid-state and molecular size depending on variation of fundamental constants.

**L. F. Pašteka<sup>1,2</sup>, A. Borschevsky<sup>3</sup>, Y. Hao<sup>3</sup>, P. Schwerdtfeger<sup>1</sup>, V. Flambaum<sup>4,1</sup>**

<sup>1</sup>*Centre for Theoretical Chemistry and Physics, Massey University, New Zealand*

<sup>2</sup>*Department of Physical and Theoretical Chemistry, Comenius University, Slovakia*

<sup>3</sup>*Van Swinderen Institute, University of Groningen, The Netherlands*

<sup>4</sup>*School of Physics, University of New South Wales, Australia*

The size-dependence of molecules or bulk materials on fundamental constants offers a new and promising direction in the study of variations of fundamental constants (VFC) and the detection of scalar dark matter to probe the physics beyond the Standard Model [1-3]. Precise experimental setups involved in the detection of VFC, scalar dark matter and gravitational waves, such as laser interferometers, resonant-mass detectors and cryogenic oscillators now reach precisions far exceeding any other spectroscopic apparatus and their performance is directly connected to material size depending on changes in fundamental constants.

We investigate the dependence of crystal lattice parameters and molecular bond lengths on the fine structure constant  $\alpha$  and proton-to-electron mass ratio  $\mu$ . We present calculated and experiment-derived estimates of  $\alpha$ - and  $\mu$ -dependence of these parameters for selected systems inspired by contemporary experimental setups. We show the sensitivity of this approach may reach several orders of magnitude smaller VFC than the current most stringent experimental constraints.

[1] A. Derevianko, M. Pospelov, *Nature Phys.* **10**, 933 (2014)

[2] Y. Stadnik, V. V. Flambaum, *Phys. Rev. Lett.* **115**, 201301 (2015)

[3] Y. Stadnik, V. V. Flambaum, *Phys. Rev. Lett.* **116**, 031102 (2016)

## Relativistic Quantum Chemistry of Heavy Elements and Hadronic Atoms and Molecules

**V. Ternovsky<sup>1,2</sup>, A. Glushkov<sup>1,2</sup>, O. Khetselius<sup>1,2</sup>, I. Serga<sup>1</sup>, A. Kvasikova<sup>2</sup>**

<sup>1</sup>*Department of Applied Mathematics and Quantum Optics, Odessa State University –  
OSEN, Lvovskaya str., 15, Odessa, 65016, Ukraine*

<sup>2</sup>*International Centre of Quantum Chemistry, Odessa State University – OSEN,  
Lvovskaya str., 15, Odessa, 65016, Ukraine*

The gauge-invariant relativistic many-body perturbation theory approach [1] to consistent calculation of the spectra for heavy and superheavy elements (isotopes) and hadronic atomic and molecular systems with an account of relativistic, correlation, nuclear, radiative effects is presented. The wave functions zeroth basis is found from the Klein-Gordon (pion system) or Dirac (electron subsystem) equation. The potential includes the core ab initio potential, the electric and polarization potentials of a nucleus (the Fermi models for charge distribution in a nucleus is used). For superheavy ions the correlation corrections of high orders are accounted for within the Green function method. The magnetic inter-electron interaction is accounted for in the lowest order, the Lamb shift polarization part is calculated in the generalized Uhling-Serber approximation and the self-energy part is calculated on the basis of the Green's function method of Dirac equation with complex energy and singular nuclear potential. There are listed the results of calculations: 1).energy levels, hfs parameters, shifts and widths of some transitions for heavy atoms (Tl, Pb, U). It is proposed a new approach to describe the characteristics of the vibrational transitions of the molecular systems based on the numerical solution of the Schrödinger (Klein-Gordon-Fock) equation with realistic Simons-Parr-Finlan potential and carried out computing the Rb, Cs, Cs<sub>2</sub> vibrational transition frequencies. The scheme developed has attractive perspectives in studying energy, radiative and spectral parameters of pion-(adron)-molecular systems such  $\pi^-$ , K-AB systems and other exotic ones, which are of a great interest for modern molecular spectroscopy and pionic chemistry.

[1] A.V. Glushkov and L.N. Ivanov, Phys. Lett. **A170**, 33 (1992); A.V. Glushkov, Adv. in the Theory of Quantum Systems in Chem. and Phys. (Berlin, Springer) **26**, 231 (2012); Frontiers in Quantum Systems in Chem. And Physics (Berlin, Springer) **18**, 505 (2008).

[2] A.V.Glushkov, In: Low Energy Antiproton Phys., AIP Serie.**796**, 206 (2005); Recent Advances in Theory of Phys. and Chem. Systems (Springer), **15**, 285 (2006).

## Consistent approach to Raman scattering of the light on metastable levels of diatomic molecules

**E.V. Ternovsky<sup>1,2</sup>, A.V. Glushkov<sup>1,2</sup>, A.A. Svinarenko<sup>1,2</sup>**

<sup>1</sup>*Department of Applied Mathematics and Quantum Optics, Odessa State University –  
OSENУ, Lvovskaya str.,15, Odessa, 65016, Ukraine*

<sup>2</sup>*International Centre of Quantum Chemistry, Odessa State University – OSENУ,  
Lvovskaya str.,15, Odessa, 65016, Ukraine*

Laser action on molecules leads to different non-linear processes, including multi-photon ionization, excitation and dissociation, Raman scattering. The elementary two-photon processes are linear coherent and combinational scattering. The intensities and polarization of lines in these spectra are defined by polarizability and derivative on inter-nuclear distance. In this paper it is considered a process of Relay and Raman vibration scattering of the light on metastable levels of molecules ( $H_2$ , HD,  $D_2$ ,  $Li_2$ ,  $Rb_2$ ,  $Cs_2$ ,  $Fr_2$ ). On the example of polarizability of metastable molecules it has been studied an effect of nuclear motion in processes of the second order of the perturbation theory. New numerical method for construction of the Green electron functions for optical electrons and electron wave functions is developed within the model potential approach in the spheroid coordinates system that allows to take into account non-spherical character of molecular field. We have carried out the calculations of molecular polarizability, its derivative on inter-nuclear distance, depolarization degree under Relay and Raman light scattering on the frequencies of the Rb, Nd lasers. Relativistic generalization of proposed approach is carried out within QED perturbation theory with account of relativistic, correlation effects [1,2]. Analysis of results of the calculation of a polarizability, its derivative on inter-nuclear distance, for example, for excited triple metastable  $c^3\Pi_u$  states of the  $H_2$ , HD,  $D_2$  molecules on the frequencies of the Rb (1,78eV) and Nd (1,18eV) lasers shows that the main contribution into polarization of the cited metastable molecules is provided by changing the electron shell under action of the external electromagnetic field. An influence of the nuclear motion terms is also studied and found to be quite little.

[1] A. Glushkov, O. Khetselius, L. Lovett, *Advances in the Theory of Atomic and Molecular Systems: Dynamics, Spectroscopy, Clusters, and Nanostructures. Series: Progr. in Theor. Chem. and Phys.*, Eds. P. Piecuch, J. Maruani, G. Delgado-Barrio, S. Wilson (Springer). **20**, 125 (2009).

[2]. A.V.Glushkov et al, *Int. Journ. Quant.Chem.* **99**, 879 (2004); **99**, 936 (2004); **109**, 3325 (2009); A.V.Glushkov, O.Yu. Khetselius, L. Lovett, *Progr. Theor. Chem. & Phys.* (Springer) **20**, 125-152 (2009).

## Theoretical Photoelectron Spectroscopy: A Versatile Tool to Understand the Electronic Structure

Gilbert Grell<sup>1</sup>, Sergey I. Bokarev<sup>1</sup>, Tobias Moehle<sup>1</sup>, Oliver Kühn<sup>1</sup>

<sup>1</sup>*Institut für Physik, Universität Rostock, Albert-Einstein-Strasse 23-24, Rostock, Germany*

Photoelectron spectroscopy (PES) is a popular tool to probe the electronic structure in different aggregation states mapping bound electronic states to the continuum. To assign and understand experimental PES data which are usually rich of features, application of advanced theoretical modelling is required. This especially applies to highly correlated systems like transition metal (TM) complexes. In this work, we employ a Dyson orbital approach [1] to estimate photoionization cross sections in conjunction with the multi-configurational restricted active space self-consistent field (RASSCF) technique and linear response TDDFT with optimally-tuned range-separated hybrid density functionals. Our protocol [2] is capable to include spin-orbit coupling which is a prerequisite for the description of core-level PES and Auger spectra.

This contribution demonstrates applications of our protocol addressing different aspects of electronic structure and photoinduced dynamics of prototypical TM compounds. For instance, in L-edge X-ray PES of TM compounds, the interplay of radiative and autoionization channels as well as solute–solvent interactions were studied [3]. Further, the interpretation of UV/vis pump - XUV photoemission probe experiments has been conducted in [4] (RASSCF) and [5, 6] (TDDFT) unraveling ultrafast photoinduced dynamics of charge transfer states in iron complexes with a special focus on spin crossover. This procedure can be also extended for description of the resonant photoemission of Auger electrons complementing the toolkit for theoretical prediction of X-ray photoionization processes.

- [1] C. M. Oana and A. I. Krylov *J. Chem. Phys.* **127**, 234106 (2007)
- [2] G. Grell, S. I. Bokarev, B. Winter, R. Seidel, et al. *J. Chem. Phys.* **143**, 7 (2015)
- [3] R. Golnak, S. I. Bokarev, R. Seidel, J. Xiao, G. Grell et al. *Sci. Rep.* **6**, 24659 (2016)
- [4] A. Mognilevski, M. Wilke, G. Grell, S. I. Bokarev et al. *Chem. Phys. Chem.* **18**, 465 (2017)
- [5] N. Engel, S. I. Bokarev, A. Mognilevski et al. *Phys. Chem. Chem. Phys.* **19**, 14248 (2017)
- [6] A. A. Raheem, M. Wilke, M. Borgwardt, N. Engel, S. Bokarev, G. Grell et al. *Struct. Dyn.* (manuscript submitted)

## Theoretical determination of the ground state of CsS and CsO

**S. Koudjeti<sup>a</sup>, K. Merabti<sup>a</sup>, S. Azizi<sup>a</sup>, B. Mehnen<sup>b</sup>, S. Ben Yaghlane<sup>b</sup>, N.E. Jaidane<sup>b</sup> and M. Hochlaf<sup>c</sup>**

<sup>a</sup> *Laboratoire de Physique Théorique, Université Abou Bekr Belkaïd, Tlemcen Algérie.*

<sup>b</sup> *Laboratoire de Spectroscopie Atomique, Moléculaire et Applications – LSAMA, Université de Tunis, Tunisie.*

<sup>c</sup> *Université Paris-Est, Laboratoire Modélisation et Simulation Multi Echelle, ,77454 Marne-La Vallée, Paris, France*

The electronic structure calculations were performed using the MOLPRO program[1]. We calculated the potential energies using highly correlated ab initio methods, namely the complete active space self-consistent field (CASSCF) approach [2] followed by the internally contracted multireference configuration interactions (MRCI) method [3].

In these calculations, different basis sets have been used for oxygen, sulfur and cesium atoms.

The spectroscopic constants such as vibrational harmonic frequency  $\omega_e$ , the internuclear distance at equilibrium  $R_e$ , the rotational constant  $B_e$  and the electronic transition energy  $T_e$  of the ground and the excited electronic states have been calculated by fitting the energy values around the equilibrium position to a polynomial in terms of the internuclear distance [4] and compared with literature values [5-6].

[1] MOLPRO is a package of ab initio programs written by H.J.Werner and P.J.Knowles.

[2] P.J.Knowles and H.J.Werner, *Chem.Phys.Lett.* **115**, 259, (1985).

[3] H.J.Werner and P.J.Knowles, *J.Chem.Phys.***89**, 5803, (1988).

[4] B. Numerov, *Publs. observatoire central astrophys. Russ.* **2**, 188, (1933).

[5] D.Kaen, M.Korek and S.N.Abdulal, *J. Mod. Phys*, **6**,1889 (2015).

[6] Partridge, H., Langhoff, S. R., & Bauschlicher Jr, C. W. *J. Chem. Phys.* **88**, 6431, (1988).

## Algorithm for calculating Bethe logarithm for two- or three- centered molecules

Ewa Palikot<sup>1</sup>, Monika Stanke<sup>1</sup>

<sup>1</sup>*Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, ul. Grudziądzka 5, Toruń, Poland*

Bethe logarithm is one of the leading quantum electrodynamic energy correction of the order of  $\alpha^3$ . Method of calculating expectation value of Bethe logarithm in alternative way to Schwartz [2] is presented. The theoretical base paper for the work was [3]. The method proposed in [3] was extended for calculate multi-electron atoms and two- or three-centered homo- or hetero-nuclear molecules. Calculations was done in Born-Oppenheimer approximation using explicitly correlated Gaussian functions. Expectation value of Bethe logarithm for H<sub>2</sub> and HeH<sup>+</sup> molecules are presented.

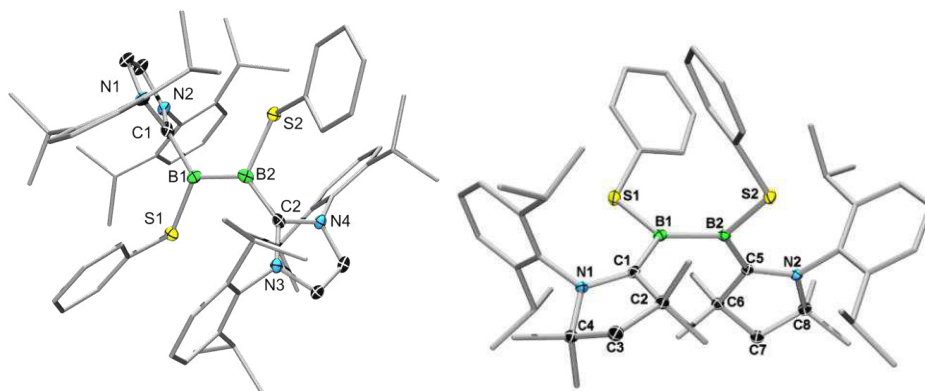
- [1] H. A. Bethe, *Phys. Rev.* **72**, 339 (1947),
- [2] C. Schwartz, *Phys. Rev.* **123**, 1700 (1961),
- [3] M. Stanke, L. Adamowicz, D. Kędziera, *Mol. Phys.* **111**, 9 (2013),
- [4] K. Piszczatowski *et al.*, *J. Chem. Theory Comput.* **5**, 3039 (2009),
- [5] V. I. Korobov, *Phys. Rev. A* **69**, 505 (2004).

## Studys of anorganic biradicals: Dependency of computational methods, electronical and sterical effects

E. Welz<sup>1</sup>, B. Engels<sup>1</sup>

<sup>1</sup>*Department of Theoretical and Physical Chemistry, University of Wuerzburg, Emil-Fischer-Straße 42, Wuerzburg, Germany*

The CAAC liganded diborene and diborane show an interesting behavior concerning their chemical behavior. Depending on the sterical effects of the ligands they appear coplanar or orthogonal. A huge role plays the CAAC ligand which causes of its sterical and electronical effects very often an open shell structure.



*Figure 1: Shows a coplanar liganded diborene on the left side and an orthogonal liganded diborane on the right side.*

For the coplanar substituted diborene it is proven that it appears as a B=B double bond, in contrast the diborane with orthogonal standing substitutes a B-B single bond is found. Now it is on great interest in what way it is possible to describe a biradical character with low cost DFT functionals, and which functionals give the best performance compared to high level CASSPT2, MR-CI methods. Another interesting point is the influence of the ligand on the boron. Therefor we take a closer look at different substituted boron systems and their influence on the structure. To get an overview over the influence of the electronic behavior we take the same skeletal structur and verify the eletronical behavior of the ligands.

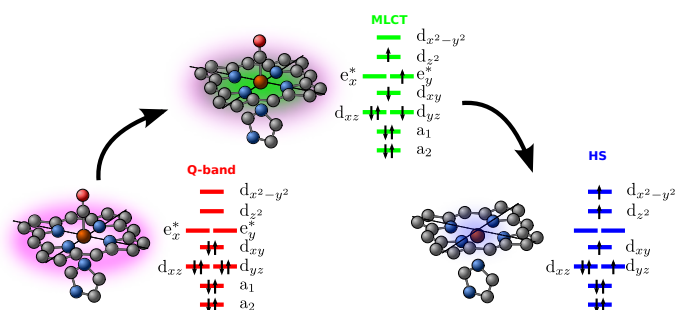
## Competition between photolysis and spin-crossover : quantum wavepacket dynamics on heme-CO organometallic complex

Miquel Huix-Rotllant<sup>1</sup>, K. Falahati<sup>2</sup>, I. Burghardt<sup>2</sup>

<sup>1</sup>*Institut de Chimie Radicale, CNRS - Aix-Marseille University, Avenue Escadrille  
Normandie-Niemen, Marseille, France.*

<sup>2</sup>*Intitut für Phys. u. Theor. Chemie, Goethe University, Max-von-Laue-Str., Frankfurt am Main,  
Germany.*

Hemoproteins are well known metalloproteins involved in storage and transport of small diatomic molecules. Recent time-resolved X-ray spectra with ultrashort pulses have revealed that the photolysis of carbon monoxide (CO) from myoglobin occurs in <50-70 fs [1]. Still, there is a discussion whether photolysis occurs before (low-spin dissociation) or after (high-spin dissociation) the spin-crossover mechanism. To resolve this, we have developed a vibronic Hamiltonian containing both the dissociation coordinate and the intersystem crossing for a manifold of singlet, triplet and quintet states. The Hamiltonian has been fitted to CASPT2 PES using a 5th-order Taylor expansion on the vibrational coordinates in addition to Morse and exponential potentials to account for anharmonicities. The model has been fitted to reproduce 180 electronic states along 12 principal vibrational coordinates, including all vibronic and spin-orbit couplings. The Hamiltonian is used to propagate wavepackets using multi-layer formulation of multi-configuration time-dependent Hartree (ML-MCTDH) method [2]. Our model reveals that strong (pseudo-)Jahn-Teller couplings induce an ultrafast transfer from the porphyrin to the metal-ligand charge transfer band (MLCT), from where dissociation occurs [3]. After photolysis, the spin-crossover acts relaxing the remaining system to a quintet state.



[1] M. Levantino et al., *Nat. Chem.* **6**, 6772 (2015).

[2] H. Wang, M. Thoss, *J. Chem. Phys.* **119**, 1289 (2003).

[3] M. Huix-Rotllant, K. Falahati, I. Burghardt, (in preparation).



## Multilevel coupled cluster theory with Cholesky- and correlated natural transition orbitals for core-excited states.

Sarai Dery Folkestad<sup>1</sup>, Ida-Marie Høyvik<sup>1</sup>, Henrik Koch<sup>1</sup>

<sup>1</sup>*Department of Chemistry, NTNU, Høgskoleringen 5, 7049 Trondheim, Norway*

In multilevel coupled cluster (MLCC) theory[1] the active regions of a molecular system, with respect to some size-intensive property, is treated at a higher level of coupled cluster (CC) theory than the inactive region. The molecular system is partitioned by a convenient selection of molecular orbitals, such as the local Cholesky orbitals[2] or by use of correlated natural transition orbitals (CNTOs)[3]. MLCC is well adapted to the treatment of size-intensive properties and facilitates computational savings while still retaining the accuracy of the higher level method, for the property of interest. The MLCC framework sets no restriction on the number of active regions, and any combination of coupled cluster methods can in theory be used to treat the system at hand.

In this work an MLCC code is implemented, with full flexibility as to the choice of system partitioning and treatment at CCS, CC2, CCSD and CC3 level of theory. Core excitations, which are local in nature and thus well suited for study with MLCC, are treated by use of the CVS approximation[4, 5]. Both Cholesky orbitals and CNTOs are used to partition the orbitals into active and inactive regions.

- [1] R. H. Myhre, A. M. Sánchez de Merás, H. Koch *J. Chem. Phys.* **141**, 224105 (2014).
- [2] A. M. Sánchez de Merás, H. Koch, I. G. Cuesta, L. Boman, *J. Chem. Phys.* **132**, 204105 (2010).
- [3] I-M. Høyvik, R. H. Myhre, H. Koch *J. Chem. Phys.* **146**, 144109 (2017).
- [4] L. S. Cederbaum, W. Domcke, J. Schirmer, *Phys. Rev. A* **22**, 206 (1980)
- [5] S. Coriani, H. Koch *J. Chem. Phys.* **143**, 181103 (2015).

**Interrogating the "B05" density functional for non-locality information.****Stephen G. Dale, Erin R. Johnson, Axel D. Becke***Department of Chemistry, Dalhousie University, 6274 Coburg Rd, Halifax, Canada*

In two papers[1, 2], Becke introduced Kohn-Sham density-functional approximations for static and dynamic correlation to be partnered with 100 percent exactly-computed exchange. Known as "B05", this was the first non-local correlation model designed to work with the full non-locality of exact (or Hartree-Fock) exchange. Non-locality issues, often referred to as the "delocalization" problem, have emerged as one of the most vexing problems in DFT today. Questions such as... how much exact exchange should be used in a hybrid functional, or... what value of the range parameter should be used in a long-range corrected functional, abound, and the answers are system dependent. The physics of non-locality is built into the B05 functional in a natural way and one wonders, therefore, if B05 might provide a mechanism to answer such questions. We are exploring a procedure, "B05min", to do this.

- [1] A. D. Becke, *J. Chem. Phys.* **119**, 2972 (2003).
- [2] A. D. Becke, *J. Chem. Phys.* **122**, 064101 (2005).

## High-accuracy extrapolated *ab initio* thermochemistry of the cyanonitrene radical

Michael E. Harding

*Institut für Nanotechnologie, Karlsruher Institut für Technologie (KIT), Campus Nord,  
Postfach 3640, D-76021 Karlsruhe, Germany*

Theoretical and experimental determinations of the heat of formation of the cyanonitrene radical, NCN, span a range of 443 to 501 kJ mol<sup>-1</sup> (see ref. [1] and references therein). Due to the fact that such discrepancies are unacceptable for a triatomic molecule, which is likely to play a key role in the formation of so-called prompt NO in combustion under fuel-rich conditions, enthalpies of formation at both 0 and 298 K were computed according to the HEAT (High-accuracy Extrapolated Ab initio Thermochemistry) protocol. [2–4]

The recommended enthalpy of formation for NCN is 451.7 ± 1.7 kJ mol<sup>-1</sup> at 0 K and 452.2 ± 1.7 kJ mol<sup>-1</sup> at 298 K, thus resolving discrepancies among the available values. The computed values are in agreement with some of the experimental values and previous computations, but the uncertainties associated with the HEAT values are considerably smaller than those based on experimental studies and earlier theoretical estimates. The study also reveals conceptual problems with the inclusion of theoretical estimations and their confidence limits into the thermochemical network of the Active Thermochemical Tables (ATcT) approach [5, 6], which is widely used as a reference for experimental and theoretical thermochemistry.

- [1] E. Goos, C. Sickfeld, F. Mauß, L. Seidel, B. Ruscic, A. Burcat, T. Zeuch, *Proc. Combust. Inst.* **34**, 657 (2013).
- [2] A. Tajti, P.G. Szalay, A. G. Császár, M. Kállay, J. Gauss, E. F. Valeev, B. A. Flowers, J. Vázquez, and J. F. Stanton, *J. Chem. Phys.*, **121**, 11599 (2004).
- [3] Y. J. Bomble, J. Vázquez, M. Kállay, C. Michauk, P. G. Szalay, A. G. Császár, J. Gauss, and J. F. Stanton, *J. Chem. Phys.*, **125**, 064108 (2006).
- [4] M. E. Harding, J. Vázquez, B. Ruscic, A. K. Wilson, J. Gauss, and J. F. Stanton, *J. Chem. Phys.*, **128**, 114111 (2008).
- [5] B. Ruscic, R. E. Pinzon, M. L. Morton, G. von Laszewski, S. Bittner, S. G. Nijsure, K. A. Amin, M. Minkoff, and A. F. Wagner, *J. Phys. Chem. A* **108**, 9979 (2004).
- [6] <http://atct.anl.gov/>

## Can wavefunction analysis support the (new) definition of oxidation state?

**Verònica Postils, Carlos Delgado-Alonso, Pedro Salvador**

*Institut de Química Computacional i Catàlisi i Departament de Química, Universitat de Girona, Maria Aurèlia Capmany 69, 17003, Girona, Spain.*

Oxidation state (OS) is a concept of utmost relevance in Chemistry that has been lacking a proper, clear cut definition. IUPAC's Gold Book still discusses a set of "agreed upon" rules, but no formal definition. Consequently, considerable debate can be found in the literature discussing over inconsistencies and alternative OS assignation in non-trivial bonding situations. Quite recently, Karen lead a IUPAC's Report [1] on the revision of the OS concept, providing a new generic definition, namely "The OS of a bonded atom equals its charge after ionic approximation", as well as algorithms for OS assignation and a vast number of illustrative examples. Despite OS is intrinsically related to the distribution of electrons around atom, the report tiptoes around the role of quantum-chemical calculations for OS assignation. The wavefunction of the system, however, should contain this type of information; one just needs to devise proper schemes to retrieve it.

Almost at the same time as Karen's work, we had introduced [2] a new and general scheme to derive OS from wavefunction analysis, the so-called effective oxidation state (EOS) analysis. It is formally applicable to any molecular system and for any level of theory. Here we present a systematic analysis of the molecular examples described in (or related with) Karen's report (more than 80 systems) using the EOS approach. Remarkably, the results of the quantum mechanical approach can be reconciled with the improved OS definition in most cases, even though the EOS analysis considers explicitly neither bonds nor Lewis structures. Moreover, no special provisions are needed when the practical application of Karen's algorithms comes with exceptions or leads to ambiguities.

Discrepancies occur and are expected when the individual bond polarization, tuned by the chemical environment, does not match with reference pairwise atomic electronegativities. Also, the rule *bonds between two atoms of the same element are divided equally* cannot always be recovered from first principles, unless the involved atoms are symmetry-equivalent.

Our analysis already reveals limitations of the new OS definition, e.g. in the assignation of OS of hapto-complexes (fundamental role of aromaticity and local spin states of the ligands), and in Fisher-type carbenes.

[1] P. Karen et al, *Pure Appl. Chem.* **86** 1017 (2014); *Angew. Chem. Int. Ed.* **54**, 2 (2015).

[2] E. Ramos-Cordoba et al. *J. Chem. Theory Comput* **11**, 1501 (2015).

## Excited states for orbital-optimized second-order perturbation theory

Eloy Ramos-Cordoba<sup>1,2</sup>, Martin Head-Gordon<sup>1</sup>

<sup>1</sup>*University of California, Berkeley, Berkeley, California 94720, (USA)*

<sup>2</sup>*Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU) and Donostia International Physics Center (DIPC), 20080 Donostia, (Spain)*

Unrestricted Hartree-Fock (UHF) wave functions with spin contamination are usually poor zero-order approximations for second-order Moller-Plesset perturbation theory (MP2). Orbital-optimized second-order perturbation theory (OOMP2) tackle this problem by using approximate Brueckner orbitals. In OOMP2 the orbitals are optimized in the presence of the mean-field energy plus the second-order many-body correlation energy. Since in OOMP2 the energy is fully minimized with respect to orbital rotations, a Hellman-Feynman condition is fulfilled and first-order properties do not present discontinuities. This method improves the description of geometries, vibrational frequencies, and relative energies. Additionally, in OOMP2 the response function does not show spurious second order poles, making it suitable for linear-response excited state properties. In this contribution, we present an extension of the OOMP2 method to excited states and we report test calculations for closed-shell systems and doublet radicals. The performance of method is compared with other second-order methods for excitation energies such as the approximate coupled-cluster singles and doubles model (CC2), configuration interaction with doubles corrections (CIS(D)), and the algebraic diagrammatic construction through second order (ADC(2)).

[1] R. C. Lochan and M. Head-Gordon, *J. Chem. Phys.* **126**, 164101 (2007).

[2] D. Stuck and M. Head-Gordon, *J. Chem. Phys.* **139**, 244109 (2013).

[2] E. Ramos-Cordoba and M. Head-Gordon, *in preparation*

## Energetic parameters of the $\text{Pt}(\text{SCN})_6^{2-}$ complex

Vladislav V. Yudanov

*Laboratory of Photochemistry, Voevodsky Institute of Chemical Kinetics and Combustion  
of SB RAS, 3 Institutskaya Str., Novosibirsk, Russian Federation*

Photosolvation of  $\text{Pt}(\text{SCN})_6^{2-}$  in water can have several possible reaction mechanisms, which are very difficult, almost impossible, to establish by experimental methods. The choice in favor of a certain mechanism of the reaction can be made only after comparing the results of quantum-chemical calculations of the intermediates with experimental spectra.

The quantum-chemical calculations of the  $\text{Pt}(\text{SCN})_6^{2-}$  complex were performed in two stages. First, the geometry of the complex in the ground state was optimized for the singlet state by RHF/LANL2DZ method. Further, the energies of the excited states, the wavelengths and strengths of the oscillators were obtained by CIS method. The most significant of them (with large oscillator strengths) are presented in the table below.

<i>Excitation energies, eV</i>	<i>Wavelengths, nm</i>	<i>Oscillator strengths</i>
0.1214	10213.91	0.1490
0.2102	5898.24	0.3913
4.8845	253.83	0.0921
4.9804	248.94	0.0859
5.1073	242.76	0.0492
5.1371	241.35	0.0309
5.2085	238.04	0.0115

Financial support from the Russian Science Foundation (Grant No. 15-13-10012) is gratefully acknowledged.

## Theoretical Study of the Methanamine Formation as Glycine Precursor in the ISM: Role of Water-Ice

Francisca Cid, Alejandro Toro-Labbé, Soledad Gutiérrez-Oliva

Laboratorio de Química Teórica Computacional (QTC), Facultad de Química,  
Pontificia Universidad Católica de Chile, Av. Vicuña Mackenna 4860, Santiago, Chile

Experimental studies have shown the possibility to hydrogenate  $C\equiv N$  bond until full saturation (See Figure 1) under interstellar conditions, to form methylamine ( $CH_3NH_2$ ) from hydrogen cyanide (HCN) [1]. The relevance of the methylamine formation is because it is a precursor to amino acids formation process in the Interstellar Medium (ISM). This theoretical study explore the gas-phase and also the process that takes place on the surface of icy particles from the reaction force perspective [2], this allow us identify different structural and electronic events through a rational partition along the reaction coordinate ( $\xi$ ). Electronic characterization of transition states are given by reaction electronic flux analysis (REF) [3].

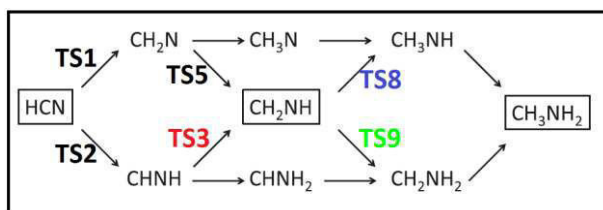


Figure 1. Hydrogenation reaction network [1]

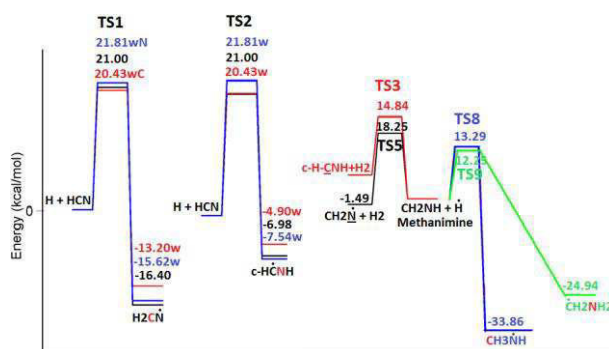


Figure 2. Energy parameters of hydrogenation reactions.

As it is shown in Figure 2, the hydrogenation reaction through carbon (TS1, TS3 and TS8) is thermodynamically favored. The reaction force analysis indicates that energy barriers are basically of structural nature. The reaction force analysis and the reaction electronic flux explain the mechanism of  $CH_2NH$  formation induced first by the weakening of the  $C\equiv N$  bond that strengthen the H-C interaction leading to the bond formation.

**Acknowledgments.** This work was supported by FONDECYT through project N° 1141098.

**Key words:** hydrogenation, water-ice, reaction force, glycine, interstellar medium.

### References

- [1] P. Theulé, F. Borget, et. al., *Astronomy and Astrophysics*, **534**, A64 (2011).
- [2] A. Toro-Labbé, *J. Phys. Chem. A*, **103**, 4398-4403 (1999).
- [3] P. Flores-Morales, S. Gutiérrez-Oliva et. al., *Comp. Theor. Chem.*, **943**, 121-126 (2010).

**Squaramide polymerization of lactide:  
Crucial role of a weak interactions network.**

**Christophe Gourlaouen<sup>1</sup>, Samuel Dagorne<sup>2</sup>**

<sup>1</sup>*Laboratoire de Chimie Quantique, Institut de Chimie UMR 7177 CNRS/Université de Strasbourg 4, rue Blaise Pascal, 67000, Strasbourg France, gourlaouen@unistra.fr*

<sup>2</sup>*Laboratoire de Synthèse, Réactivité et Catalyse Organométalliques, Institut de Chimie UMR 7177 CNRS/Université de Strasbourg 4, rue Blaise Pascal, 67000, Strasbourg France, dagorne@unistra.fr*

Newly synthesized substituted squaramides have been successfully used as organocatalyst for lactide ring-opening polymerization (ROP) [1]. The amino-functionalized squaramide [Figure 1] leads to ROP of L-lactides under mild conditions in the presence of benzyl alcohol. Experimental data prove that both Hydrogen-bond acceptor and donor sites are critical for the catalyst activity: the absence of amino group inhibits the reaction. The catalyst is also selective; it is inactive in the presence of other cyclic molecules such as  $\epsilon$ -caprolactone. DFT calculations were undertaken to determine the precise mechanism of the ROP. We successfully computed a three main steps mechanism and highlighted the role played by each part of the molecule. As proposed by the experimentalist the three nitrogen atoms act as anchor to fix the alcohol and the monomer. However, we put in evidence the more active role played by the amino group. Then we also prove that the fluorinated part also contribute to the thermodynamic balance of the reaction. Finally, the selective activity of the catalyst was explained through the modification of the H-bond network induced by the change of the monomer.

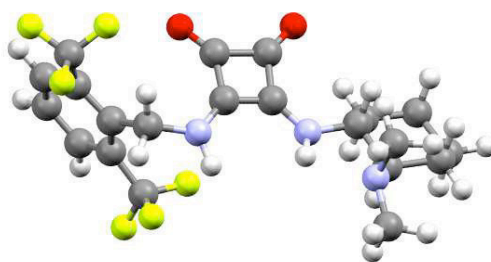


Figure 1: Structure of the amino-squaramide

[1] S. Dagorne, *ChemCatChem*. **9**, accepted (2017).



## Excited State Transition Energies and Properties in Solution from a Smooth Dielectric Model

**J. Coleman Howard<sup>1</sup>, James C. Womack<sup>2</sup>, J. Dziedzic<sup>2</sup>, Chris-Kriton Skylaris<sup>2</sup>, T. Daniel Crawford<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, Virginia Tech, Blacksburg, Virginia, United States*

<sup>2</sup>*School of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, United Kingdom*

A quantum mechanical solvation model is presented for a solute embedded in a polarizable dielectric medium, where the solute cavity is determined from an electronic isodensity surface in a smooth two-parameter model previously implemented in plane-wave-based density functional theory computations. In this work, solvent-solute interactions are incorporated into a Hartree-Fock framework and captured via numerical solution of the nonhomogenous Poisson equation on a real-space grid through an interface between PSI4 and the DL\_MG multigrid solver library. The method is applied here to compute excited state transition energies and properties with the equation-of-motion coupled-cluster singles and doubles method (EOM-CCSD). Results are presented for solvated water, as well as formaldehyde, acetone and *trans*-acrolein, which have low-lying  $n \rightarrow \pi^*$  transitions and associated blue shifts in aqueous solution. Comparisons are made with other theoretical approaches, including popular implicit solvation models and QM/MM methods, in addition to available experimental data.

## On the Chirality of Antimalarial Drug Candidates

**Kirk C. Pearce<sup>1</sup>, Yongle Du<sup>1</sup>, Yumin Dai<sup>1</sup>, Priscilla Krai<sup>3</sup>, Seema Dalal<sup>3</sup>, Maria B. Cassera<sup>2,3</sup>, Michael Goetz<sup>4</sup>, T. Daniel Crawford<sup>1</sup>, David G. I. Kingston<sup>1,2</sup>**

<sup>1</sup>*Department of Chemistry, Virginia Tech, Blacksburg, Virginia, United States*

<sup>2</sup>*Virginia Tech Center for Drug Discovery, Virginia Tech, Blacksburg, Virginia, United States*

<sup>3</sup>*Department of Biochemistry, Virginia Tech, Blacksburg, Virginia, United States*

<sup>4</sup>*Natural Products Discovery Institute, Doylestown, Pennsylvania, United States*

A dichloromethane extract of *Trichospira verticillata* from the Natural Products Discovery Institute was discovered to have good antiplasmodial activity. After purification, four new germacranolide-type sesquiterpene lactones named trichospirolides A-D (**1** - **4**) were isolated from *Trichospira verticillata*. The structures of the new compounds were elucidated by analysis of their 1D and 2D NMR spectra and MS data. The relative and absolute configurations were assigned based on a comparison of calculated and experimental ECD and UV spectra, specific rotations, and internuclear distances for all possible diastereomers for each compound. Herein, we report the stereochemical assignment of these four compounds.

## Electrochemistry via Liquid Photoemission Spectroscopy: Insight from Molecular Simulations

Veronika Jurásková<sup>1</sup>, Petr Slavíček<sup>1, 2</sup>

<sup>1</sup>*Department of Physical Chemistry, University of Chemistry and Technology Prague,  
Technická 5, Prague 6, Czech Republic*

<sup>2</sup>*J. Heyrovský Institute of Physical Chemistry, Academy of Science of the Czech Republic, v.v.i.,  
Prague 8, Czech Republic*

Photoemission spectroscopy (PES) with liquid microjets represents relatively new powerful method enabling measurements of photoemission spectra in liquid phase. It opens a way to study electronic structure of liquid water and aqueous solutions of different molecules in general. [1] PES can also provide information on the oxidation half reactions.

In this presentation, we focused on modeling of photoemission spectra in aqueous solution using *ab initio* molecular dynamics simulations (AIMD) combined with static calculations of vertical ionization energy. [2] Our main goal was to invent a protocol reproducing the measured spectra and enabling the calculations of redox potentials. The redox potentials are directly connected with the Gibbs free energy of oxidation. This quantity can be estimated from the calculated vertical ionization energy and reorganization energy which is related to the spectral width. In our calculations, we studied the effect of different solvent models and nuclear quantum effects on these properties.

Due to the relation between reorganization energy and spectral width, we discuss the possibility of direct extraction of redox potentials from photoemission spectra. This represents a complex problem requiring the information on the solute and solvent reorganization energy and the characteristic vibrational frequencies responsible for the reorganization. Here, we calculated the solvent reorganization using the equilibrium and non-equilibrium continuum models. We also showed the possibility of the estimation of the solvent frequency from experimental data on refractive index of liquid water.

[1] B. Winter; M. Faubel, *Chem. Rev.* **106**, 1176 (2006).

[2] M. Rubešová; V. Jurásková; P. Slavíček *J. Comput. Chem.* **38**, 427 (2017).

## Numerically converged Hyperfine Coupling Constants using a similarity transformed Hamiltonian and a Multiwavelet basis set

Stig Rune Jensen<sup>1,2</sup>, Luca Frediani<sup>1,2</sup>

<sup>1</sup>*Centre for Theoretical and Computational Chemistry*

<sup>2</sup>*Department of Chemistry, UiT - The Arctic University of Norway, N-9037 Tromsø*

Hyperfine coupling constants (HFCCs) are among the most challenging molecular properties to compute when it comes to basis set convergence. The reason for this is that the property depends explicitly on the spin density at the nuclear position (through the Fermi-Contact operator), where it is well known that the standard basis sets of computational chemistry are inadequate. Even the fully adaptive and highly flexible multiwavelet basis[1] shows a rather slow convergence for the density value at the nuclear cusp, and very large computational resources are needed to reach numerically converged results in a brute force manner. The spin density is particularly challenging as is it computed as the difference between two large and almost equal numbers (the spin-up and spin-down density values), putting hard demands on the absolute precision of the calculation.

Using a similarity transformed Hamiltonian[2] we can analytically remove the nuclear cusps of the wavefunction, leaving only a smoothly varying part to be represented in the numerical basis set. We show that this retains the fast convergence of the density value also at the nuclear positions, which makes it possible to obtain numerically converged values for HFCCs within Density Functional Theory using a multiwavelet basis set.

[1] S. R. Jensen, *et al.*, *J. Phys. Chem. Lett.* **8**, 7 (2017).

[2] F. Bischoff, *J. Chem. Phys.* **141**, 184105 (2014).

## Interactions of binary twinned-icosahedral $[B_{21}H_{18}]^-$ with cyclodextrins

Saltuk M. Eyrilmez<sup>1,2</sup>, Martin Lepsik<sup>1</sup>, Pavel Hobza<sup>1,3</sup>, Jindřich Fanfrlík<sup>1</sup>,  
Drahomír Hnyk<sup>4</sup>

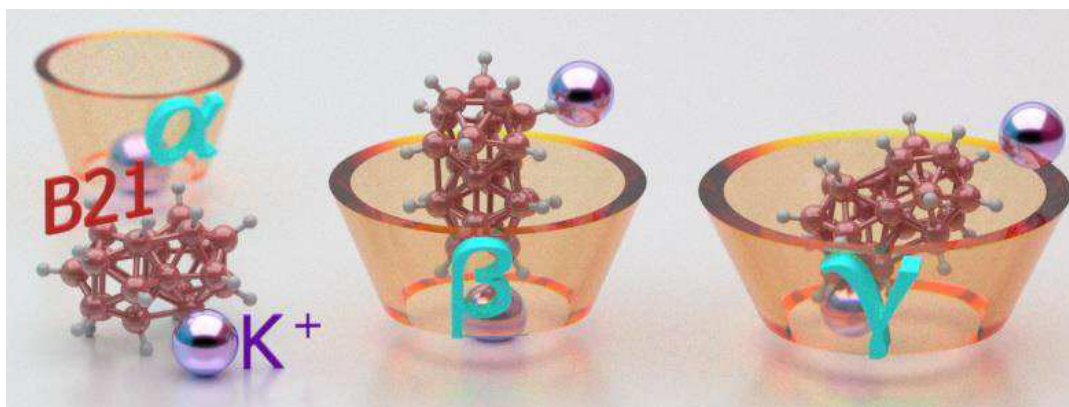
<sup>1</sup>*Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences,  
Flemingovo nám. 2, CZ-16610 Prague 6, Czech Republic*

<sup>2</sup>*Department of Physical Chemistry, Palacký University, CZ-77146 Olomouc, Czech  
Republic*

<sup>3</sup>*Regional Center of Advanced Technologies and Materials, Department of Physical  
Chemistry, Palacký University, CZ-77146 Olomouc, Czech Republic*

<sup>4</sup>*Institute of Inorganic Chemistry of the Czech Academy of Sciences, v.v.i. CZ-25068  
Husinec-Řež, Czech Republic*

In this project, we study the spectroscopic evidence of gas-phase complexes of *closo,closo*- $[B_{21}H_{18}]^-$  (B21;  $D_{3h}$  symmetry) with  $\beta$ - and  $\gamma$ -cyclodextrin (CD) by using quantum-chemical computations, showing that  $\beta$ - and  $\gamma$ -CD are able to interact with B21 due to their larger cavities, in contrast to the smaller  $\alpha$ -CD. The hydridic B–H vectors of the B21 anion interact with  $K^+$  counterions and, *via* dihydrogen bonding, also with the partially positively charged hydrogens of the CD sugar units in the modeled  $\beta$ - and  $\gamma$ -CD complexes. In summary, the combination of spectrometric and computational analysis shows that macropolyhedral boron hydride anions with two counter-ions can form stable complexes with  $\beta$ - and  $\gamma$ -CD in the gas phase, offering a new perspective for the future investigation of this remarkable anion in the areas of supramolecular and medicinal chemistries [1].



[1] S. M. Eyrilmez et al., *Phys. Chem. Chem. Phys.* **19**, 11748, (2017).

## Understanding and Utilizing the Role of London Dispersion Interactions in Catalysis

Lijuan Song<sup>1</sup>, Henrik Quanz<sup>1</sup>, and Peter R. Schreiner<sup>1</sup>

<sup>1</sup>*Institute of Organic Chemistry, Justus-Liebig University, Heinrich-Buff-Ring 17, Giessen, Germany*

London dispersion (LD) interactions constitute the attractive part of the van-der-Waals potential and they have been found to provide decisive stabilization in sterically bulky molecules and to enhance catalytic reactivity.<sup>[1]</sup>

We present a systematic study on quantifying LD interactions by correlating LD interactions energies with the intrinsic properties (size and polarizability) of so-called dispersion-energy donors (DEDs).<sup>[2]</sup> We employed dispersion-corrected density functional theory that allows to size the significance of LD contributions.<sup>[3]</sup> A group scan of various DEDs illustrates the “DED-strength”, which can be applied to catalyzed chemical reactions as LD helps understand the contribution of DEDs in the reactivity and selectivity of chemical reactions. The notion of selectivity control by specific rate acceleration through LD stabilization rather than by inhibitory means enables LD interaction to be developed as a control element in the design of catalyzed chemical reactions.

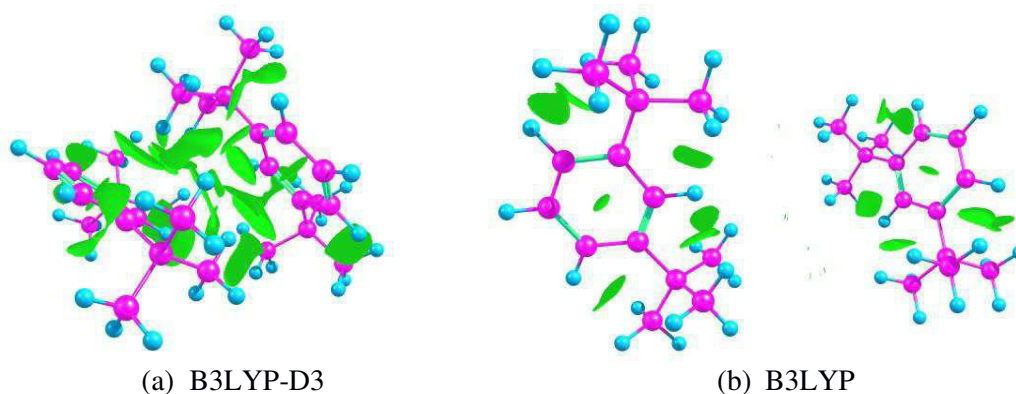


Figure 1. NCI plot of 1,3-Di-tert-butylbenzene dimer with and without dispersion correction.

[1] **Review:** J. P. Wagner, P. R. Schreiner, *Angew. Chem. Int. Ed.* **54**, 12274 (2015).

[2] S. Rösel, C. Balestrieri, P. R. Schreiner, *Chem. Sci.* **8**, 405 (2017).

[3] S. Grimme, A. Hansen, J. G. Brandenburg, C. Bannwarth, *Chem. Rev.* **116**, 5105 (2016).

## Molecular dynamics simulations on the aggregation of Keggin-type polyoxometalate ions in aqueous solution.

**A. Chaumont and G. Wipff**

<sup>1</sup>*Universite de Strasbourg, UMR 7140, Chimie de la Matiere Complexe,  
4, rue B. Pascal, 67000 Strasbourg, France*

Aqueous solutions of polyoxometallate ( $\alpha$ -PW<sub>12</sub>O<sub>40</sub><sup>3-</sup>) Keggin anions have been simulated by molecular dynamics, comparing between solutions with different neutralizing M<sup>n+</sup> counterions (Cs<sup>+</sup>, NBu<sub>4</sub><sup>+</sup>, UO<sub>2</sub><sup>2+</sup>, Eu<sup>3+</sup>, H<sub>3</sub>O<sup>+</sup> and H<sub>5</sub>O<sub>2</sub><sup>+</sup>). They reveal marked counterion effects. While the hydrophobic NBu<sub>4</sub><sup>+</sup> cations tend to surround  $\alpha$ -PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> anions via loose contacts, leading to "phase separation" between water and an overall neutral humid salty domain, the other studied cations are more hydrophilic and generally separated from the  $\alpha$ -PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> anions. The most important finding concerns the aggregation of  $\alpha$ -PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> anions, mostly as dimers with short contacts but also as higher ( $\alpha$ -PW<sub>12</sub>O<sub>40</sub><sup>3-</sup>)<sub>n</sub> oligomers (n = 3 to 5) with the proportion of the aggregates ranging from ca. 9 to 46%, depending on the counterion. While Eu<sup>3+</sup> and UO<sub>2</sub><sup>2+</sup> are fully hydrated and interact at short distances with  $\alpha$ -PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> as solvent-separated ion pairs, Cs<sup>+</sup> can form contact ion pairs, as well as solvent-separated ions.

Free energy profiles, obtained via potential of mean force "PMF" calculations, as a function of the P ... P distance show a flat profile with a tiny minimum at ca. 11 Å as the anions approach each other, showing that the anions can form "contact ion pairs" in the presence of either H<sub>3</sub>O<sup>+</sup>, UO<sub>2</sub><sup>2+</sup> or Eu<sup>3+</sup> counterions.

The role of water is demonstrated by comparing PMFs in water and in methanol solution where there is no contact ion pair, but a free energy minimum at ca. 17 Å, corresponding to an ion separated pair  $\alpha$ -PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> ... Eu(MeOH)<sub>9</sub><sup>3+</sup> ...  $\alpha$ -PW<sub>12</sub>O<sub>40</sub><sup>3-</sup>.

## Spin-orbit coupling matrix elements from the Hermitian formulation of coupled cluster response theory

Aleksandra Tucholska<sup>1</sup>, M. Lesiuk<sup>1</sup>, Robert Moszynski<sup>1</sup>

<sup>1</sup>*Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*

In high resolution spectroscopy, the interpretation of experimental spectra requires inclusion of both the relativistic effects and electron correlation at a high level. Relativistic effects, especially the spin-orbit interaction, are responsible for the fine structure splitting, existence of intercombination transitions, and phosphorescence. They also affect the shape of the potential energy surfaces of systems containing heavy atoms.

In this work we are focused on the computation of the spin-orbit coupling matrix elements using the Hermitian formulation of coupled cluster response theory [1,2]. In contrast to the existing coupled cluster approaches, the resulting electron transition moments satisfy the necessary symmetry conditions.

We present a derivation and implementation of the spin-orbit coupling matrix elements within the CC3 approximation of the coupled cluster amplitudes. The results are obtained with Gaussian and Slater basis sets. We present preliminary numerical results and compare them with the MRCI values and experimental data. Additionally, we present computed lifetimes for various states of atomic and diatomic closed-shell systems.

The code for spin-orbit matrix elements, transition moments between excited states, as well as the previously implemented code for transition moments from the ground state, will be incorporated into KOŁOS: A general purpose ab initio program for the electronic structure calculation with Slater orbitals, Slater geminals, and Kołos-Wolniewicz functions.

Acknowledgments: This work was supported by the The National Science Centre within the grant No. D112/501/66GR5365

- [1] A. M. Tucholska, M. Lesiuk, R. Moszynski *J. Chem. Phys.* **146** (2017) 034108
- [2] A. M. Tucholska, M. Modrzejewski and R. Moszynski *J. Chem. Phys.* **141** (2014) 12409
- [3] B. Jeziorski and R. Moszynski, *Int. J. Quantum Chem.* **48** (1993) 161.
- [4] R. Moszynski, P. S. Zuchowski and B. Jeziorski, *Collect. Czech. Chem. Commun.* **70** (2005) 1109.



## Upgrading existing GGA functionals to range-separated hybrid meta-GGAs

**Marcin Modrzejewski<sup>1</sup>, Michał Hapka<sup>1</sup>, Małgorzata M. Szcześniak<sup>2</sup>, Grzegorz Chalaśiński<sup>1</sup>**

*<sup>1</sup>Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*

*<sup>2</sup>Department of Chemistry, Oakland University, Rochester, Michigan 48309-4477, United States*

We present a general scheme for converting an existing exchange functional into its range-separated hybrid form with long-range Hartree-Fock exchange. The main difference with the existing approaches is that the underlying Becke-Roussel-type exchange hole has the exact second-order expansion in the interelectron distance. Consequently, the short-range part of the range-separated exchange energy depends on the kinetic energy density and the Laplacian even if the base functional is a simple GGA. The range-separation parameter can be fixed by the requirement that the spurious self-interaction energy of the hydrogen atom vanishes. An example constructed using this scheme is LC-PBETPSS, which combines the PBE exchange and the TPSS correlation energies. Numerical tests show remarkably robust performance of the method for noncovalent interactions, barrier heights, excitation energies, and energy differences involving compounds with transition metals.

Acknowledgments: This work was supported by the The National Science Centre within the grant No. 2014/15/N/ST4/02170.

[1] M. Modrzejewski, M. Hapka, G. Chalasinski, and Małgorzata M. Szcześniak, *J. Chem. Theory Comput.* **12**, 3662 (2016).

**High-energy photochemistry in liquid solutions:  
Ultrafast proton and electron transfer initiated by X-rays**

**Daniel Hollas<sup>1</sup>, Marwin Pohl<sup>2</sup>, Bernd Winter<sup>3</sup>, Tsveta Miteva<sup>4</sup>, Nicolas Sisourat<sup>4</sup>,  
Petr Slavíček<sup>1</sup>**

<sup>1</sup>*Department of Physical Chemistry, University of Chemistry and Technology Prague,  
Technická 5, Prague, Czech Republic*

<sup>2</sup>*Department of Physics, Freie Universität Berlin, Arnimallee 14, D-141595, Berlin, Germany*

<sup>3</sup>*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195, Berlin,  
Germany*

<sup>4</sup>*UMR 7614, Laboratoire de Chimie Physique Matière et Rayonnement, Sorbonne Universités,  
UPMC University Paris 06, France*

High energy radiation is routinely used in various areas of science and technology yet the ultrafast processes following the core ionization of atoms or molecules remain poorly understood. In addition to well-known Auger decay and X-ray fluorescence, new non-local relaxation processes such as Intermolecular Coulombic Decay (ICD) were discovered only recently. In collaboration with liquid beam photoemission experiments, we investigated ultrafast electronic and nuclear relaxation pathways in liquid solutions.

A new relaxation pathway in liquid water was recently identified (so called PTM-CS process).[1] We have shown that the same process is taking place also in other hydrogen bonded systems such as hydrogen peroxide[2], glycine[3] and ammonia solutions[3, 4]. Since the different relaxation pathways result in different transient reactive species, our findings may lead to a better understanding of biomolecular radiation damage.

- [1] S. Thürmer, M. Ončák, N. Ottosson, R. Seidel, U. Hergenhausen, S. E. Bradforth, P. Slavíček, B. Winter, *Nat. Chem.* **5**, 590 (2013).
- [2] I. Unger, S. Thürmer, D. Hollas, E. F. Aziz, B. Winter, P. Slavíček, *J. Phys. Chem. C* **118**, 29142 (2014).
- [3] I. Unger, D. Hollas, R. Seidel, S. Thürmer, E. Aziz, P. Slavíček, B. Winter, *J. Phys. Chem. B* **119**, 10750 (2015).
- [4] D. Hollas, M. Pohl, R. Seidel, E.F. Aziz, P. Slavíček, B. Winter, *Sci. Rep.* **7**, 756 (2017).

**Lewis acid bulkiness effect on the stereoselectivity of cycloaddition reactions  
between acyclic dienes and  $\alpha,\beta$ -enals.**

**Diana Yepes<sup>1</sup>, Patricia Pérez<sup>1</sup>, Pablo Jaque<sup>1</sup>, Israel Fernández<sup>2</sup>**

<sup>1</sup>*Departamento de Ciencias Químicas, Facultad de Ciencias Exactas, Universidad Andres Bello, Av. República 275, Santiago, Chile.*

<sup>2</sup>*Departamento de Química Orgánica I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040-Madrid, Spain.*

The factors controlling the reactivity and endo/exo selectivity of Lewis acid-catalyzed Diels–Alder reactions between highly substituted open-chain 1,3-dienes and  $\alpha,\beta$ -enals have been explored computationally by means of density functional theory calculations. In agreement with previous experimental observations [1], it is found that the  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed cycloaddition reaction leads almost exclusively to the corresponding exo-cycloadduct, whereas the analogous  $\text{AlCl}_3$ -mediated process is highly endo-selective. The effect of Lewis acid bulkiness on stereoselectivity has been quantitatively analyzed by means of a combination of the activation strain model of reactivity and the energy decomposition analysis methods [2,3]. In contrast to the current view, the exo-selectivity promoted by the bulky  $\text{B}(\text{C}_6\text{F}_5)_3$  catalyst does not result from the steric destabilization of the corresponding endo-transition state but from the interplay between the less destabilizing strain energy and the stronger interaction between the deformed reactants along the entire reaction coordinate. In addition, non-covalent interactions are found to play a crucial role in stabilizing the exo-approach. These results allow us to not only quantitatively understand the effect of the Lewis acids in the process, but also predict new catalysts leading to highly exo-selective Diels–Alder reactions [4].

- [1] J.-H. Zhou, B. Jiang, F.-F. Meng, Y.-H. Xu, T.-P. Loh, *Org. Lett.* **17**, 4432 (2015).
- [2] F. M. Bickelhaupt, *J. Comput. Chem.* **20**, 114 (1999).
- [3] K. Morokuma, *J. Chem. Phys.* **55**, 1236 (1971).
- [4] D. Yepes, P. Pérez, P. Jaque, I. Fernández, *Org. Chem. Front.* DOI: 10.1039/c7qo00154a.

**Acknowledgments**

The authors acknowledge financial support from the FONDECYT (No. 3150249 to D. Y., No. 1140341 to P.P. and No. 1140340 to P. J.) and the Spanish MINECO-FEDER (Grant No. CTQ2013-44303-P, CTQ2014- 51912-REDC and CTQ2016-78205-P to I. F.).

## NMR magnetic shielding in halogen bonding and cooperative effects in $(\text{BrF})_n$ clusters.

Blatter, Sandra Patricia<sup>1, 2</sup>, Maldonado, Alejandro<sup>1</sup>, Aucar, Gustavo<sup>1, 2</sup>

<sup>1</sup>FaCENA - UNNE - Corrientes - Argentina

<sup>2</sup>Physics Department, Natural and Exact Science Faculty, Northeastern University of Argentina and Institute of Modelling and Innovative Technology, IMIT, Corrientes, Argentina

In this work we study the NMR nuclear magnetic shielding linear molecules containing halogen atoms  $XY$  ( $X, Y = \text{F, Cl, Br, I}$ ) and the magnitude of relativistic effects in such property. We also analyze dimer molecules with the same linear molecules in order to find a relationship among the strength of halogen bonding and the NMR parameter. As a particular case, we study deeper the cooperative effects on the magnetic shielding constant in cyclic clusters  $\text{FBr}_n$  ( $n = 1 - 5$ ) molecular systems.

We applied the relativistic polarization propagator approach (Rel-PPA)[1] for the nuclear magnetic shielding constant as implemented in Dirac code.[3] We also performed nonrelativistic calculations making the speed of light ( $c$ ) tend to infinity in order to obtain such values with the same scheme of calculations.

The bond length of monomers,  $XY$  ( $X, Y = \text{F, Cl, Br, I}$ ), used in this work were taken from experimental measurements. The gauge atomic including orbitals (GIAO) was used in shielding calculations to avoid the gauge dependence and ensure the basis set convergence. In the first step we analyzed the magnetic shielding of halogen in monomers, and after that the same properties in dimers in order to analyze the effect of halogen bonding. The next step was the calculations of the magnetic shielding in  $(\text{FBr})_n$  clusters taken from early study[2] and the look for cooperative effects on one nucleus due the rest of halogen atom conforming the clusters.

Keyword: Relativistic effects; Cooperative effects; Magnetic shielding; Polarization propagators

[1] G. A. Aucar, R. H. Romero, and A. F. Maldonado. *Int. Rev. on Phys. Chem.*, 29:1, 2010.

[2] R. D. Parra. *Comp. Theor. Chem.*, 1066:47, 2015.

[3] DIRAC, a relativistic ab initio electronic structure program, Release DIRAC13 (2013), written by L. Visscher, H. J. Aa. Jensen, R. Bast, and T. Saue. (see <http://www.diracprogram.org>).

[4] K. Sutter, G. A. Aucar, and J. Autschbach. *Chem. European J.*, 21:18138, 2015.

## Reaction Force Constant Analysis Applied in Organic and Organometallics Multi-Bond Reactions.

Pablo Jaque<sup>1</sup>

<sup>1</sup>*Departamento de Ciencias Química, Facultad de Ciencias Exactas, Universidad Andres Bello, Santiago, Chile; e-mail: pjaque@unab.cl*

A main goal in chemistry is to rationalize the controlling factors on the reaction barrier heights, thermodynamic driving force and the reaction mechanisms of a chemical interconversion since this can lead to an improved capability for guiding the chemical processes. In this regard, several interpretative models have been proposed and successful applied in a large variety of chemical reactions. The potential energy profile  $V(\xi)$  along any reaction coordinate  $\xi$  (typically the intrinsic reaction coordinate) contains the kinetical and thermodynamical information. In addition, the exploration of the shape of  $V(\xi)$  through its derivative allows to describe what physically happens in a chemical reaction. Therefore, the reaction force  $F(\xi)$  [1] and the reaction force constant  $\kappa(\xi)$  [2] defined, respectively, as the first- and the second-order derivative of  $V(\xi)$  of the reacting system along  $\xi$ , provide a useful frame to characterize the “mechanic” aspects. While the former provide a rational partition of the energy barrier into structural and electronic factors [3] the latter has been proposed as a suitable indicator of the degree of synchronicity/asynchronicity in bond-breaking/bond-forming processes [4]. In the present communication we will present the last results of organic and organometallic multi-bond reactions.

**Acknowledgments.** The authors acknowledge FONDECYT project number 1140340.

- [1] A. Toro-Labbé, *J. Phys. Chem. A* **103**, 4398 (1999).
- [2] P. Jaque, A. Toro-Labbé, P. Politzer, P. Geerlings, *Chem. Phys. Lett.* **456**, 135 (2008).
- [3] P. Politzer, A. Toro-Labbé, S. Gutiérrez-Oliva, J. S. Murray, *Adv. Quantum Chem.* **64**, 189 (2012).
- [4] D. Yepes, J. S. Murray, P. Politzer, P. Jaque, *Phys. Chem. Chem. Phys.* **14**, 11125 (2012). D. Yepes, O. Donoso-Tauda, P. Pérez, J. S. Murray, P. Politzer, P. Jaque, *Phys. Chem. Chem. Phys.* **15**, 7311 (2013). D. Yepes, J. S. Murray, P. Pérez, L. R. Domingo, P. Politzer, P. Jaque, *Phys. Chem. Chem. Phys.* **16**, 6726 (2014).

**DLPNO-CCSD(T) based compound methods for accurate thermochemistry****Dimitrios G. Liakos<sup>1</sup> and Frank Neese<sup>1</sup>**

*<sup>1</sup>Max-Planck Institute for Chemical Energy Conversion, Stiftstr. 34-36 D-45470 Muelheim  
a.d. Ruhr Germany*

DLPNO-CCSD(T) methods provide an efficient way to calculate energies with CCSD(T) accuracy. Nevertheless, sources of error still remain that need to be addressed in order to achieve experimental accuracy. In an attempt to reach thermochemical accuracy, we present a combination of methods that attempts to address most of the potential errors like the basis set incompleteness, inaccurate initial geometries and relativistic effects. The resulting methods are all implemented in the ORCA package and can be used in a black box manner. The calculated energies can now be used as a reference for calibration of approximate methods.

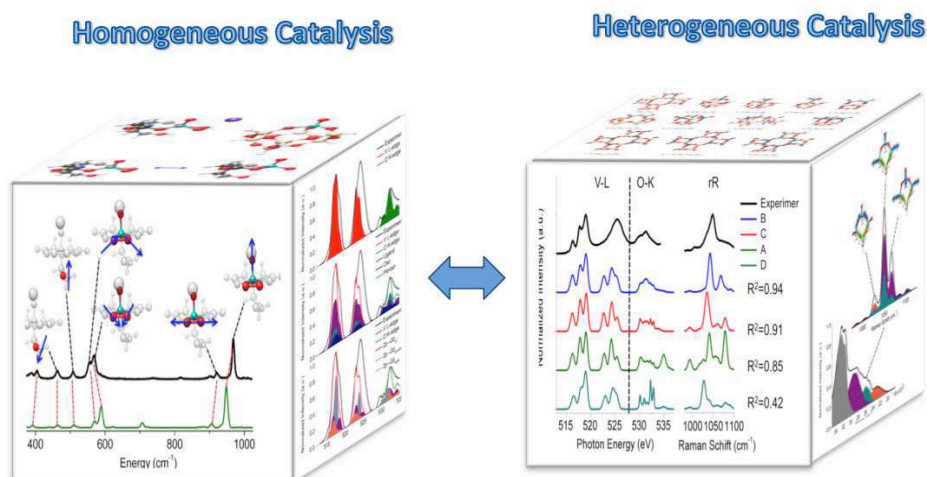
## Insights into heterogeneous catalysts from theoretical spectroscopy and accurate binding energies

Dimitrios Maganas and Frank Neese

<sup>1</sup> Max Planck Institute for Chemical Energy Conversion, Stiftstr. 34-36, D-45470 Mülheim an der Ruhr

\*: presenting author, email: dimitrios.maganas@cec.mpg.de

The structural characterization of catalytically active structures in heterogeneous catalysis is a particularly difficult problem. In many cases, spectroscopic data taken under in-situ conditions is available. However, developing the full information content of these spectroscopic data has been proven to be exceptionally difficult. This is partially due to the fact that many different structural motifs contribute to the spectra and partially is due to a lack of reliable theoretical tools that are able to simulate spectra with predictive accuracy and therefore allow for structure/spectra correlations. In addition entry into the field of catalytic reactivity is required in order to cross-correlate spectroscopic properties with accurate energetics in an effort to identify key reaction functionalities of a particular catalytic system. We will present herein illustrative examples on metal oxide<sup>1,2</sup> based catalysts.



(1) A unified view on heterogeneous and homogeneous catalysts through a combination of spectroscopy and quantum chemistry Dimitrios Maganas, Annette Trunschke, Robert Schlögl and Frank Neese Faraday Discuss., **2016**, 188, 181-197

(2) Surface Adsorption Energetics Studied with “Gold Standard” Wave-Function-Based Ab Initio Methods: Small-Molecule Binding to TiO<sub>2</sub>(110) Adam Kubas, Daniel Berger, Harald Oberhofer, Dimitrios Maganas, Karsten Reuter, and Frank Neese J. Phys. Chem. Lett., **2016**, 7, 4207-4212

**Energy decomposition analysis for studying covalent bonds.**

Daniel S. Levine, Martin Head-Gordon

Kenneth S. Pitzer Center for Theoretical Chemistry, Department of Chemistry, University of California, Berkeley, California 94720, United States

Energy Decomposition Analysis (EDA) is a technique to describe the interactions between fragments of molecules in terms of chemically meaningful terms (e.g. electrostatics, dispersion, Pauli repulsion, charge transfer, etc.). Few EDAs are applicable to systems in which the fragmentation of the supersystem into separate interacting parts breaks covalent bonds. We present an EDA method specifically designed for this class of problem using absolutely localized molecular orbitals (ALMOs). This EDA method gives terms describable as frozen interactions (further decomposable into electrostatics, Pauli repulsion, dispersion components), spin-coupling, induced polarization, and charge-transfer stabilization. A variety of simple and complex molecules (including dispersion-assisted bonds and metal-metal bonds) are analyzed by this method and the results lend insight into the nature of the interactions.



## Exact Single-Electron Approach to the Dynamics of Molecules in Strong Laser Fields

Axel Schild<sup>1</sup>, E.K.U. Gross<sup>2</sup>

<sup>1</sup>*Laboratorium für Physikalische Chemie, ETH Zürich, Switzerland*

<sup>2</sup>*Max Planck Institute of Microstructure Physics, Halle (Saale), Germany*

We present an exact single-electron picture that describes the correlated electron dynamics in strong laser fields. The picture is based on the idea to factor the many-electron wavefunction as a product of a marginal amplitude and a conditional amplitude. The marginal amplitude is constructed such that it yields the exact one-electron density and current density. If the equation of motion for the many-electron wavefunction is a Schrödinger equation, then the equation of motion for the marginal amplitude is also a Schrödinger equation, albeit for a single effective particle (with the mass of an electron) and with the many-electron interaction given by a time-dependent effective potential. Thus, the resulting marginal amplitude may be called a single-electron wavefunction, but it yields properties of the full many-electron system.

Our approach is relevant for the description of strong field phenomena, because they are often interpreted in a single-electron picture. We present results for 2- and 3-electron model systems in strong laser fields and illustrate how an exact single-electron picture of ionization or high-harmonic generation looks like, and how many-electron interactions are represented as the time-dependence of an effective single-electron potential. Additionally, we present a first step towards a new computationally feasible approximation for the theoretical treatment of the dynamics of realistic molecules in laser fields.

[1] Axel Schild, E.K.U. Gross, *Phys. Rev. Lett.* **118**, 163202 (2017).

## When magnetism meets reactivity: Hydrogen generation via a bi-metallic mechanism with spin exchange.

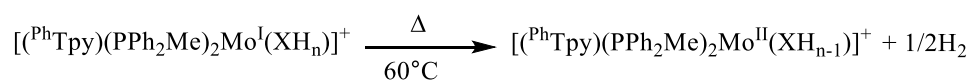
**Nuno A. G. Bandeira<sup>1,2,3</sup>, Luís F. Veiros<sup>2</sup>, Carles Bo<sup>1</sup>**

<sup>1</sup> *Institute of Chemical Research of Catalonia (ICIQ) - Avda. Països Catalans, 16- 43007 Tarragona, Spain.*

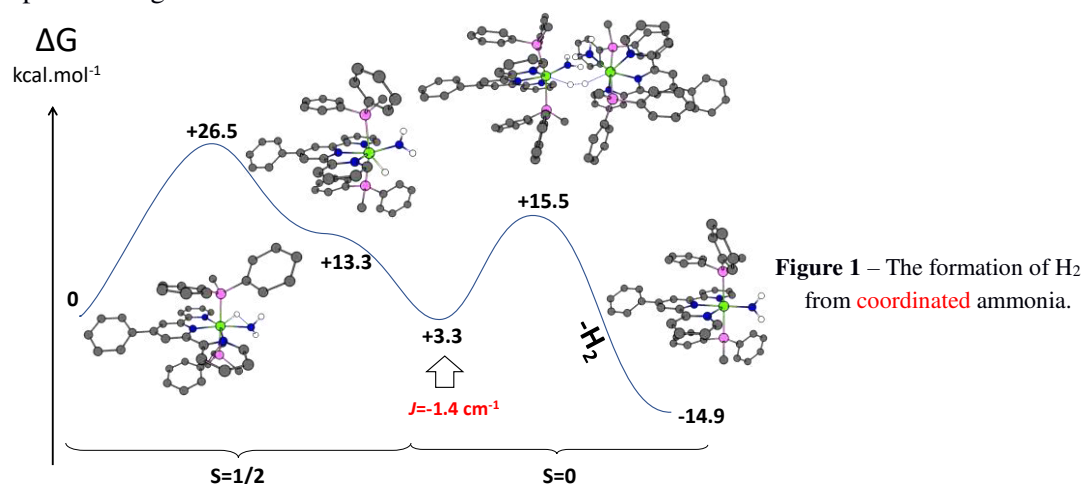
<sup>2</sup> *Centro de Química Estrutural - Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.*

<sup>3</sup> *Centro de Química e Bioquímica - Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal.*

The very recent report by Chirik and others [1] of a novel transition metal complex  $[(^{\text{Ph}}\text{Tpy})(\text{PPh}_2\text{Me})_2\text{Mo}^{\text{I}}(\text{XH}_n)]^+$  ( $^{\text{Ph}}\text{Tpy}$ , 4'-Ph-2,2',6',2''-terpyridine,  $\text{XH}_n = \text{NH}_3$ ,  $\text{OH}_2$ ,  $\text{NH}_2\text{NH}_2$ ) capable of generating molecular hydrogen from an  $\text{XH}_n$  ligand as a hydrogen source is an interesting leap forward towards sustainable energy research in the homogeneous phase:



We explored three mechanistic routes for this process and examined their feasibility with Density Functional Theory (PBE-D3BJ/TZP+DZP) to pinpoint the most favourable one. The rate limiting step takes place initially by an oxidative addition of the X-H bond (Figure 1) but the subsequent step must involve a bi-metallic association with concomitant spin exchange.



[1] M. J. Bezdek, S. Guo, and P. J. Chirik, *Science* **354**, 730 (2016).

**FeNO<sup>2+</sup> as a model system for spin–state energetics.****Constantine N. Sakellaris<sup>1</sup>, Christoph R. Jacob<sup>1</sup>**<sup>1</sup>*Institute of Physical and Theoretical Chemistry, TU Braunschweig,  
Gaußstr. 17, 38106 Braunschweig, Germany.*

Iron–nitrosyl complexes, containing an NO ligand perpendicular to the plane of a porphyrin–like N<sub>4</sub> cavity, feature a rather complicated electronic structure; on top of an open–shell iron cation we have an NO ligand, a "non–innocent" ligand [1–3]. Consequently, iron–nitrosyl compounds provide a challenging test case for the development of quantum–chemical methods, particularly for the density functional theory.

Here, we propose a FeNO<sup>2+</sup> moiety [4], embedded in a square grid of point–charges,  $q$ , as a model system for spin–state energetics [5]. The grid serves as a means of charge perturbations, resembling ligand fields of different strength in the actual complex. We report the CASSCF/CASPT2 and DFT spin–state energetic transitions between the high–intermediate and low–intermediate spin states, i.e. sextet to quartet and doublet to quartet. We span across a total charge of  $Q = +3$  to  $-3$ , for which the three spin states are calculated with nine different active spaces.

It is shown that calculated energies for spin–state crossovers with relatively large active spaces become oblivious to any amelioration, expected to either be brought about by the CASPT2 correction, or to their increase in size by means of additional orbitals. Thus, we find that these active spaces are quenched, or energetically converged and can provide reliable excitation energies at least for such a model system.

In addition to the grid of fixed Fe– $q$  distances, we expand (or shrink) the square–plane by varying the distance between the Fe atom and the four point charges. Moreover, we choose to perturb the point–charge perturbation grid itself by keeping its total charge fixed but the relative distribution over the individual four point–charges *not* uniform. As a final parameter in our study, we vary the Fe–N–O angle from 0 to 180 degrees.

The FeNO<sup>2+</sup> model system established here and the reference data obtained for a wide range of parameters can serve as a benchmark to guide future developments in spin–DFT.

- [1] D. Sakow, B. Böker, K. Brandhorst, O. Burghaus and M. Bröring, *Angew. Chem. Int. Ed.* **52**, 4912 (2013).
- [2] J. Conradie and A. Gosh, *J. Phys. Chem. B* **111**, 12621 (2007).
- [3] M. Radon and K. Pierloot, *J. Phys. Chem. A* **112**, 11824 (2008).
- [4] K. Boguslawski, Ch. R. Jacob and M. Reiher, *J. Chem. Theory Comput.* **7**, 2740 (2011).
- [5] C. N. Sakellaris and Ch. R. Jacob, *to be submitted for publication* (2017).

## Orbital relaxation and electronic transitions What is the nature of Handy's Z-vector?

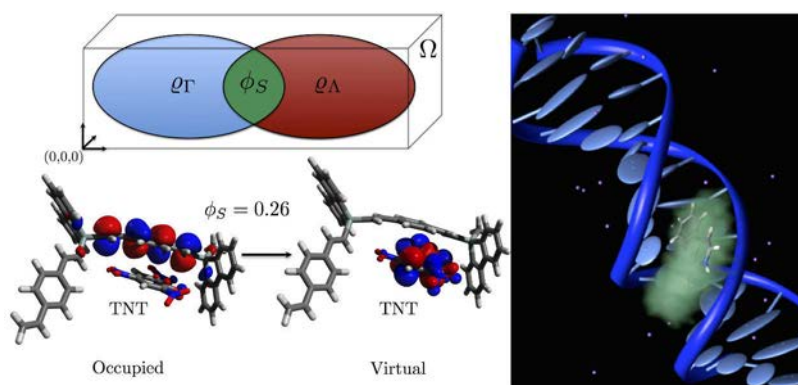
Mariachiara Pastore<sup>1,2</sup>, Antonio Monari<sup>1,2</sup>, Xavier Assfeld<sup>1,2</sup>, Thibaud Etienne<sup>3</sup>

<sup>1</sup>Université de Lorraine – Nancy, France (Théorie-Modélisation-Simulation SRS MC)

<sup>2</sup>CNRS (Théorie-Modélisation-Simulation SRS MC) – CNRS : UMR7565

<sup>3</sup>Chimie Théorique, Méthodologies, Modélisation – Institut Charles Gerhardt, Université de Montpellier, France

Providing a quantitative insight into light-induced electronic structure reorganization of complex chromophores remains a challenging task that has attracted a substantial attention from theoretical communities in the past few years. Indeed, a potential knowledge related to the ability of a chromophore to undergo a charge transfer caused by photon absorption or emission is of seminal importance for designing novel dyes with highly competitive optoelectronic properties. These target systems are at the center of the main societal issues of our time such as public health with anti-cancer phototherapy, sustainable energy with high-performance solar cells, or homeland security with explosive probes for example. In this context, we elaborated systematic and tractable strategies for qualitatively and quantitatively assessing the electronic cloud polarization of complex molecular structures upon a transition to or from electronic excited states and improve our understanding of the electronic transition process[1, 2, 3]. In addition to providing a clear picture of complex charge transfer processes, our topological metrics are able to act as reliable diagnostic instruments for the exchange-correlation functionals used within the time-dependent density functional theory framework, and therefore constitute a precious tool for computational chemists. After introducing the theoretical elaboration of our strategy and applying it to the aforementioned hot topics, this contribution will detail for the first time the generalization of our topological analyses to fully relaxed excited states density matrices including the so-called Z-vector. Finally, the way our developments allowed us to unravel the physical nature of Handy's Z-vector itself [4] will be reported.



- [1] T. Etienne, X. Assfeld, A. Monari, *J. Chem. Theory Comput.* **10**, 3896 & 3906 (2014).
- [2] T. Etienne, *J. Chem. Theory Comput.* **11**, 1692 (2015).
- [3] T. Etienne, *J. Chem. Phys.* **142**, 244103 (2015).
- [4] M. Pastore, A. Monari, E. Mosconi, X. Assfeld, T. Etienne, *J. Chem. Phys.*, *Submitted*.

## Stochastic-CASSCF and Multiconfiguration Pair-Density Functional Theory for Spin Challenges in organometallic and organic chemistry

**G. Li Manni, N. Bogdanov, A. Alavi**

*Department of Electronic Structure Theory, Max-Planck Institute for Solid State Research, Heisenbergstrasse 1, 70569 Stuttgart, Germany*

Spin magnetism, of great relevance in the field of energy storage and conversions, poses enormous challenges to well established theoretical methods in quantum chemistry, due to the complex electronic structures of ground and excited states, often involving orbital and states degeneracies and in general multiconfigurational in nature. Advanced ab initio theoretical methods currently available are not able to meet this challenge and density functional theory (DFT) has been for a long time the only computational tool to complement experimental findings. Methods for strongly correlated systems are urged. In this talk, I will present two novel methods: **(a)** The Stochastic-CASSCF [1] approach, that uses a Quantum Monte-Carlo algorithm to solve the CI secular problem and the Super-CI scheme to variationally optimizing the molecular orbitals and **(b)** the Multiconfiguration Pair-Density Functional Theory (MC-PDFT) [2] method, a post-SCF scheme that combines the advantages of multiconfigurational wave function theory and density functional theory to recover static and dynamic electron correlation. The two methods are complementary and have been coupled together. By these approaches (a) much larger active spaces, easily up to 50 electrons and 50 orbitals, (b) larger basis set expansions (via density fitting techniques), up to several thousand contracted functions and, (c) molecular systems of a few hundred atoms are accessible and both non-dynamical and dynamic correlation effects can be recovered. These methods are completely general and can be applied to any kind of molecular system. In this talk, their application to several chemical systems of practical interest will be presented, with special focus on the Fe(II)-Porphyrin and the chain of polyacenes.



Figure 1: Fe(II)-Porphyrin (*left*), and dodecacene (*right*), CAS(50,50) treated via Stochastic-CASSCF/MC-PDFT.

- [1] G. Li Manni, S. D. Smart, A. Alavi, *J. Chem. Theory Comput.* **12**, 1245 (2016).
- [2] L. Gagliardi, D. G. Truhlar, G. Li Manni, R. K. Carlson, C. E. Hoyer, J. L. Bao, *Acc. Chem. Res.* **50**, 66 (2017).

## Putting the squeeze on: First-principles melting of Hg, Cd and Zn under pressure

K.G. Steenbergen<sup>1</sup>, F. Calvo<sup>2</sup>, E. Pahl<sup>1</sup>, P. Schwerdtfeger<sup>1</sup>

<sup>1</sup>*Centre for Theoretical Chemistry and Physics, The New Zealand Institute for Advanced Study, Massey University (Auckland), Private Bag 102904, 0632 Auckland, New Zealand*

<sup>2</sup>*Laboratoire Interdisciplinaire de Physique, Université Grenoble Alpes and CNRS, St Martin d'Hères, France*

As the only elemental metal that exists in the liquid state at standard temperature and pressure, mercury's thermodynamic properties have been of significant interest to the scientific community for over 60 years. In Hg, scalar relativity leads to a significant contraction of mercury's 6s shell, which stabilises the 6s orbital while destabilising the 5d shell. Using density functional theory and the recently-developed interface pinning method for bulk melting (graphically illustrated in Figure 1),[1] we have recently proven that mercury is, in fact, a liquid at room temperature due to relativistic effects.[2] We obtain a relativistic simulated melting temperature ( $T_m$ ) of 241 K, in excellent agreement with the experimental value of 234 K. The non-relativistic model melts at 402 K: an increase of 160 K! Here, we present the results of first-principles melting simulations at 0, 10 and 20 GPa, using the Hg relativistic and non-relativistic models, in order to compare how relativity effects solid state properties under pressure. We also include and compare results for cadmium and zinc at the same pressures. With a first glimpse at relativistic effects at nonstandard pressures and temperatures, as well as a comprehensive comparison of thermodynamic effects across the group-12 metals for the liquid and solid states, this work gives a deeper understanding of how relativity and pressure affect macroscopic properties of metals.

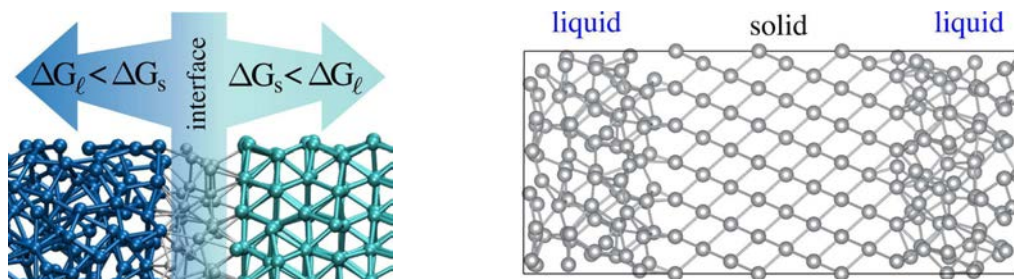


Figure 1: Interface pinning exploits the fact that the Gibbs free energy difference ( $\Delta G$ ) between the solid and liquid phase is zero at  $T_m$ : (left) graphical illustration of interface melting; (right) first-principles bulk melting supercell for Hg.

[1] UR Pedersen, F Hummel, G Kresse, G Kahl, C Dellago. *Phys. Rev. B* **88**, 094101 (2013).

[2] KG Steenbergen, E Pahl, P Schwerdtfeger. *J. Phys. Chem. Lett.* **8**, 1407–1412 (2017).

## Oxygen Induced Diffusion of Ni Atoms in Ni-Au Clusters

Ralf Meyer<sup>1</sup>, Andreas W. Hauser<sup>1</sup>

<sup>1</sup>*Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, A-8010  
Graz, Austria*

Bimetallic nanoparticles are a topic of special interest due to their unique physical and chemical properties. Potential applications for this new class of materials range from optics and catalysis to biomedicine. Recent experimental results of the Ernst group, who is able to grow highly inert mixed-metallic nanoparticles in superfluid helium nanodroplets,[1, 2] caught our interest and triggered a series of theoretical investigations of Ni-core/Au-shell nanoclusters with the aim to explain the observed inversion of the core-shell structure after heating to 400°C and subsequent cooling. The experimental investigations were based on *in-situ* transmission electron microscopy and included spatially resolved EDX and EELS measurements allowing for an element-specific characterization of the nanoparticle structure as a function of temperature. However, the advantage of this direct imaging technique comes at the cost of an inevitable oxidation of the particles during observation, which leads to an interesting interplay between oxidation reactions and phase transitions. It is our aim to describe these features via a combination of Monte Carlo and molecular dynamics calculations with density functional theory. Preliminary results indicate that the oxidation of the nickel atoms at the surface is responsible for locking the bimetallic particles in a Au-core/Ni-shell structure. The diffusion of Ni atoms to the surface of the core-shell particle seems to be significantly enhanced by the adsorption of oxygen on the surface of the nanoparticles.

- [1] P. Thaler, A. Volk, F. Lackner, H. Steurer, D. Knez, W. Grogger, F. Hofer, and W. E. Ernst, *Phys. Rev. B*, **90**, 155442 (2014).
- [2] G. Haberfehlner, P. Thaler, D. Knez, A. Volk, F. Hofer, W. E. Ernst and G. Kothleitner, *Nat. Commun.*, **6**, 8779 (2015).

## Adsorption of post-Combustion Gases by *Mg-MOF-74*

F. Keshavarz, O. Sánchez, D. Bahamón, P. Gamallo, X. Giménez and R. Sayós

Departament de Ciència de Materials i Química Física

Universitat de Barcelona

Separation of  $\text{CO}_2$  from gas streams is imperative in sour natural gas wells and power-plant flue gases [1]. Such separation may be performed during post-combustion, with the gas stream at 1 atm. and between 313 to 333 K, consisting of  $\text{CO}_2$  (15%),  $\text{N}_2$  (75%),  $\text{H}_2\text{O}$  (6%),  $\text{O}_2$  (4%),  $\text{NO}_x$  (53 ppm) and  $\text{SO}_2$  (80 ppm), all percentages being v/v [2]. An interesting candidate for the capturing task is a metal-organic framework, *Mg-MOF-74*. It exhibits exceptional  $\text{CO}_2$  storage capacity, strong physisorption interaction, but facile  $\text{CO}_2$  release and thermodynamic selectivity [3]. Despite these positive features, *Mg-MOF-74* capacity may decrease dramatically if exposed to mixtures of gases under dynamic conditions, as would be the case of post-combustion [4]. Though it has been revealed that  $\text{SO}_2$  is a significant threat to  $\text{CO}_2$  adsorption, and gases such as  $\text{H}_2\text{O}$ ,  $\text{NO}_2$ ,  $\text{NO}$  and  $\text{O}_2$  are major concerns, most experimental and simulation studies have ignored the effect of these gases on the adsorption behavior.

Therefore, this study considers the influence of minor gases on  $\text{CO}_2$  adsorption capability. The best force field, for isotherm analysis of post-combustion gases, was first verified through *Grand Canonical Monte Carlo* (GCMC) simulations (pressure: 0.1 to 1 atm.), including Lennard-Jones 6-12, Coulomb interactions and Ewald summation method for van der Waals, short- and long-range electrostatic interactions, respectively. The best force field parameters for *Mg-MOF-74*, reproducing both experimental and simulated isotherms, have been determined.

Then, pure gas isotherms at several temperatures above and below 323 K were retrieved for all the gases (except  $\text{H}_2\text{O}$ , that is usually trapped before the adsorption unit) from GCMC simulations. Two- and three-gas mixtures, corresponding to all combinations, at several pressure and temperatures, have been also studied, so that the influence on  $\text{CO}_2$  adsorption could be determined in detail. Mixture results show a moderate to low ability of minor gases to diminish  $\text{CO}_2$  adsorption on *Mg-MOF-74*, in contradiction to prior statements in the literature. More specific results will be presented at the meeting.

### References:

- [1] Zou, R., et al. "Storage and separation applications of nanoporous metal-organic frameworks", *Cryst. Eng. Comm* 12 (2010) 1337-1353.
- [2] Espinal, L., et al. "Measurement, standards, and data needs for  $\text{CO}_2$  capture materials: a critical review", *Env. Sci. Technol.* 47 (2013) 11960-11975.
- [3] Sircar, S., T. C. Golden, and M. B. Rao. "Activated carbon for gas separation and storage", *Carbon* 34 (1996) 1-12.
- [4] Britt, D., et al. "Highly efficient separation of carbon dioxide by a metal-organic framework replete with open metal sites", *Proc. Nat. Acad. Sci.* 106 (2009) 20637-20640.
- [5] Pham, T., et al. "Capturing the  $\text{H}_2$ -Metal Interaction in *Mg-MOF-74* Using Classical Polarization" *J. Phys. Chem. C* 118 (2014) 22683-22690.



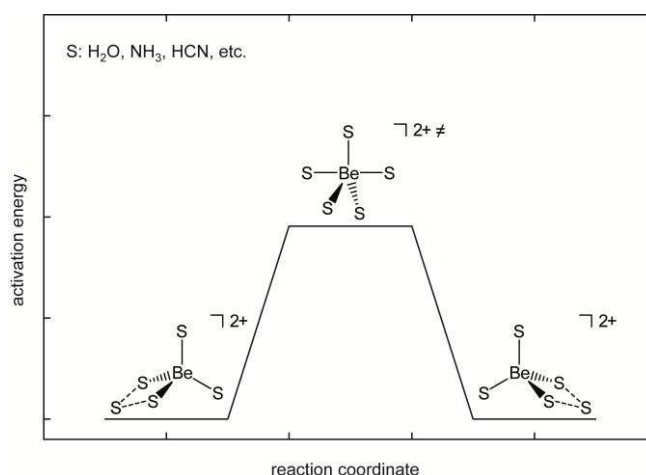
## LiEBe<sup>2+</sup> - Ligand Exchange at Beryllium dications

Ralph Puchta<sup>1,2</sup>

<sup>1</sup>Department Chemie und Pharmazie, Institut für Anorganische Chemie,  
Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 1,  
91058 Erlangen, Deutschland

<sup>2</sup> Department Chemie und Pharmazie, Computer Chemie Centrum,  
Friedrich-Alexander-Universität Erlangen-Nürnberg, Nögelsbachstraße 25,  
91052 Erlangen, Deutschland

Beryllium is supposed to be the most toxic non-radioactive metal in the periodic table, while parallel it is applied in various technical applications.[1] Due to the toxicological concerns only a few experimental studies in (bio)inorganic chemistry and related mechanisms are known. While solvent exchange reactions are the most fundamental substitution processes that a solvated metal ion can undergo and do not necessarily lead to a chemical conversion, they contribute fundamentally to our understanding of reactivity and substitution mechanisms. Experiments will lead to knowledge about reactions under realistic conditions, in contrast to quantum chemical calculations that permit detailed investigations unbiased by external effects.



In the presented work ligand exchange reactions on [BeS<sub>4</sub>]<sup>2+</sup>-ions were investigated and rationalized by DFT and MP2 calculations, focusing on solvent molecules (S),[2] bio-relevant ligands and ligands with differently hybridized donor atoms.

[1] R. Puchta, *Nat. Chem.* **3**, 413 (2011).

[2] R. Puchta, N. v. Eikema Hommes, R. v. Eldik, *Helv. Chim. Acta*, **88**, 911, (2005).

# Hydride-enhanced ligand nucleophilicity for metalloorganic catalytic reactivities

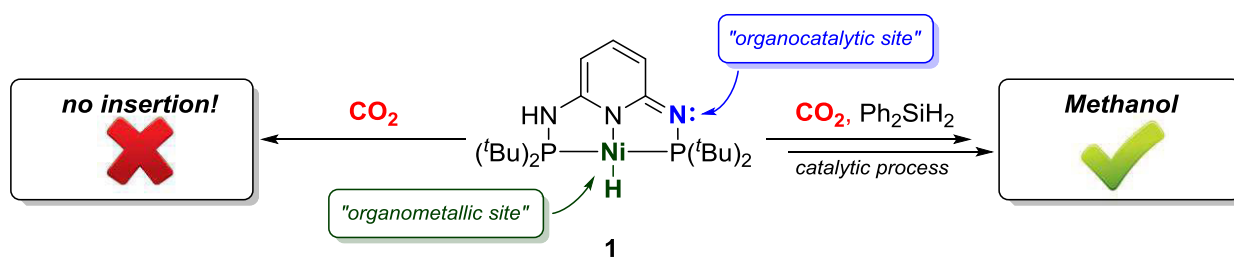
Theo P. Gonçalves<sup>a</sup>, Huaifeng Li and Kuo-Wei Huang<sup>b</sup>

King Abdullah University of Science and Technology (KAUST)  
KAUST Catalysis Center (KCC), and, Physical Science and Engineering Division (PSE),  
Thuwal, 23955-6900, Saudi Arabia

<sup>a</sup>E-mail: theo.goncalves@kaust.edu.sa

<sup>b</sup>E-mail: hkw@kaust.edu.sa

In this work, we disclose the computational study of unexpected reaction mechanism with our dearomatized Ni-H pincer complex **1** that promotes CO<sub>2</sub> reduction without direct participation of the metal center.<sup>[1]</sup> The reactivity has been attributed to the presence of the iminic arm moiety which acts as a strong electron donor, and in consequence, activates silane for hydride transfer. In contrast to commune observed reactivity,<sup>[2]</sup> our DFT and CCSD(T) calculations support that the complex itself is unable to perform CO<sub>2</sub> insertion to Ni-H bond in experimental conditions. Further analysis of the transition states confirm experimental finding that the nucleophilicity of the nitrogen is enhanced when electron donating spectator ligands are coordinating to the Ni metal. Therefore the dearomatized PN<sup>3</sup>P nickel complexes are capable of catalyzed efficiently transformations which typically belongs to the organocatalyst domain.



**Scheme 1.** Reactivity of the **1**, PN<sup>3</sup>P\*Ni-H complex.

## References (use Times New Roman 10)

- [1] H. Li, Q. Zhao, T. P. Gonçalves, D. Gong, B. Zheng, L. Yao, Z. Lai, Z. Wang, J. Zheng, K. W. Huang, *unpublished data*.
- [2] a) S. Chakraborty, J. Zhang, J. A. Krause, H. Guan, *J. Am. Chem. Soc.* **2010**, 132, 8872-8873; b) K. J. Jonasson, O. F. Wendt, *Chem. Eur. J* **2014**, 20, 11894-11902.

## **Influence of odd/even alkyl side-chain substitution on the morphology and charge-transport of benzothieno-benzothiophenes (BTBT)**

**M. Alkan, I. Yavuz<sup>1</sup>**

<sup>1</sup> *Department of Physics, Marmara University, 34722, Ziverbey, İstanbul, Turkey.*

Recent measurements show that organic materials with a benzothieno-benzothiophene (BTBT) core exhibit unprecedented charge-carrier mobilities but dramatically influenced by the size of side-chains. Recently, the crystal structures of a series of even ( $C_n$ -X- $C_n$ ) and odd ( $C_n$ -X) alkylated BTBTs have been obtained [1]. Using a multitude of computational tools, we calculate the molecular ordering and charge-transport of these materials to understand the side-chain dependence. The mobilities are typically on the order of 1-100  $\text{cm}^2/\text{Vs}$ , therefore we employ both band transport models using deformation-potential theory based on DFT-D3 methodology and hopping transport using kinetic Monte Carlo simulations employing Marcus-Levich-Jortner charge-transfer theory. Band transport calculations are performed in a perfect lattice, while hopping transport calculations are performed for both perfect lattices and disordered morphologies based on molecular dynamics simulations.

[1] H. Minemawari *et al.*, *Chem. Mater.* **29**, 1245–1254 (2017).

## Calculation of Molecular Properties from Relativistic Electron Dynamics

**Lukas Konecny<sup>1</sup>, Marius Kadek<sup>2</sup>, Stanislav Komorovsky<sup>3</sup>, Olga L. Malkin<sup>1,3</sup>,  
Vladimir G. Malkin<sup>3</sup>, Kenneth Ruud<sup>2</sup>, Michal Repisky<sup>2</sup>**

<sup>1</sup>*Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University,  
Ilkovicova 6, Bratislava, Slovakia*

<sup>2</sup>*The Centre for Theoretical and Computational Chemistry, Department of Chemistry, UiT The  
Arctic University of Norway, NO-9037, Tromsø, Norway*

<sup>3</sup>*Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dubravska cesta 9, Bratislava,  
Slovakia*

We present an implementation and applications of relativistic electron dynamics for molecular property calculations as an alternative to response theory approach. The electron dynamics methodology is based on a direct stepwise time propagation of an electronic state, represented by an one-electron density matrix. Time dependence of molecular properties can be obtained in the course of the simulation and afterwards processed to spectra in various regions including near resonant frequencies. This is possible without the need to explicitly evaluate the response kernels. If molecules of interest contain atoms of heavy elements or exhibit strong spin-orbit coupling, relativistic Hamiltonians have to be considered. Our implementation utilizes the matrix representation of the four-component Dirac–Coulomb Hamiltonian in the basis of restricted kinetically balanced Gaussian functions exploiting the noncollinear Kramers unrestricted formalism, as well as the quasirelativistic two-component X2C Hamiltonian. The latter leads to a 7-fold acceleration practically without the loss of accuracy.

The selected applications include the calculations of electron absorption and circular dichroism spectra by Fourier transform of the time-dependent induced electric or magnetic dipole moment, respectively. We focus on various spectral regions including the UV/Vis [1] and X-ray near L-edge structure [2]. Moreover, we compute molecular hyperpolarizabilities by a time-dependent finite-field method [3]. To overcome the absence of an analysis tool for spectra we have developed the dipole-weighted transition analysis to identify the nature of electronic transitions. In addition, to eliminate non-physical excitations that arise as artefacts of finite basis representation particularly in the high-frequency regions we propose the orbital-selective perturbation.

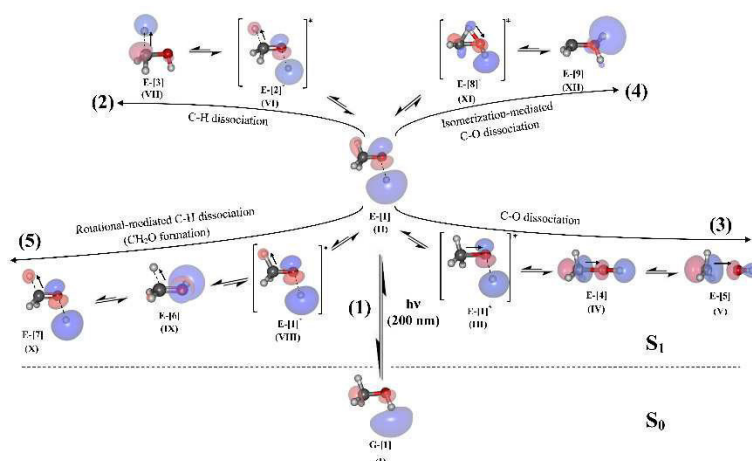
- [1] M. Repisky, L. Konecny, M. Kadek, S. Komorovsky, O. L. Malkin, V. G. Malkin, K. Ruud, *J. Chem. Theory Comput.* **11**, 980 (2015).
- [2] M. Kadek, L. Konecny, B. Gao, M. Repisky, K. Ruud, *Phys. Chem. Chem. Phys.* **17**, 22566 (2015).
- [3] L. Konecny, M. Kadek, S. Komorovsky, O. L. Malkin, K. Ruud, M. Repisky, *J. Chem. Theory Comput.* **12**, 5823 (2016).

## Dynamics of Photo-fragmentation of Methanol

Pannipa Panajapo, Kittipan Siwawannapong, Kritsana Sagarik\*

School of Chemistry, Institute of Science, Suranaree University of Technology,  
111 University Avenue, Nakhon Ratchasima 30000,  
Thailand.

**ABSTRACT:** Photo-fragmentation of methanol ( $\text{CH}_3\text{OH}$ ) has been of interest, because the product radicals are reactive intermediates in industrial, combustion and atmospheric processes [1,2]. Based on a theoretical method [3], the photo-fragmentation of  $\text{CH}_3\text{OH}$  in the  $S_1$  state was studied using TD-DFT and ADC(2) calculations with the aug-cc-pVDZ basis set and BOMD simulations over the temperature range of 200–2100 K. Because a minimum was found on the  $S_1$  relax-scan potential energy surface, the photo-fragmentation processes were suggested for the first time to take place through the  $[\text{CH}_3\text{O}]^\cdot-[\text{H}]^\cdot$  radical pair, which is also a common intermediate for the C-H and C-O bond dissociations, as well as for the formation of formaldehyde ( $\text{CH}_2\text{O}$ ) through a rotational-mediated dissociation process. These findings are different from the previous theoretical study [2], in which a homolytic cleavage of the O-H bond along a purely repulsive potential surface was predicted from a freeze-scan method. The BOMD results suggested that in the  $S_1$  state, the photo-fragmentation of  $\text{CH}_3\text{OH}$  and the formation of  $\text{CH}_2\text{O}$  are kinetic-control processes.



- [1] M. Yang, P. D. Nightingale, R. Beale, P. S. Liss, B. Blomquis, C. Fairall, *Environ. Sci.* **110**, 20034 (2013).
- [2] R. J. Buenker, G. Olbrich, H. P. Schuchmann, B. L. Schuermann, C. V. Sonntag, *J. Am. Chem. Soc.*, **106**, 4362 (1984).
- [3] J. Thisuwan, P. Suwannakham, C. Lao-ngam, K. Sagarik, *Phys. Chem. Chem. Phys.*, **18**, 5564 (2016).

**Acknowledgement:** The Royal Golden Jubilee (RGJ) Ph.D. Program of the Thailand Research Fund (TRF) (Grant No. PHD/0139/2554) and the Development and Promotion of Science and Technology Talents Project (DPST).

## Investigating the molecular structure and hydrogen bonding in single-chain polymer nanoparticle self-assembly binding motifs

**Peter A. Limacher<sup>1</sup>**, Wim Klopper<sup>1</sup>

<sup>1</sup>*Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany*

Figure 1 shows the intermolecular binding between a Hamilton wedge and cyanuric acid, frequently employed binding motifs to achieve self-assembly of single-chain polymer nanoparticles.

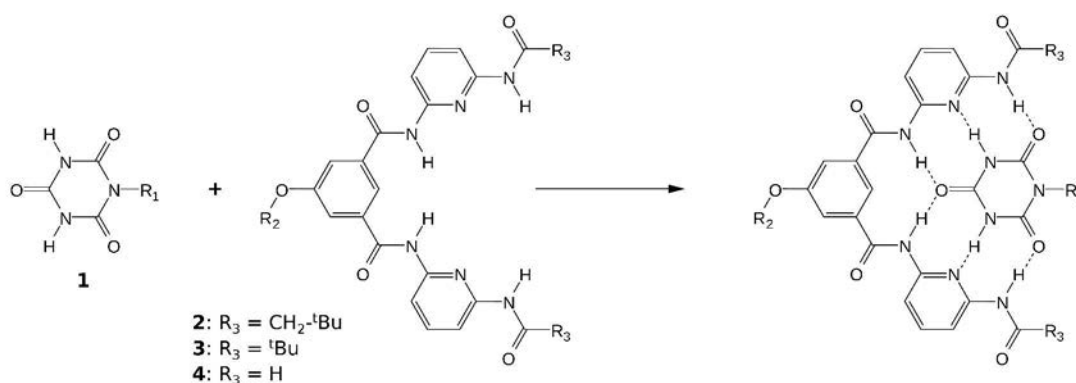


Figure 1: The hydrogen bonding pattern in a Hamilton wedge/cyanuric acid binding motif

In a recent study, we performed a conformational analysis of the isolated compounds and the hydrogen-bonded complex.[1] We found several low-energy structures, which are characterized based on their non-planarity and binding energy. New hypothetical binding motifs are proposed and proven to possess a superior binding energy, when becoming planar.

In addition, we compared NMR chemical shifts calculated on the B3LYP, BP86 and MP2 level with experimentally available data with a good qualitative agreement. Cases of quantitative disagreement between experiment and theory are traced back to solvent effects for isolated substituents or to thermally stretched intermolecular bonds for hydrogen-bonded species. When comparing the calculated NMR chemical shifts with their corresponding intermolecular hydrogen bond length, strong linear correlations can be found. This will allow experimentalists to predict exact geometrical distances from their measured NMR spectra in the future.

[1] P. A. Limacher, W. Klopper, *Soft Matter*, **submitted**.

## Recent developments in domain local pair natural orbital electron correlation approaches.

Christoph Riplinger<sup>1,2</sup>, Frank Neese<sup>1</sup>

<sup>1</sup>*Department of Molecular Theory and Spectroscopy, Max Planck Institute for Chemical Energy Conversion, Stiftstr. 34 – 36, D-45470 Mülheim an der Ruhr, Germany*

<sup>2</sup>*FAccTs GmbH, Rolandstr. 67, D-50677 Köln, Germany*

An overview on recent advances in method development employing the domain local pair natural orbital (DLPNO) framework is given. The DLPNO framework, first published in 2013, has been used to implement methods for open and closed shell CCSD(T) energy calculations and for closed shell CCSD(T) electron density calculations for the calculation of first-order molecular properties.[1-5] A multilevel implementation (DLPNO-CCSD(T), DLPNO-MP2, HF) has been established to treat different parts of a chemical system at different accuracy.[6] E.g. one part of a system can be treated at DLPNO-CCSD(T) level, while being embedded in an environment treated at DLPNO-MP2 or HF level.

A very efficient implementation of DLPNO-NEVPT2 yields accurate results for multi-reference cases.[7]

Overall, systems consisting of hundreds of atoms have been modeled in a routine fashion using the various DLPNO implementations. Chemical accuracy compared to the results obtained with the parent methodologies or compared to experimental data is achieved.

[1] C. Riplinger, F. Neese, *J. Chem. Phys.* **138**, 034106 (2013).

[2] C. Riplinger, B. Sandhöfer, A. Hansen, F. Neese, *J. Chem. Phys.* **139**, 134101 (2013).

[3] M. Saitow, U. Becker, C. Riplinger, E. F. Valeev, F. Neese, *J. Chem. Phys.* **146**, 164105 (2017).

[4] C. Riplinger, P. Pinski, U. Becker, E. F. Valeev, F. Neese, *J. Chem. Phys.* **144**, 024109 (2016).

[5] D. Datta, S. Kossmann, F. Neese, *J. Chem. Phys.* **145**, 114101 (2016).

[6] M. Sparta, M. Retegan, P. Pinski, C. Riplinger, U. Becker, F. Neese, *J. Chem. Theory Comput.* Just Accepted Manuscript.

[7] Y. Guo, K. Sivalingam, E. F. Valeev, F. Neese, *J. Chem. Phys.* **144**, 094111 (2016).

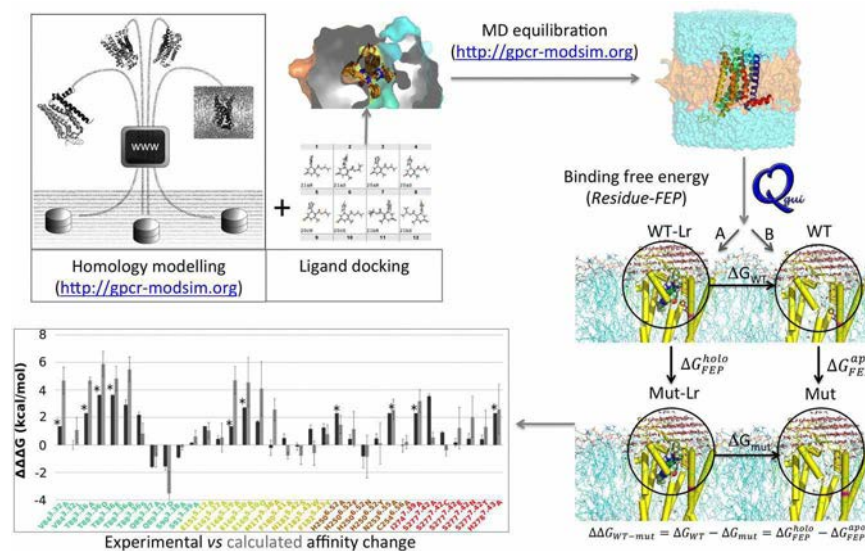
## Res-FEP: A tool for in silico site-directed mutagenesis in ligand-binding

Hugo Gutiérrez de Terán, Willem Jaspers, Silvana Vasile, Johan Åqvist.

Department of Cell and Molecular Biology, Uppsala University, Biomedical Center, Box 596, SE-751 24 Uppsala, Sweden. E-mail: hugo.gutierrez@icm.uu.se

Site-directed mutagenesis (SDM) is a powerful and widely used tool to characterize ligand-binding at the structural and molecular level. The characterization of ligand binding affinities against a set of mutant proteins, interpreted by computational modeling, is a process that has been used in the hit-to-lead optimization of many drug targets, with GPCRs being a paradigmatic example due to the traditional lack of structural information.

In this poster, I will outline our recently developed computational scheme, based on free energy perturbation (FEP) simulations, to quantitatively and routinely assess the effects of point-mutations on ligand binding as well as the structure-activity relationships (SAR) of congeneric series of ligands [1-2] (Fig 1). The procedure is based on an MD sampling of the protein-ligand binding site, using spherical boundary conditions centred on the binding site, which makes it computationally efficient. This method, which we call Res-FEP is now automated and will be soon released as part of the Q-gui graphical interface of our MD software Q. I will present recent results from three biological systems belonging to the GPCR superfamily of membrane receptors: agonist design for the type 2 (Y2) neuropeptide Y receptor; antagonist design on the A<sub>2A</sub> and A<sub>3</sub> adenosine receptors, and deorphanization of receptor GPR139 [3]. In some cases, we have complemented our simulations with classical FEP simulations on the ligands, providing a full picture of the energetics of ligand binding in the scope of SDM data or ligand-SAR from the literature or from collaborators. Indeed, all the three examples presented are framed into collaborative projects with medicinal chemists and pharmacologists, both from the academia or from the pharmaceutical industry.



## References

- [1] Keranen, H.; Åqvist, J.; Gutierrez-de-Teran, H. ChemComm (2015), 51:3522
- [2] Boukharta, L.; Gutierrez-de-Teran, H.; Åqvist, J. PLOS Comp. Biol (2014) 10:e1003585 and Xu, Vasile et al, Manuscript in preparation
- [3] Nøhr AC, Jaspers W, Shehata MA, et al. *Sci Rep.* (2017) 7:1128.



## Virtual-reality view on chemistry and materials science

**Rubén Jesús García-Hernández<sup>1</sup>, Claudia Draxl<sup>2,3</sup>, Matthias Scheffler<sup>3</sup>, Dieter Kranzlmüller<sup>1</sup>**

<sup>1</sup>*Leibniz Supercomputing Centre, Boltzmannstr 1, Garching by Munich, Germany*

<sup>2</sup>*Humboldt-Universität zu Berlin, Zum Großen Windkanal 6, 12489 Berlin*

<sup>3</sup>*Fritz-Haber-Institut Berlin, Faradayweg 4-6, 14195 Berlin*

We present a multi-platform tool that allows us to explore materials in Virtual Reality (VR) which has been developed within the Novel Materials Discovery (NOMAD) Laboratory, a European Centre of Excellence (<https://nomad-coe.eu>). The so far implemented functionality covers (Fig. 1) crystal structures, Fermi surfaces, molecular-dynamics trajectories, and electron-hole pairs (excitons). The latter are 6-dimensional objects where VR can show its potential to visualize effects that otherwise are hard to capture. We demonstrate the power of our implementation on the large variety of data from the *NOMAD Repository*, *Archive*, and *Encyclopedia* which host several millions of calculated materials properties. We will give a live demonstration of molecular adsorption on surfaces and excitons in an organic-inorganic hybrid material.

Our platform can be utilized to view various types of datasets commonly used in chemistry and materials science. The tools run on various state-of-the-art VR setups – from extremely low cost to extremely high cost, adjusting the rendering quality according to the equipment. Our goal is to offer the system that suits the users' budget and needs best. This may range from Google Cardboard (a few Euro) to smartphone-based Samsung GearVR (order 200 Euro) and PC-based HTC-Vive (order 1000 Euro) to room-sized CAVE-like<sup>i</sup> equipment (order Mio. of Euro).

The project received funding from the European Union's Horizon 2020 research and innovation program under grant agreement no. 676580 with The Novel Materials Discovery (NOMAD) Laboratory, a European Center of Excellence.

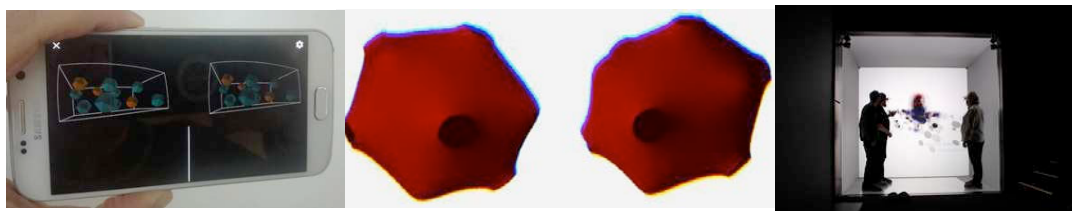


Fig. 1: Crystal structure of  $\text{Nb}_8\text{As}_4$  (as visualized in Cardboard glasses); Fermi surface of Ag in a Vive system, and adsorption of  $\text{CO}_2$  in CaO, as explored in a CAVE system.

<sup>i</sup> CAVE<sup>TM</sup> is a trademark of the University of Illinois Board of Trustees. We use the term CAVE to denote both the original system at Illinois and the variants developed by multiple organizations.

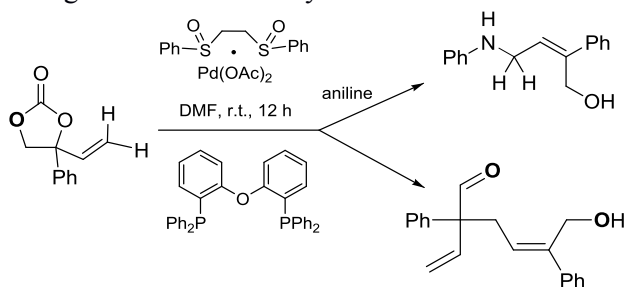
## Selective Transformation of Cyclic Vinyl Carbonates to Allylic Amines and Aldehydes - A DFT Study

Rositha Kuniyil,<sup>a</sup> Feliu Maseras,<sup>a,b</sup>

<sup>a</sup>*Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, Av. Països Catalans, 16, Tarragona (Spain)*

<sup>b</sup>*Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra (Spain)*

Cyclic vinyl carbonates are one of the most promising initial products from CO<sub>2</sub> activation. Several applications are being developed for the transformation of cyclic carbonates to various kinds of useful compounds. Allylic amines and allylic aldehydes represents a class of functional olefins which are of greater importance in organic chemistry. Even though significant progress has been observed in recent years for their synthesis, stereoselective synthesis of multi-substituted allylic amines and aldehydes remains a challenging target. Palladium catalyzed decarboxylative approaches from cyclic vinyl carbonates enables the construction of them which are characterized by excellent stereoselectivity, operational simplicity, mild reaction conditions, and wide scope in reaction partners (Scheme 1) [1]. DFT studies were performed to rationalize the stereocontrol in these reactions, and evidence is provided that the formation of a six-membered palladacyclic intermediate has a great role in controlling the stereoselectivity of reaction.



Scheme1. Conversion of cyclic vinyl carbonates to allylic amines and allylic aldehydes

[1] (a) W. Guo, L. Martínez-Rodríguez, R. Kuniyil, E. Martín, E. C. Escudero-Adán, F. Maseras, A. W. Kleij, *J. Am. Chem. Soc.* **138** 11970 (2016) (b) W. Guo, R. Kuniyil, J. E. Gomez, F. Maseras, A. W. Kleij (manuscript in preparation)



# AUTHOR INDEX



## Author Index

### A

Aav R.	PO3-131	Antol I.	<b>PO2-5</b>
Abbott A.	<b>PO3-123</b>	Antonietti M.	PO1-27
Abe M.	PO3-98	Antonio F.C.T.	PO1-107, <b>PO2-55</b> , C-094
Abramov P.	PO1-85	Antony J.	<b>PO3-210</b>
Abudoukadeer A.	<b>PO1-103</b>	Antušek A.	I-412
Acher E.	<b>PO3-188</b>	Aoki S.	PO1-247
Acke G.	<b>PO1-39</b>	Aoki Y.	PO1-141
Adamo C.	<b>I-202</b> , PO2-163	Aono C.M.	<b>PO1-100</b>
Agee M.M.	I-301, PO3-183	Apeloig Y.	<b>I-074</b>
Agostini F.	I-114	Apfel U.-P.	PO3-239
Aguilar-Galindo F.	<b>PO2-158</b>	Aquino A.J.A.	PO1-120
Aguilera-Porta N.	<b>PO1-99</b>	Åqvist J.	<b>I-362</b>
Aguzzi C.	PO2-155	Aradi B.	PO3-105
Ahlrichs R.	PO3-84	Aragó J.	PO1-53
Ahlstrand E.	C-023	Aragonès A.	C-062
Ahn-Furudate M.	PO3-193	Aranda Moratalla J.	<b>PO2-152</b>
Ajani H.	PO2-290	Aravena D.	<b>C-062</b>
Akiyama H.	PO1-135	Arbuznikov A.V.	PO2-51
Alabugin I.	<b>I-411</b>	Arismendi Arrieta D.J.	<b>PO1-102</b>
Alarco J.	C-105	Arnarson L.	IN-7
Alavi A.	<b>I-141</b> , PO3-202, PO3-230, PO3-295	Aroua S.	PO2-135
Alcamí M.	PO1-262	Arpa González E.M.	<b>PO1-185</b>
Aldongarov A.	<b>PO2-106</b>	Artiukhin D.	<b>PO1-170</b>
Alessandri R.	C-132, <b>PO3-167</b>	Arulmozhiraja S.	PO3-53
Alessio M.	<b>PO2-150</b>	Arvanitidis A.	<b>PO3-191</b>
Aliaga-Alcalde N.	C-062	Asahara H.	PO2-141
Alikhani E.	PO1-49	Ásgeirsson V.	<b>PO3-164</b> , PO2-265
Alimonti A.	PO1-132	Ashcroft N.W.	C-104
Alizadeh Sanati D.	<b>PO2-102</b>	Aspuru-Guzik A.	<b>I-241</b> , PO3-146, PO3-150
Alkorta I.	<b>I-064</b>	Assfeld X.	C-178, PO3-294
Allgäuer S. D.	PO2-141	Assilbekova A.	PO2-106
Almeida A.L.d.	C-014	Atanasov M.	PO3-213
Almora Díaz C.X.	<b>PO3-143</b>	Atlam F.	PO1-37, <b>PO1-38</b>
Alonso G.	PO1-50	Attia A.	PO1-34, PO2-107
Alonso M.	<b>C-061</b>	Aucar G.A.	<b>I-063</b> , PO3-21, PO3-284
Altun Z.	PO1-114, <b>PO1-71</b>	Aucar M.G.	<b>PO3-155</b>
Álvarez D.	PO2-12	Auth T.	<b>PO2-105</b>
Álvarez Barcia S.	<b>PO2-16</b>	Avanzini F.	<b>PO2-142</b>
Alvarez-Idaboy R.	<b>C-052</b>	Aviyente V.	PO3-247
Alves T.	<b>PO2-43</b>	Awad M.	<b>PO1-37</b> , PO1-38
Alves de Castro A.	<b>PO3-226</b>	Ayers P.	<b>I-305</b> , PO2-230
Amaral de Faria J.	PO3-226	Ayub R.	<b>PO2-90</b>
Amgoune A.	PO1-118, PO1-237	Ayyappan A.	<b>C-046</b>
Amine B.	PO2-226	Azarias C.	<b>PO1-263</b>
Amitay Z.	PO1-200	Aziz E.F.	C-103
Anas S.	PO2-76	Aziz S.	PO3-242
Anda A.	C-037	Azizi S.	<b>PO3-261</b>
Andrada D.	<b>PO2-148</b>	Azofra L.M.	<b>PO1-180</b>
Andrae D.	PO1-226		
Andrikopoulos P.C.	<b>PO1-22</b> , C-086, PO2-289	<b>B</b>	
Andris E.	C-086	Bacchus M.-C.	<b>PO1-42</b>
Andruniów T.	PO1-119	Bae H.	PO1-106
Andrushchenko V.	C-064	Baek H.	<b>PO2-195</b>
Andrzejak M.	<b>PO1-201</b>	Baer R.	<b>I-143</b> , PO1-12, PO1-219
Añez R.	PO1-147	Bagherpoor Helabad M.	C-057
Ang S.J.	<b>PO1-76</b>	Bahamón D.	PO1-50, PO3-299
Antalik A.	I-344, PO3-230	Bahlke M.P.	<b>PO2-219</b>
Antes I.	<b>PO3-120</b> , PO3-222, PO3-25, PO3-43	Bahmann H.	PO2-51
Antipov S.	PO3-110, <b>PO3-116</b>	Bai L.	C-056
		Bai S.	<b>PO1-212</b>

## Author Index

Baiardi A.	C-145, <b>PO3-107</b>	Berraud-Pache R.	C-137, <b>PO2-160</b>
Baik M.-H.	PO1-11	Berry J.	PO1-87
Bajaj A.	C-072	Berski S.	<b>PO1-131</b>
Bakó I.	<b>PO2-2</b> , PO2-268	Berta D.	<b>PO2-268</b>
Baldauf C.	<b>C-082</b>	Besley E.	PO3-46
Baldofski M.	<b>PO2-214</b>	Besley N.	PO3-46
Baldoni M.	PO3-46	Beton P.	PO3-46
Balta B.	PO2-73, <b>PO3-247</b>	Beuerle M.	<b>PO2-273</b>
Bande A.	<b>C-103</b>	Beyle F.	<b>PO3-221</b>
Bandeira N.A.G.	<b>PO3-292</b>	Beyle F.E.	PO3-252
Banerjee S.	I-174	Bhalodia P.	PO3-245
Bannwarth C.	PO2-72	Bhat H.	<b>PO1-2</b>
Baptista L.	PO1-147, PO2-61, PO3-80	Bhati A.P.	<b>PO1-36</b>
Baranek P.	PO2-94	Bhattacharyya D.	C-046
Barbatti M.	PO2-117, PO2-292, PO3-101	Bickelhaupt F.M.	<b>I-254</b> , PO1-84, PO2-78
Barca G.	<b>PO3-94</b>	Biczysko M.	<b>C-143</b>
Barcza G.	I-083, <b>PO3-178</b>	Bieberle-Hütter A.	PO1-6
Bargholz A.	<b>PO3-48</b>	Biele R.	PO2-239
Baric D.	<b>PO2-248</b>	Bielewicz T.	PO2-280
Barnard A.	PO2-192	Biermann S.	<b>I-373</b>
Barone V.	C-145, PO3-107	Bieske E.	C-176
Barquera-Lozada J.E.	<b>C-171</b>	Bilgin N.	PO3-247
Barrales-Martínez C.	<b>PO2-60</b>	Bilonda M.K.	PO1-285
Barroso J.	<b>PO1-296</b>	Bim D.	<b>PO1-306</b>
Bartlett R.	<b>I-341</b>	Binder R.	I-112
Barton D.	PO1-153	Bisha I.	<b>PO3-222</b>
Bassi A.	PO3-140	Bistoni G.	<b>PO1-234</b>
Batebi H.	<b>PO3-165</b>	Bjornsson R.	<b>C-023</b>
Battaglia S.	<b>PO1-226</b>	Blanco-Rey M.	C-088
Battistini F.	PO2-164	Blase X.	PO1-263
Bauer C.	<b>PO2-265</b>	Blaško M.	I-412
Bauer F.	<b>PO2-33</b>	Blatter S.P.	<b>PO3-284</b>
Bauer P.	PO1-43	Bleda E.A.	<b>PO1-114</b> , PO1-71
Bauerfeldt G.F.	<b>PO3-78</b> , PO3-79, PO3-80	Bleiziffer P.	<b>PO3-220</b>
Bayne M.	C-154	Bley M.	<b>PO2-88</b>
Baz J.	C-115	Bloino J.	C-143, C-145
Bazhenov A.S.	<b>PO3-142</b> , PO1-80	Blum V.	<b>I-374</b>
Bearpark M.J.	PO1-126	Blumberger J.	<b>I-025</b> , PO1-60, PO1-160
Beattie N.	<b>PO2-144</b>	Bo C.	PO3-292
Beaumont C.	PO1-239	Bochenkova A.	PO3-119
Beck A.K.	PO2-246	Bock L.V.	I-195
Beck M.E.	<b>IN-3</b>	Böckers M.	PO1-153
Becke A.	<b>I-302</b> , PO3-266	Bocola M.	<b>PO3-23</b>
Becker M.	<b>PO2-30</b>	Bodenstein T.	PO2-169, <b>PO3-5</b>
Begic I.	C-078	Boereboom J.	<b>PO3-236</b>
Begusic T.	<b>PO3-134</b>	Boese A.D.	<b>PO2-97</b>
Belinassi A.R.	PO2-43	Bofill J.M.	C-047, PO1-218
Bellili A.	<b>PO3-100</b>	Bogdanov N.	<b>PO3-202</b> , PO3-295
Bellinger D.	<b>PO2-36</b> , PO3-162	Boggio-Pasqua M.	<b>C-165</b> , PO2-45
Belpassi L.	<b>C-174</b>	Boguslawski K.	PO1-133
Ben Amor N.	C-038	Bohle F.	<b>PO3-176</b>
Benda Z.	<b>PO2-224</b>	Bois J.	<b>PO1-220</b>
Benediktsson B.	C-158	Boisson J.-C.	I-314, PO3-113, PO3-135
Ben-Shalom I.	I-285	Bokarev S.	<b>PO3-233</b> , PO3-242
Beran G.	<b>I-375</b> , PO1-93	Bold B.	<b>PO3-252</b>
Bereau T.	<b>C-022</b> , PO2-206	Bollini M.	PO3-155
Berger D.	I-355	Bols M.	PO1-68
Berger R.	<b>I-162</b> , PO1-157, PO1-301, PO1-97	Bolvin H.	<b>C-084</b>
Bernardi M.	<b>I-024</b>	Borge J.	C-101
Bernasconi L.	PO1-155	Borges-Martinez M.	<b>PO3-72</b>

## Author Index

Borgis D.	C-036	Buyadzhi V.	<b>PO3-255</b>
Borisov A.	PO2-158	Byon H.-R.	PO1-11
Borovik A.S.	I-045		
Borrego-Sánchez A.	<b>PO2-155</b>	<b>C</b>	
Borrego-Varillas R.	PO3-128	Cabellos J.L.	PO1-66
Borschevsky A.	PO3-257	Caffarel M.	C-073
Bortoli M.	<b>PO2-78</b>	Cafiero M.	PO1-57, PO1-58, PO1-59, PO1-63, PO1-65
Bottoni A.	PO2-120	Calatayud M.	PO1-188
Bouaouli S.	<b>PO3-254</b>	Calbo J.	<b>PO1-53</b>
Boulanger E.	<b>PO3-17</b>	Caldeweyher E.	<b>PO2-137</b>
Bouledroua M.	PO1-4	Calhorda M.J.	PO3-169
Bourissou D.	PO1-118, PO1-237	Call A.	PO1-142
Bouteloup R.	<b>PO2-250</b>	Calvaresi M.	PO2-120
Bowman J.	<b>I-161</b>	Calvelo Souto M.	<b>PO3-38</b>
Boyd R.	<b>I-315</b>	Calvo F.	PO3-296
Boyle P.D.	PO1-196	Campetella M.	PO3-228
Boz E.	<b>PO2-118</b>	Canola S.	I-262, <b>PO2-124</b>
Brabec J.	I-344, <b>PO3-136</b> , PO3-225	Cantatore V.	<b>PO3-96</b>
Braeuer A.	PO2-131	Canuto S.	PO1-109, PO2-305
Braïda B.	PO1-39	Cao X.	PO3-64
Brakestad A.M.	I-152	Cao Z.	C-156, <b>I-181</b>
Brandão I.	PO3-234	Cappelli C.	<b>I-321</b> , PO3-208
Brandbyge M.	PO2-274	Caprasecca S.	PO2-80, PO3-228
Brandejs H.	I-083	Carazo E.	PO2-155
Brandenburg G.	<b>PO1-13</b>	Cárdenas Morales D.J.	PO1-185
Branzanic A.	<b>PO1-229</b>	Cardenas-Jiron G.	<b>PO2-194</b> , PO3-72
Brauer C.-A.	PO1-202	Cardoso C.	PO3-80
Bredas J.-L.	<b>I-023</b>	Carneiro J.W.d.M.	PO1-84, PO1-206
Breher F.	PO3-34	Carniato S.	PO2-35
Brehm M.	<b>PO2-11</b>	Carof A.	PO1-160, <b>PO1-60</b>
Bremer M.	<b>IN-9</b>	Carsky P.	<b>I-095</b>
Brenner V.	<b>C-038</b>	Casademont Reig I.	<b>PO1-142</b>
Brickel S.	<b>PO1-184</b>	Casadevall C.	PO1-142
Brinck T.	<b>I-053</b>	Casado J.	PO2-76
Brinkmeier A.	PO2-256	Casanova D.	PO1-136, PO1-190
Brites G.	PO3-80	Casasnovas R.	<b>PO3-145</b>
Brkljača Z.	PO3-256	Cassam-Chenaï P.	<b>PO2-20</b>
Broer R.	C-132, PO1-24	Cassera M.	PO3-274
Brothers E.	C-112, PO3-200	Castro A.C.	<b>PO2-229</b>
Brown J.	<b>PO1-300</b>	Castro M.A.	PO3-234
Browne W.R.	I-045	Castro R.	PO3-78
Browning N.J.	PO2-277	Castro Ramalho T.	PO3-67
Brüggemann J.	PO1-258	Catak S.	PO2-296, PO3-81
Bruno Goncalves P.F.	PO2-117	Caux J.-S.	PO2-230
Brzęk F.	<b>PO1-133</b>	Cavalli A.	PO1-132
Buehl M.	<b>I-062</b>	Cavallo L.	PO1-180
Bulo R.	PO3-236	Cavasotto C.N.	PO3-155
Bultinck P.	PO1-39, PO1-86	Ceccato A.	<b>PO2-130</b>
Buma W.J.	PO2-77	Cederbaum L.S.	<b>I-164</b>
Bumüller D.	PO3-84	Cederquist H.	PO3-103
Bunge C.F.	PO3-143	Celestino A.	PO2-269
Bunting P.	PO3-213	Cembran A.	PO2-283
Burghardt I.	<b>I-112</b> , PO3-264	Ceriotti M.	<b>I-242</b>
Burke K.	<b>I-203</b>	Cerón-Carrasco J.P.	<b>C-114</b>
Burow A.M.	C-013, PO2-153	Cerqueira N.M.F.S.A.	PO1-239
Burrows A.	PO1-167	Cerullo G.	PO3-128
Bursch M.	<b>PO1-186</b>	Cervinka C.	<b>PO1-93</b>
Burton H.	<b>PO3-76</b>	Ceulemans A.	PO3-215
Buš V.	PO3-60	Cezar H.	<b>PO1-109</b>
Busch M.	I-252	Chadwick F.M.	PO3-52

## Author Index

Chakrabarty S.	PO1-179	Comba P.	PO2-212, PO2-298, PO2-304, PO3-15, PO3-207
Chakraborty A.	<b>C-154</b>	Goncalves T.P.	<b>PO3-301</b>
Chalasinski G.	PO3-281	Condic-Jurkic K.	<b>PO2-197</b>
Champagne B.	<b>I-403</b> , PO1-298, PO2-191	Conic D.	<b>PO1-303</b>
Champion J.	PO1-288	Conti I.	PO3-128
Chan B.	I-073, PO1-246, <b>PO1-91</b>	Contini A.	<b>C-054</b> , PO1-264
Chan C.H.	<b>PO3-102</b>	Contreras-García J.	<b>I-314</b> , PO3-113
Chan G.	<b>I-012</b>	Cooper A.	<b>PO1-253</b>
Chang H.	PO1-112	Coote M.	<b>I-055</b>
Chang M.-W.	PO1-182	Copéret C.	I-061, PO3-115
Changotra A.	<b>PO1-72</b>	Corentin L.	I-314
Chaumont A.	<b>PO3-279</b>	Coriani S.	<b>I-404</b>
Chavarot-Kerlidou M.	PO2-42	Corminboeuf C.	<b>I-252</b> , PO2-159, PO2-46
Chedid J.	C-074	Cornard J.P.	PO3-192
Cheeseman J.R.	PO3-208	Corni S.	C-135, PO1-260
Chen G.	<b>I-214</b> , <b>PO3-183</b>	Corno M.	<b>PO2-171</b>
Chen G.P.	I-301	Corral I.	PO1-239, PO1-99
Chen J.	PO1-132	Corral Pérez I.	PO1-185
Chen L.	<b>PO3-249</b>	Correa J.D.	C-066
Chen P.	<b>PO3-240</b>	Correia A.N.	PO1-127
Chen Q.	PO2-141	Cortés-Arriagada D.	PO1-146, PO2-60
Chen W.-C.	<b>PO1-254</b>	Cortese R.	<b>PO1-14</b>
Cheng Y.C.	PO1-166	Cossi M.	PO2-171
Chermette H.	<b>PO1-81</b>	Cossío F.P.	PO2-58, PO3-203
Chiş V.	PO2-98	Costa França T.C.	PO3-67
Chibotaru L.F.	PO1-252	Coto P.B.	<b>PO2-4</b> , PO2-50
Chilton N.F.	PO3-219	Coughtrie D.	<b>PO1-284</b>
Chitpakdee C.	<b>PO2-223</b>	Coutinho K.	PO1-109
Chiu C.-C.	<b>PO1-35</b>	Coveney P.V.	PO1-36
Chołuj M.	<b>PO2-203</b>	Cowley R.E.	PO1-22
Choi H.	<b>PO1-106</b>	Cozar I.B.	PO2-98
Choi S.	PO2-182, PO2-228, PO2-70	Crawford T.D.	<b>I-402</b> , PO2-156, PO3-175, PO3-273, PO3-274, PO3-51
Chou C.-P.	PO1-233, PO1-305, <b>PO2-68</b>	Crespo-Otero R.	PO2-119, PO2-161
Christian M.	<b>PO2-176</b>	Crestoni M.E.	PO3-37
Christiansen O.	<b>I-345</b> , PO2-209, PO2-210, PO2-236, PO2-79, PO3-198	Cristina de Assis L.	PO3-226
Chug O.L.W.	<b>C-067</b>	Cristofol-Clough M.	PO3-114
Chunchen L.	PO1-190	Crnković L.	PO2-5
Chung L.W.	PO1-110	Croce R.	PO2-225
Ciarlariello N.	PO2-124	Crovetto A.	PO2-274
Cid Mora F.A.	<b>PO3-271</b>	Csaszar A.	<b>I-413</b>
Çifci G.	PO3-247	Cui Q.	<b>I-363</b>
Cilpa-Karhu G.	<b>PO2-204</b>	Cukrowski I.	<b>C-177</b> , PO2-108
Ciofini I.	<b>I-123</b>	Cunha A.	<b>PO3-118</b>
Cirera J.	C-108	Cupellini L.	PO3-174, <b>PO3-228</b>
Civalleri B.	PO2-94	Curchod B.F.E.	<b>C-096</b>
Claeys P.	PO2-230	Curutchet A.	C-095
Clark T.	<b>I-182</b>	Custer T.	PO3-95
Clary D.	<b>I-111</b>	Cytter Y.	<b>PO1-219</b>
Clavaguera C.	<b>PO1-259</b>	Czapla M.	<b>PO1-25</b>
Clavaguéra C.	PO2-278		
Coccia E.	<b>C-135</b>		
Cochrane B.	PO1-240	<b>D</b>	
Coelho M.	PO1-124	Da Silveira E.F.	PO1-147
Coitiño Izaguirre E.L.	<b>I-282</b>	Dabjartsdóttir F.B.	PO3-164
Colebatch A.	PO2-144	Dai Y.	PO2-124, PO3-274
Coles J.	<b>PO3-211</b>	Dalal S.	PO3-274
Colombi Ciacchi L.	PO3-36	Dale S.	<b>PO3-266</b>
Comas-Vives A.	PO3-115	D'Amore L.	<b>PO2-256</b>
		Dang T.T.M.	<b>PO1-244</b>



## Author Index

Dang Y.	PO2-188	Dognon J.-P.	<b>PO1-113</b>
D'Angelo G.	<b>PO3-103</b>	Dohm S.	<b>PO3-231</b>
Daniel C.	<b>I-153</b> , PO2-109	Dokainish H.	<b>PO1-249</b>
Dans P.D.	PO2-164	Dolbundalchok P.	C-103
Darre L.	PO2-164	Dolg M.	PO3-64
Daru J.	<b>C-116</b> , PO3-11	Dolgonos G.A.	PO2-97
Das S.	<b>PO2-167</b>	Domcke W.	PO1-30, PO2-101, PO2-175
Davari M.D.	PO3-23	Domingues Coutinho-Neto M.	PO2-149
David G.	C-102, <b>PO2-262</b>	Dominguez A.	PO3-105
Dawid A.	<b>PO2-247</b>	Domínguez M.M.	PO1-306
Daza M.	C-053	Dommett M.	<b>PO2-119</b> , PO2-161
De Azevedo Santos L.	<b>PO2-179</b> , PO2-180	Domratcheva T.	PO1-149
De Baerdemacker S.	PO1-39, <b>PO2-230</b>	Dong Y.	PO2-13
De Brito Sá É.	PO3-35	Dononelli W.	<b>PO3-88</b>
De Bruin T.	<b>PO1-250</b>	Dopieralski P.	<b>C-055</b> , PO2-258
De Castro Ramalho T.	PO2-179, PO3-226	Doran A.E.	I-381
De Costa S.	PO2-197	Dornbach M.	<b>PO3-205</b>
De Cózar A.	PO3-203	Doublet M.-L.	PO1-287
De Lange J.H.	C-177, PO2-108	Dragelj J.	<b>PO2-40</b>
De Lara-Castells M.P.	C-051	Dragičević I.	PO2-248
De Lima-Neto P.	PO1-127	Dral P.O.	<b>PO3-62</b> , PO2-85
De Mesmaeker A.	PO2-296, PO3-81	Draxl C.	<b>I-232</b>
De Oliveira Silva D.	PO2-49	Dresselhaus T.	PO1-153
De Vico L.	<b>C-037</b>	Dreuw A.	<b>I-333</b> , PO1-292, PO2-140, PO2-162, PO3-196, PO3-29
De Vivie-Riedle R.	PO1-279, PO2-121, PO2-125, PO2-127, PO2-157, PO2-201	Driant T.	<b>PO1-43</b> , PO2-128
De Vries A.H.	PO3-167	Du Y.	PO3-274
DeBeer S.	PO1-46	Dube H.	PO2-157
Dedecek J.	C-147	Duboué-Dijon E.	<b>PO1-62</b>
Deeth R.J.	PO3-180	Dubrovskaya Y.	PO3-255
Deffner M.	<b>PO2-251</b>	Duca D.	PO1-14
Deglmann P.	<b>IN-1</b>	Duchemin I.	PO1-263
Dehnen S.	PO3-50	Dufrêche J.-F.	PO2-88
Delgado-Alonso C.	PO3-250, PO3-268	Dumon A.S.	<b>PO2-133</b>
Dellago C.	<b>I-103</b>	Dumont E.	PO3-102
Delle Piane M.	<b>PO3-36</b>	Dums J.	<b>PO2-136</b>
Delor M.	PO3-216	Duran M.	C-162
Demel O.	I-344, I-371, <b>PO3-225</b>	Durán R.	PO1-146, <b>PO1-178</b>
Denzel A.	<b>PO1-261</b>	Durbeej B.	<b>C-035</b>
Derat E.	PO1-43, <b>PO2-128</b>	Dutta A.K.	<b>PO2-170</b>
Desch S.	PO1-299	Dutta Banik S.	<b>PO3-111</b>
Deumal M.	<b>C-101</b>	Dutton J.	C-176
Deustua J.E.	I-395	Duvail M.	PO2-88
Dhoke G.V.	PO3-23	Dvorak M.	<b>PO2-147</b>
Di Luca A.	<b>PO3-121</b>	Dyduch K.	PO1-217
Di Remigio R.	C-127, C-128	Dziedzic J.	PO3-273
Diamantis P.	<b>PO1-199</b>		
Diaz N.	<b>PO1-32</b>	<b>E</b>	
Díaz L.	<b>PO1-147</b> , <b>PO2-307</b>	East A.	<b>C-117</b>
Díaz-Tendero S.	PO2-158	Easton C.	I-073
Diefenbach M.	PO2-105, PO2-241	Ebata T.	PO1-29
Diestler D.J.	PO1-164	Eckhardt A.K.	<b>PO1-145</b>
Dietl N.	PL-4	Eckl T.	<b>IN-10</b>
Dietschreit J.	<b>PO3-26</b>	Eda M.	PO1-140
Dietzek B.	PO2-42	Edwards B.	PO3-219
Díez-Pérez I.	C-062	Egidi F.	<b>C-145</b> , PO3-208
Dimitrova M.	<b>PO3-190</b>	Ehara M.	PO1-29
Dina N.E.	PO2-98	Ehrmaier J.	<b>PO1-138</b>
Dmitriev A.	<b>PO1-85</b>	Eisenstein O.	<b>I-061</b>
Dobi Z.	PO2-116	Eisert J.	I-083



## Author Index

El Bakouri O.	PO2-76, PO2-90	Ferrari A.	PO1-132
Eliav E.	<b>PO3-168</b>	Ferraro Gómez F.	<b>PO3-39</b>
Elleuchi S.	PO3-169	Ferré N.	C-102, PO2-262
Elm J.	PO2-300	Ferreira de Moraes L.H.	<b>PO2-49</b>
Elsen H.	<b>PO1-77</b>	Feskov S.	<b>PO3-56</b>
Elstner M.	<b>I-281</b> , PO1-203, PO3-105, PO3-221, PO3-252	Feyrer A.	PO3-34
Embry C.	PO1-65	Fingerhut B.	I-121
Eng J.	I-153	Fink K.	<b>PO2-169</b> , PO3-34
Engels B.	PO3-162, PO3-199	Fink R.	PO2-124, <b>PO3-147</b>
Ensing B.	PO3-7	Finkelmann A.	PO1-205
Epifanovsky E.	PO1-297, <b>PO3-248</b>	Finzel K.	<b>PO1-86</b>
Ercan S.	PO3-247	Fiorot R.	<b>PO1-206</b>
Erdmannsdörfer J.	PO3-162	Fischer J.M.	<b>PO2-200</b>
Eriksen J.J.	<b>PO2-297</b>	Fischer R.A.	PO1-51
Erlebach A.	<b>PO1-210</b>	Fischermeier D.	PO2-136
Ernst W.E.	PO1-158	Flambaum V.	PO3-257
Ernzerhof M.	<b>I-275</b>	Fletcher G.	<b>C-124</b>
Escamilla-Roa E.	PO2-26	Fleurat-Lessard P.	PO3-236
Escudero D.	<b>PO1-176</b>	Fliegl H.	<b>PO2-222</b> , PO3-190
Eshuis H.	<b>C-074</b>	Florindo C.	<b>PO3-140</b>
Espinal J.F.	<b>C-066</b>	Flöser B.	<b>PO1-82</b>
Espinosa E.	I-064	Földes T.	<b>PO2-116</b>
Espinosa de Oliveira T.	<b>PO1-274</b>	Folkestad S.D.	<b>PO3-265</b>
Esser B.	PO3-176	Föller J.	I-122
Estep M.	<b>PO3-71</b> , PO3-77	Fonseca T.L.	PO3-234
Esteves da Silva J.C.G.	PO1-242	Fontecave M.	PO2-135
Estevez L.	PO1-118	Fontes Ferreira da Cunha E.	PO2-179, PO3-226
Etienne M.	PO2-53	Foppa L.	<b>PO3-115</b>
Etienne T.	<b>C-168</b> , PO1-287, PO3-294	Formoso E.	<b>PO1-111</b>
Etinski M.	<b>PO3-7</b>	Förster M.	<b>PO2-134</b>
Eulenstein A.	PO3-50	Fouroutan-Nejad C.	C-064
Evangelista F.	<b>PL-9</b>	Fox T.	<b>IN-5</b>
Evangelisti S.	PO1-226	Franck O.	<b>PO3-69</b>
Evans R.	<b>PO1-63</b>	Franco L.R.	PO3-234
Eveleens C.	<b>PO1-129</b>	Frank I.	<b>PO1-144</b>
Eyrilmez S.M.	<b>PO3-277</b>	Frank M.	<b>PO3-189</b>
<b>F</b>		Franke R.	PO1-174
Fabian M.D.	<b>PO1-12</b>	Franzoni I.	C-068
Faginas-Lago N.	PO1-226	Frau J.	PO3-145
Falahati K.	PO3-264	Frauenheim T.	PO3-105
Falsig H.	<b>IN-7</b>	Frediani L.	<b>C-127</b> , C-128, PO3-276
Faltermeier D.	<b>PO2-304</b>	Fregoni J.	<b>PO1-260</b>
Fan C.	<b>PO1-172</b>	Freitag L.	<b>PO2-269</b>
Fanfrlík J.	<b>PO2-87</b> , PO2-290, PO3-277	Frenking G.	<b>I-312</b> , PO1-47, PO1-51, PO2-148
Fantuzzi F.	PO3-129, <b>PO3-61</b>	Freund M.S.	C-011
Faraji S.	<b>C-031</b>	Frezzato D.	PO2-130
Fasshauer E.	<b>PO3-184</b>	Friedman R.	<b>C-158</b>
Fässler T.F.	PO2-136	Friese D.H.	<b>PO3-181</b>
Feixas F.	<b>C-111</b> , PO2-76	Fujie T.	PO2-226
Feldt J.	<b>PO1-243</b>	Fujinami M.	<b>PO1-280</b>
Feldt M.	<b>PO2-245</b>	Fujioka A.	PO2-23
Fennimore M.	I-334	Fujita T.	<b>C-093</b>
Fensterbank L.	PO2-128	Fujiyoshi J.	PO1-298
Ferch L.S.	C-011	Fukushima T.	PO1-269
Ferenc D.	<b>PO1-15</b> , PO2-268	Fukuzawa K.	<b>PO3-86</b> , PO3-87
Ferenczy G.G.	PO2-82	Fumagalli V.	C-054
Fernandes P.A.	<b>I-351</b> , PO1-116	Fumanal M.	I-153, PO2-109
Fernandez I.	<b>PO1-31</b>	Furche F.	<b>I-301</b> , PO3-149, PO3-183
Ferrara N.	C-074	Fuse M.	C-145

## Author Index

### G

Gagliardi L.	<b>I-225</b>	Gill P.M.W.	<b>I-011</b> , PO1-294, PO1-297
Gajsek O.	PO2-301	Gillet N.	<b>PO1-203</b>
Galano A.	C-052, <b>I-414</b> , PO1-101	Gil-Mestres A.	<b>PO3-169</b>
Galembeck S.E.	PO2-77	Gilmour J.	<b>PO2-63</b>
Galland N.	PO1-288, PO2-28	Giménez X.	<b>PO3-299</b> , PO1-50
Gallandi L.	<b>PO2-14</b>	Gimferrer M.	C-111
Gallego J.	C-066	Gindensperger E.	I-153
Galli G.	<b>PL-6</b>	Ginsbach J.	PO1-22
Galván I.F.	I-152	Giovannini T.	<b>PO3-208</b>
Gamallo P.	PO1-50, PO3-299	Giraldo Nohra F.	<b>PO1-256</b>
Gamarnik A.V.	PO3-155	Giribet C.	PO3-21
Gámez V.	<b>PO1-101</b>	Giussani A.	<b>PO2-287</b>
Gamiz-Hernandez A.P.	<b>PO2-103</b> , PO1-137	Glaser M.	PO3-120
Ganesh Balasubramani S.	I-301	Glasovac Z.	PO2-5
Gani T.Z.H.	C-072	Glebko N.	<b>PO2-99</b>
Ganzer L.	PO3-128	Glenn R.	<b>PO3-175</b>
Gao J.	<b>I-192</b>	Gloaguen E.	C-038
Gao M.	C-085, <b>PO2-291</b>	Glover W.	<b>C-097</b>
Gao Y.	<b>I-352</b>	Glushkov A.	<b>PO3-251</b> , PO3-255, PO3-258, PO3-259
Garavelli M.	PO3-128, PO3-174	Godtliessen I.H.	PO3-198
García S.P.	PO1-218	Goerigk L.	<b>C-152</b> , PO1-295
Garcia Meseguer R.	<b>PO3-160</b>	Goetz M.	PO3-274
Garcia-Borràs M.	C-111	Gogan O.M.	PO1-8
Garcia-Hernandez R.J.	<b>PO3-308</b>	Gohlke H.	<b>I-285</b>
Garcia-Iriepa C.	C-137	Golding B.T.	PO2-248
Garcia-Rodeja Y.	PO1-31	Goldmann D.	PO1-205
Garniron Y.	C-073	Göller A.H.	<b>PO1-205</b> , PO2-54
Garofalo M.	PO1-132	Golze D.	<b>PO2-286</b>
Gaston N.	PO2-64	Gómez H.	<b>PO2-164</b> , PO2-152
Gatchell M.	PO3-103	Gomez Pech C.	<b>PO2-28</b>
Gattuso H.	<b>C-178</b> , PO2-109	Gomez Rodriguez S.	<b>PO2-240</b>
Gaul K.	<b>PO1-97</b>	Gonthier J.F.	<b>PO3-137</b>
Gauld J.W.	PO3-194	González L.	<b>I-151</b> , PO2-45, PO2-109, PO2-113, PO2-140, PO2-240, PO2-301
Gauss J.	<b>I-013</b> , PO2-297	Gonzalez Campos A.	C-062
Gebhard L.G.	PO3-155	Gonzalez Herrero L.	PO2-95
Geerke D.	<b>PO2-123</b>	Gopalakrishna T.Y.	PO1-190
Geerke D.P.	PO2-303	Góra R.W.	<b>C-136</b> , PO2-146, PO3-224
Geiß A.	PO3-199	Gordon M.	<b>I-145</b>
Geng C.	PL-4	Görling A.	<b>I-304</b>
Georg H.	<b>PO3-234</b>	Gorritz R.	C-057
Gerber R.B.	<b>I-163</b> , PO1-221, PO1-302, PO3-159	Goto H.	PO2-17
Gerbig D.	PO1-145, <b>PO1-299</b>	Götte L.	<b>PO1-174</b>
Geronimo I.	<b>PO1-235</b>	Gourlaouen C.	<b>PO3-272</b>
Ghafarian Shirazi R.	<b>PO1-286</b>	Govind N.	PO3-136
Ghane T.	C-057	Grabarek D.	<b>PO1-119</b>
Gherman A.M.R.	<b>PO2-98</b>	Grad J.-N.	<b>PO3-49</b>
Ghorai S.	<b>PO1-278</b>	Gräfe S.	PO2-42
Ghose K.K.	<b>PO1-293</b>	Graham C.M.E.	PO1-196
Ghosh D.	<b>C-033</b>	Grande Aztatzi R.	<b>PO1-282</b>
Ghuman K.	<b>PO1-194</b>	Granucci G.	PO1-260, PO1-99
Giacomozzi L.	PO3-103	Grazioso G.	PO1-132
Giampapa R.	PO1-59	Grebenshchikov S.Y.	PO2-175
Giannini S.	<b>PO1-160</b>	Green M.	PO2-57
Gianotti E.	PO2-171	Gregory K.	C-024, <b>PO2-69</b>
Gierada M.	<b>PO1-216</b>	Gregson M.	PO2-197
Giereth R.	PO1-284	Grell G.	<b>PO3-260</b>
Giesen S.M.	<b>PO1-301</b>	Grimme S.	<b>I-132</b> , PO1-186, PO2-265, PO2-54, P O2-72, PO3-176, PO3-231
Gilbert A.	<b>PO2-196</b>	Gritsan N.	PO1-21, PO1-85
Gilbert A.T.B.	PO1-297		

## Author Index

Groenhof G.	PO1-115	Hansen M.B.	<b>PO2-236</b>
Groll M.	PO2-131	Hansen N.	<b>C-115</b>
Gronowski M.	<b>PO3-95</b>	Hansen O.	PO2-274
Gross E.K.U.	I-114, <b>I-034</b> , PO3-291	Hansen T.	C-037
Grotjahn R.	<b>PO2-41</b>	Hansmann A.-K.	<b>PO1-157</b>
Grubmüller H.	<b>I-195</b>	Hanulikova B.	<b>PO1-281</b>
Grübner I.	PO2-105	Hanževački M.	<b>PO1-257</b>
Gruden M.	PO2-217	Hao Y.	PO3-257
Grundeir M.	<b>PO2-153</b>	Hapka M.	PO3-281
Grüneis A.	PO1-163	Harabuchi Y.	C-042, PO1-29
Gryn'ova G.	I-055	Harding M.	<b>PO3-267</b>
Gsänger S.	<b>PO1-18</b>	Harish H.	<b>PO2-141</b>
Guarnetti Prandi I.	<b>PO3-67</b>	Harris A.	<b>PO2-57</b>
Gückel S.	C-151	Harrison E.	<b>PO1-56</b>
Guggolz L.	<b>PO3-50</b>	Harting J.	I-355
Gui X.	<b>PO3-45</b>	Hartke B.	PO2-221, PO2-38
Guido C.A.	<b>PO3-127</b> , PO3-228	Harvey J.N.	<b>I-071</b> , PO2-245, PO3-17, PO3-19
Guihéry N.	<b>C-102</b> , PO2-262	Hase W.L.	<b>I-255</b> , PO3-37
Guilbaud P.	PO2-88	Hashmi M.A.	<b>PO1-304</b>
Guillaumont D.	PO3-188	Hatanaka M.	<b>PO3-90</b>
Gül Ş.	PO3-247	Hättig C.	PO1-198, PO2-213, PO3-109, PO3-189
Gunnarsson O.	PO3-202	Hauser A.W.	<b>C-051</b> , PO1-158, PO3-297
Gunst T.	PO2-274	Havenith R.W.A.	<b>C-132</b> , PO1-24, PO3-167
Guo N.	PO1-288	Hayami M.	PO1-268
Guo Y.	<b>PO1-23</b> , PO3-252	Hayamizu K.	PO3-53
Gupta A.K.	<b>PO1-168</b>	Head-Gordon M.	<b>I-015</b> , PO3-137, PO3-269, PO3-290
Gupta P.K.	C-116, <b>PO3-11</b>	Head-Gordon T.	<b>I-191</b>
Gupta T.	<b>PO2-298</b>	Hecht S.	C-082
Guthmuller J.	<b>PO1-265</b> , PO2-154, PO2-285	Hegely B.	C-123
Gutierrez O.	<b>PO3-89</b>	Hegemann P.	PO3-252
Gutierrez de Teran H.	<b>PO3-307</b>	Hehn A.-S.	<b>PO3-84</b>
Gutiérrez-Flores J.	<b>PO2-65</b>	Heidar-Zadeh F.	I-305
Gutiérrez-Oliva S.	PO1-146, PO2-60, PO3-182, PO3-271	Heilos A.	<b>PO3-199</b>
Gutten O.	<b>PO2-232</b>	Heimermann A.	PO2-169
Guzmán-Angel D.	<b>PO3-182</b>	Heindl M.	PO2-95
Gwee E.	<b>PO1-248</b>	Heine T.	PO1-104
<b>H</b>		Heinz N.	<b>PO3-64</b>
Haasler M.	PO2-51	Heiska J.	C-017
Hada M.	PO3-98	Hekal H.	PO1-37
Hadad C.	C-053	Helgaker T.	<b>PL-3</b>
Hagebaum-Reignier D.	<b>PO3-193</b>	Helmich-Paris B.	<b>PO3-74</b>
Hahn D.F.	<b>PO3-40</b>	Henchman R.	<b>I-361</b>
Hahn R.	PO3-176	Hénin J.	PO2-211
Haines B.	C-025	Hénon E.	I-314, <b>PO3-113</b> , PO3-135
Häkkinen H.	PO1-80	Henry D.	<b>C-167</b>
Haldar S.	PO2-290	Henschel H.	<b>PO1-173</b>
Hall M.	C-112, PO3-200	Heras-Domingo J.	<b>PO3-18</b>
Hallaert S.	<b>PO1-68</b>	Herbert J.	<b>I-335</b>
Hamann J.	PO2-212	Hermann G.	PO1-164, <b>PO3-99</b>
Hamerton I.	PO1-33	Hermann M.	PO1-47
Hammerschmidt L.	<b>PO2-64</b>	Hermansson K.	C-023
Hammes-Schiffer S.	<b>I-033</b>	Hermesen M.	<b>PO2-212</b>
Hammoutène D.	<b>PO3-85</b>	Hernandes Barrozo A.	<b>PO2-166</b>
Hamza A.	<b>PO2-32</b>	Hernández-Haro N.	C-148
Han N.	<b>PO3-195</b>	Hernández-Laguna A.	<b>C-148</b>
Handzlik J.	PO1-216	Hernández-Lemus E.	PO2-65
Hanni M.	PO1-173	Hernando J.	PO1-139
Hansen E.	C-025	Herrera B.	PO1-178
		Herrmann C.	<b>C-092</b> , PO1-266, PO2-237, PO2-251, PO2-280

## Author Index

Herrmann N.	PO3-64	Hühn C.	<b>PO2-27</b>
Heuer M.A.	<b>PO1-117</b>	Huix-Rotllant M.	<b>PO3-264</b>
Heuser J.	C-128, <b>PO2-86</b>	Hummel F.	PO1-163
Heyda J.	PO3-44	Hummer G.	<b>I-365</b>
Heyden M.	<b>I-283</b>	Hünenberger P.H.	PO3-40
Hidalgo Cardenuto M.	<b>PO2-305</b>	Husch T.	<b>PO2-246</b>
Hieringer W.	<b>C-015</b>	Huwig K.	PO1-172, <b>PO2-13</b>
Higham J.	I-361	Huynh H.M.	<b>PO3-9</b>
Hilal R.	PO3-101	Hwang S.-Y.	PO2-182, PO2-228, <b>PO3-24</b>
Hildebrand N.	PO3-36	Hynes J.T.	PO3-160
Hinkley J.	PO1-293		
Hiraga K.	PO1-268	<b>I</b>	
Hirata S.	<b>I-381</b>	Iannuzzi M.	PO3-115
Hirshberg B.	<b>PO3-159</b>	Iffland L.	PO3-239
Hitzenberger M.	<b>PO2-264</b>	Ikabata Y.	<b>PO1-268</b> , PO1-269
Hiyama M.	PO1-135	Imamura Y.	PO3-54
Hnyk D.	PO3-277	Imberti S.	PO1-155
Ho E.	<b>PO1-287</b>	Imhof P.	<b>C-057</b> , PO3-165, PO3-91
Hobza P.	<b>PL-7</b> , PO2-290, PO3-277	Ingolfsson H.I.	PO3-6
Hochlaf M.	PO3-100	Ingr M.	<b>PO3-60</b>
Hodecker M.	<b>PO2-162</b>	Irgibaeva I.	PO2-106
Höfener S.	<b>C-128</b> , PO2-86	Irlé S.	PO1-129, PO1-152
Hoffmann D.	PO3-49	Iron M.	<b>C-161</b>
Hoffmann F.	<b>PO2-151</b>	Ishida T.	<b>C-107</b>
Hoffmann K.	PO1-164	Ishii T.	PO2-23
Hoffmann R.	C-104	Ishimura K.	<b>PO2-189</b>
Hofierka J.	<b>PO2-253</b>	Işık M.	PO3-247
Hogan C.	C-176	Islas R.	<b>PO2-165</b>
Hollas D.	<b>PO3-282</b>	Ito K.	PO1-228
Holm C.	PO2-281	Ito S.	C-091, PO3-53
Hölscher M.	<b>PO1-69</b>	Ivanov S.	<b>C-146</b>
Holthausen M.C.	PO2-134, PO2-241, PO2-294, PO2-48, PO2-81	Ivashchenko D.	<b>PO1-239</b>
Holub D.	PO1-203, <b>PO3-158</b>	Iwahara N.	PO1-252
Holzer C.	<b>PO2-138</b> , PO3-45	Iwasa T.	C-085, <b>C-144</b>
Holzmann N.	<b>PO1-155</b>	Iwata S.	PO1-223
Homem-de-Mello P.	<b>C-094</b> , PO1-100, PO1-107, PO1-127, PO2-55	Iwata T.	PO1-249
Hong K.	PO2-182	Izgorodina E.	PO1-248
Honkala K.	PO1-80	Izsák R.	PO2-170
Honma T.	PO3-87		
Hooper J.	<b>PO3-12</b>	<b>J</b>	
Hornung J.	<b>PO1-51</b>	Jackson C.	PO3-197
Hough M.A.	PO1-204	Jacob C.R.	PO1-123, PO1-202, PO1-258, PO3-293
Houk K.	<b>I-075</b> , PO1-1, PO2-229	Jacquemin D.	<b>I-383</b> , PO1-263
Howard J.C.	<b>PO3-273</b>	Jagau T.-C.	<b>PO2-44</b> , PO2-224
Howlin B.J.	PO1-33	Jahn B.O.	PO2-76
Hoyau S.	C-038	Jahn E.	<b>PO2-289</b>
Høyvik I.-M.	PO3-265	Jahn U.	PO2-289
Hrnčířík J.	PO3-60	Jalife-Jacobo S.	<b>PO1-79</b>
Hršák D.	<b>PO2-132</b>	James A.M.	<b>PO3-51</b> , PO3-175
Hsu C.-P.	PO2-218	Jamshidi Z.	<b>C-087</b>
Hu X.	C-054, <b>PO1-264</b>	Janet J.P.	C-072
Huang B.-J.	PO1-35	Jang J.	<b>C-056</b>
Huang G.-T.	PO1-9	Jani Thaviligu D.	PO3-192
Huang P.	PO2-76	Janicki M.	C-136, <b>PO2-146</b>
Huang R.	PO1-110	Janoš P.	<b>PO3-133</b>
Huang X.	C-025, <b>I-185</b>	Jansen G.	PO1-256
Huber L.	PO2-157	Jansen T.L.C.	PO3-118
Huh J.	<b>C-126</b>	Jaoul A.	PO1-259, <b>PO2-278</b>
		Jaque P.	<b>PO3-286</b>
		Jarraya K.	PO3-169

## Author Index

Järvinen T.	<b>PO2-258</b>	Kar T.	<b>PO1-241</b>
Jaworska M.	<b>PO2-252</b>	Karadeniz U.	<b>PO3-81</b>
Jelinek S.	<b>PO1-57</b>	Karancsiné Menyhárd D.	PO2-82
Jemmis E.	<b>I-294</b>	Karandashev K.	<b>PO3-235</b>
Jena N.K.	C-138	Karbalaeei Khani S.	<b>PO2-213</b>
Jensen F.	<b>I-133</b> , PO1-183	Karlov D.	C-113
Jensen H.J.A.	<b>I-394</b>	Karlsson H.O.	I-152
Jensen J.H.	<b>I-135</b>	Karmodak N.	<b>PO1-275</b>
Jensen S.R.	<b>PO3-276</b>	Karppinen M.	C-017
Jerabek P.	PO1-51, <b>PO2-181</b>	Karsili T.N.V.	I-334, PO2-101
Jesus D.	PO3-80	Karton A.	C-151, PO1-151, PO1-246, PO2-104, PO3-55
Jeung G.-H.	PO3-193	Karttunen A.J.	<b>C-017</b> , PO2-110, PO2-99, PO2-136
Jeziorski B.	<b>I-291</b>	Kasamatsu S.	PO2-10, <b>PO2-83</b>
Jha P.	PO1-2	Kashef Ol Gheta S.	<b>PO3-217</b>
Ji L.	<b>PO3-232</b>	Kästner J.	<b>I-293</b> , PO1-253, PO1-41, PO2-16, PO2-19
Jia D.	PO1-164	Kato T.	PO2-83
Jiang F.	PO3-209	Katoh K.	PO2-8
Jiao H.	<b>PO3-152</b>	Katouda M.	<b>PO3-54</b>
Jimenez-Oses G.	PO1-1	Kats D.	<b>PO3-41</b>
Johansson M.P.	<b>C-157</b>	Kaupp M.	<b>C-151</b> , PO2-41, PO2-51, PO2-52
Johnson E.R.	<b>I-274</b> , PO1-211, PO2-176, PO3-163, PO3-266	Kawasaki A.	<b>PO2-29</b>
Jones C.	PO1-47	Keal T.W.	PO1-204
Jones G.	<b>IN-6</b> , <b>PO1-1</b>	Keane T.	<b>PO3-216</b>
Jónsson H.	<b>I-272</b> , PO2-275, PO3-164	Keefer D.	<b>PO2-125</b> , PO2-127
Jorgensen P.	<b>I-014</b>	Keremu A.	<b>PO1-88</b>
Jorner K.	<b>PO2-76</b> , PO2-90	Kerfoot J.	PO3-46
Jornet-Somoza J.	C-101, <b>PO2-239</b>	Kesharvani M.K.	<b>PO3-55</b>
Jovanovic M.	I-311, <b>PO3-83</b>	Keshavarz F.	PO3-299
Judd M.	PO2-199	Keskin F.E.	PO2-73
Juhasz G.	<b>PO2-187</b>	Khartabil H.	I-314, PO3-113, <b>PO3-135</b>
Jungwirth P.	<b>I-364</b> , PO1-62	Khazaei S.	<b>PO2-295</b>
Junkaew A.	PO2-223	Khedkar A.	<b>PO3-239</b>
Jurásková V.	<b>PO3-275</b>	Khetselius O.	PO3-251, <b>PO3-253</b> , PO3-255, PO3-258
Jurinovich S.	PO3-174, PO3-228	Khomyakov P.	PO2-275
<b>K</b>		Kılıç M.	<b>PO2-277</b>
Kaczmarek-Kedziera A.	<b>PO1-267</b> , PO3-125	Kim C.S.	PO2-190
Kadek M.	I-041	Kim C.W.	<b>PO2-202</b>
Kähler S.	<b>PO2-22</b>	Kim H.W.	C-056, <b>PO1-112</b>
Kaila V.R.I.	<b>I-284</b> , PO1-137, PO2-131, PO3-13, PO3-222	Kim J.	<b>PO2-182</b> , PO2-183, PO2-195, PO2-228, PO2-70
Kaiser D.	PO2-301, <b>PO3-162</b>	Kim K.S.	<b>I-022</b>
Kaldre D.	PO2-301	Kim W.Y.	<b>C-045</b> , PO2-182, PO2-228, PO2-70, PO3-24
Kalemos A.	<b>C-175</b>	Kim Y.-H.	PO2-184
Kallay M.	C-123	King R.B.	PO1-34, PO2-107
Kalmykov S.	PO2-18	Kingston D.G.I.	PO3-274
Kaloni T.P.	C-011	Kinzel D.	PO2-154
Kaltsoyannis N.	PO3-219	Kipouros I.	PO1-22
Kalvet I.	<b>PO2-284</b>	Kiran Y.B.	PO1-206
Kamerlin S.C.L.	<b>I-194</b> , PO1-43	Kiselev V.	<b>PO1-21</b>
Kaminský J.	C-064	Kishi R.	C-091, PO1-298, PO2-191
Kamisaka K.	PO3-87	Kiss D.J.	<b>PO2-82</b>
Kamorzin B.	<b>PO3-119</b>	Kitagawa Y.	C-091, PO1-247, <b>PO2-8</b>
Kandori H.	PO1-249	Kitao A.	PO1-249
Kanekal K.	C-022	Kitaoka Y.	PO1-140
Kang S.	PO2-182, <b>PO2-228</b>	Klahr K.	PO1-153, <b>PO1-171</b>
Kanger T.	PO2-111	Klamroth T.	I-174
Kannath S.	<b>PO1-61</b>	Klein A.	PO2-177
Kappes M.M.	PO3-84	Klimes J.	<b>C-075</b> , PO2-253
Kar M.	<b>PO1-165</b>	Klinke C.	PO2-280
		Klinting E.L.	<b>PO2-299</b>
		Klöffel T.	<b>PO2-173</b>

## Author Index

Klopper W.	<b>I-385</b> , PO2-138, PO3-45	Kühne T.D.	<b>C-021</b> , PO3-66
Klüner T.	PO1-161, PO1-162, PO1-7, PO3-88	Kuklin M.S.	<b>PO1-80</b>
Knapp E.-W.	PO2-40	Kukułka M.	PO1-201
Knecht S.	PO2-269, PO3-74	Kulik H.	<b>C-072</b>
Knippenberg S.	<b>C-138</b>	Kumar A.	<b>PO2-156</b>
Knowles P.J.	<b>I-175</b> , I-381, PO1-270	Kumar K.	<b>PO2-178</b>
Ko Y.-K.	PO2-190	Kumawat A.	<b>PO1-179</b>
Koča J.	PO3-133	Kundu A.	<b>PO2-143</b>
Kolos R.	PO3-95	Kuniyil R.	<b>PO3-309</b>
Kobayashi M.	<b>C-085</b> , PO2-218	Kunz L.	IN-10
Koch C.P.	PO1-200	Kuo J.-L.	PO1-35
Koch H.	<b>I-125</b>	Kupfer S.	PO2-154, PO2-42
Koenis M.	PO2-77	Kurashige Y.	<b>I-393</b>
Koepl C.	PO1-195	Kuritka I.	PO1-281
Koerzdoerfer T.	<b>C-134</b>	Kuroda Y.	<b>PO2-218</b>
Koga N.	<b>PO1-135</b>	Kurtén T.	PO2-300
Kohaut S.	<b>PO3-34</b>	Kussmann J.	<b>PO2-220</b> , PO2-273, PO3-28
Kohguchi H.	PO1-29	Kutáľková E.	PO3-60
Kohls E.	<b>PO2-266</b>	Kuznetsova A.	PO3-251, PO3-253
Köhn A.	<b>I-342</b> , PO1-175, PO1-284, PO2-24, PO2-33, PO3-48	Kvasikova A.	PO3-258
Koistinen O.-P.	PO3-164	Kwon S.-K.	PO2-184
Kolar M.H.	I-195	<b>L</b>	
Kolleth A.	PO2-296, PO3-81	Laage D.	PO3-1, PO3-160
Kollmar C.	<b>PO2-89</b>	Laasonen K.	PO2-172, PO2-204
Komorovsky S.	I-041	Labat S.	PO2-53
Konecny L.	<b>PO3-303</b>	Lafond F.	<b>PO2-94</b>
Kongsted J.	<b>I-322</b> , PO2-132	Lagardère L.	PO2-80
König C.	PO2-210, <b>PO2-79</b>	Lagones T.A.	PO2-199
Köpl C.	I-082	Laio A.	PO3-222
Köprülüoğlu C.	<b>PO2-290</b>	Lamberts T.	<b>PO1-41</b>
Korolokov V.	PO3-46	Lan J.	C-067
Körzdörfer T.	PO1-220, PO2-14	Lang L.	<b>PO2-1</b>
Kosloff R.	PO1-200	Langer R.	PO1-64
Koslowski A.	PO2-85	Lankau T.	PO1-214
Kossoski F.	<b>PO2-292</b>	Lans I.	C-053
Koszinowski K.	PO2-105	Larrañaga O.	<b>PO3-203</b>
Kovačević B.	PO2-248	Larsson H.R.	<b>PO2-38</b>
Kovács Á.	PO1-15	Lasorne B.	PO1-287
Kozłowska M.	PO2-173, <b>PO3-125</b>	Lauritsen J.	IN-7
Kozmon S.	PO3-133	Lautens M.	C-068
Kraemer T.	I-054, <b>PO3-52</b>	Lavrov M.	C-113
Krai P.	PO3-274	Łazarski R.	C-013
Kraka E.	<b>I-221</b>	Le T.A.	<b>PO2-122</b>
Kranz J.J.	<b>PO3-105</b>	Le Bahers T.	<b>C-095</b>
Krause P.	I-173, I-174	Le Bras L.	<b>PO2-163</b>
Kreisbeck C.	PO3-146	Leal E.S.	PO3-155
Kremer K.	C-022, <b>I-101</b> , PO2-206	LeBlanc L.	<b>PO1-211</b>
Kreplin D.A.	<b>PO1-270</b>	Lecours M.	I-371
Kreppel A.	<b>PO3-20</b>	Ledendecker M.	PO1-27
Kresse G.	<b>I-372</b>	Lee K.	PO1-83
Kříž K.	<b>PO2-255</b>	Lee M.E.	PO2-275
Kruegener M.	C-057	Lee S.G.	<b>PO1-83</b> , PO2-190
Krumnow C.	I-083	Lefebvre C.	PO3-113
Kruse H.	<b>PO3-16</b>	Lefebvre J.-F.	PO2-42
Krylov A.	<b>I-331</b>	Legault C.	<b>PO3-68</b>
Krzemińska A.	<b>PO1-17</b>	Legeza Ö.	<b>I-083</b> , I-344, PO2-7, PO3-230
Kubas A.	<b>PO2-75</b>	Leherte L.	<b>C-027</b>
Kubo T.	C-091	Lei J.	C-025
Kühn O.	<b>C-032</b> , PO3-242	Lein M.	<b>C-065</b> , PO1-304



## Author Index

Leininger T.	PO1-226	Lu B.	PO2-205
Lelièvre T.	PO2-211	Lu L.	PO1-230
Lepšák M.	PO2-290, PO3-277	Luber S.	<b>C-142</b>
Lesiuk M.	PO3-280	Lüchow A.	PO1-117
Letz M.	<b>IN-8</b>	Ludwig M.	PO2-242
Levandowski B.	PO1-1	Luis J.M.	<b>PO1-208</b> , PO3-126, PO3-250
Levin L.	PO1-200	Lumbroso A.	PO2-296, PO3-81
Levine D.S.	<b>PO3-290</b>	Lundell J.	PO2-258
Lewenstein M.	PO2-247	Lupan A.	<b>PO1-34</b>
Lewis C.	<b>PO3-229</b> , PO3-57	Lutsker V.	PO3-105
Li J.	PL-4, PO1-10, <b>PO1-5</b>	Luy J.-N.	<b>PO2-139</b>
Li J.-H.	<b>PO3-238</b>	Luyt A.S.	PO1-95
Li J.-W.	<b>PO3-82</b>	Lyalin A.	C-085, <b>PO3-97</b>
Li S.	<b>I-343</b>	Lyskov I.	I-122
Li T.	<b>PO3-172</b>	Lyu P.	C-168
Li W.	I-173, PO2-205		
Li X.	<b>I-332</b> , PO2-186, <b>PO2-188</b>	<b>M</b>	
Li Z.	PO2-141	Ma Q.	I-082, <b>PO1-195</b>
Li Manni G.	PO3-202, <b>PO3-295</b>	Ma Y.	PO2-269
Liakos D.G.	<b>PO3-288</b>	Macaluso V.	<b>PO3-37</b>
Liang W.	<b>I-235</b>	Macgregor S.A.	<b>I-054</b> , PO2-144, PO3-52
Liao Q.	I-173	Machado F.B.C.	PO1-120
Liedl K.R.	PO2-234	Machado G.	PO3-78
Liégeois V.	PO1-298	Maciel C.	<b>PO2-149</b>
Ligouri N.	PO2-225	Mackinnon I.	<b>C-105</b>
Lim C.	<b>I-354</b>	Madarász Á.	PO1-15, PO2-116, PO2-268
Lim J.	PO2-182, PO2-228, <b>PO2-70</b>	Mader S.	<b>PO2-131</b>
Lima M.A.P.	PO2-292	Madsen A.Ø.	C-037
Limacher P.A.	<b>PO3-305</b>	Madsen D.	<b>PO2-210</b> , PO2-79
Limpouchová Z.	PO3-130	Madsen N.K.	<b>PO3-198</b>
Lin K.-H.	<b>PO2-46</b>	Maeda S.	C-042, C-044, C-085, <b>I-124</b> , PO1-143, PO1-159, PO1-29, PO2-293, PO3-106
Linderberg J.	<b>PO3-171</b>	Maffucci I.	C-054
Lindh R.	<b>I-152</b>	Magalhães A.	<b>C-063</b> , PO1-239
Lindner J.	<b>PO3-8</b>	Magalhães C.	PO1-242
Linguetti R.	PO3-100	Maganas D.	<b>PO3-289</b>
Linnera J.	C-017, <b>PO2-110</b>	Magee C.	<b>PO1-58</b> , PO1-65
Lins I.A.	PO2-43	Magistrato A.	PO3-222
Lipparini F.	PO2-297, PO2-80	Mahata A.	I-264, PO1-134
Lischka H.	PO1-120, PO3-51	Mai S.	<b>PO2-109</b> , PO2-140
Liu C.	<b>PO1-154</b> , PO3-186	Maier T.M.	PO2-41, <b>PO2-51</b> , PO2-52
Liu W.-J.	<b>I-043</b> , PO2-124	Maitra N.	<b>I-032</b>
Liu Z.-P.	<b>I-213</b> , PO2-283, PO2-309	Mak A.M.	PO1-76
Lloret J.	PO1-142	Maldonado A.F.	PO3-284
Loboda O.A.	PO2-97	Maldonado-Dominguez M.	<b>PO3-223</b>
Loco D.	<b>PO2-80</b>	Malenov D.	C-112
Lode A.U.J.	PO3-184	Malhado J.P.	PO1-126
Loffreda D.	PO3-102	Mammino L.	<b>PO1-285</b>
Loher C.	PO2-34	Manby F.	<b>I-324</b>
Löhle A.	<b>PO1-255</b>	Mandal D.	I-251
Long J.R.	PO3-213	Manrique-Moreno M.	C-053
Longo E.	PO1-92	Mansarliysky V.	PO3-253
Loos P.-F.	<b>C-073</b>	Mansikkamäki A.	<b>PO1-252</b>
Lopes L.J.S.	<b>PO2-211</b>	Manz J.	<b>PO1-164</b>
Lopez N.	<b>I-052</b>	Marazzi M.	C-178, PO3-252
Lopez X.	<b>C-028</b> , PO1-111	Marchese L.	PO2-171
López R.	<b>PO2-12</b> , PO2-194	Mardyukov A.	<b>PO1-73</b>
López Carballeira D.	<b>PO1-136</b>	Marefat Khah A.	<b>PO3-109</b>
Lopez-Tarifa P.	I-031, PO2-225	Marforio T.D.	<b>PO2-120</b>
Lotfikatooli L.	<b>PO3-58</b>	Margetić D.	PO2-5
Low P.J.	C-151		

## Author Index

Margraf J.	<b>PO2-243</b>	Meijer A.	PO3-216
Margreiter M.A.	<b>PO1-207</b>	Meisner J.	<b>PO2-19</b>
Marian C.	<b>I-122</b>	Meister P.	<b>PO3-194</b>
Mariani Silla J.	PO2-180	Melo A.	<b>PO3-148</b>
Marín Pérez M.D.C.	<b>PO1-197</b> , PO3-215	Melse O.	PO3-120, <b>PO3-43</b>
Marin-Luna M.	<b>PO2-71</b>	Menche M.	PO2-81
Marion A.	PO3-120, <b>PO3-25</b> , PO3-43	Mendoza C.I.	PO2-65
Markmeyer M.	<b>PO2-39</b>	Menegon Arantes G.	PO2-49
Marković M.	<b>PO2-145</b> , PO2-34	Menéndez Rodríguez M.I.	<b>PO1-209</b> , PO2-12
Markussen T.	PO2-274	Meng L.	<b>PO2-186</b> , PO2-205
Marques C.	PO1-274	Menger M.	<b>PO1-215</b>
Marrink S.-J.	<b>I-134</b> , PO3-6, PO3-167	Menichetti R.	C-022
Marsoner Steinkasserer L.E.	<b>PO2-249</b>	Mennucci B.	<b>PL-2</b> , PO2-80, PO3-174
Martin A.	C-108	Mera-Adasme R.	PO3-72
Martin B.	<b>PO3-207</b>	Merieux G.	PO3-135
Martin F.	<b>I-171</b>	Merino G.	<b>I-222</b> , PO1-66
Martin J.M.L.	<b>C-121</b> , PO2-104, PO3-55	Mester D.	C-123
Martinez F.	I-063	Metin D.	<b>PO2-198</b>
Martinez T.	<b>PL-1</b>	Metsala A.	<b>PO2-111</b>
Martinez-Nunez E.	PO3-37	Matthews D.A.	I-295
Martín-Rodríguez A.	C-062	Meuwly M.	<b>I-183</b> , PO1-122, PO1-184, PO1-251
Martins J.B.L.	<b>C-014</b> , PO1-92	Mewes J.-M.	<b>PO1-292</b>
Martin-Somer A.	<b>PO3-33</b>	Mewes S.A.	PO2-140
Martin-Torres J.	PO2-26	Meyer B.	PO1-18, PO1-27, PO2-173, <b>PO3-42</b>
Martynow M.	<b>PO2-285</b>	Meyer F.	PO2-256
Marusczyk A.	IN-10	Meyer L.	<b>PO2-48</b>
Marx D.	C-116, PO3-11, PO3-31	Meyer R.	PO1-158, <b>PO3-297</b>
Maryasin B.	<b>PO2-301</b>	Meyerhenke H.	PO1-123
Maschio L.	<b>C-012</b>	Michalak A.	PO1-217
Masella M.	PO3-188	Michels B.	PO3-162
Mason P.E.	PO1-62	Michl J.	<b>I-311</b> , PO2-41, PO3-83
Massolle A.	<b>PO2-37</b>	Mihaylov T.	<b>PO3-227</b>
Mata I.	I-064	Mikkelsen K.V.	<b>I-325</b>
Mata R.A.	<b>C-122</b> , PO1-243, PO1-271, PO2-21, PO2-245, PO2-74	Miletto I.	PO2-171
Mathieu D.	PO2-250	Millán L.	<b>PO3-21</b>
Matito E.	<b>C-076</b> , PO1-142, PO1-44, PO3-126	Mills D.P.	PO3-219
Matsika S.	<b>I-334</b>	Min S.K.	I-114
Matsui H.	<b>PO2-191</b>	Miqueu K.	<b>PO1-118</b> , PO1-237, PO2-53
Matsunaga S.	PO1-140	Miriyala V.M.	<b>PO2-235</b>
Matsuzaki Y.	PO1-181	Mitchell I.	<b>PO1-152</b>
Matveev P.	PO2-18	Mitchell J.	<b>PO3-197</b>
Matxain J.M.	<b>C-018</b>	Mitric R.	<b>I-113</b> , PO3-8
Matz O.	<b>PO1-188</b>	Mitrofanov A.	<b>PO2-18</b>
Maulide N.	PO2-301	Mitzinger S.	PO3-50
Maurer M.	PO2-242	Miyazaki Y.	PO1-29
Maurice R.	<b>PO1-288</b> , PO2-28	Mo L.	PO2-186
Maximowitsch E.	<b>PO1-149</b>	Modrzejewski M.	<b>PO3-281</b>
Mayer I.	<b>C-155</b> , PO2-2	Moe S.	<b>PO2-283</b>
Mayhall N.	<b>C-131</b>	Mohr S.	PO3-66
Mayr H.	PO2-141	Moiseyev N.	PO2-177
Mazumdar A.	PO3-6	Molins E.	I-064
McCaslin L.	<b>PO1-221</b>	Møller K.B.	PO3-59
McConnell S.	<b>PO2-9</b>	Monari A.	C-178, PO2-109, PO3-294
McDonald A.R.	I-045	Moncho S.	PO3-200
McKay A.I.	PO3-52	Moncomble A.	<b>PO3-192</b>
McKemmish L.	<b>PO3-22</b>	Mondragón-Solórzano G.	PO1-296
McKenzie S.	<b>PO1-297</b>	Mons M.	C-038
McLean B.	<b>PO1-130</b>	Montavon G.	PO1-288
Medina F.	<b>PO1-116</b>	Montero M.	I-063
		Mookherjee M.	C-148



## Author Index

Moon J.	<b>PO2-183</b>	Natori Y.	<b>PO1-247, PO2-8</b>
Moore K.	PO3-123	Natrajan L.	PO3-219
Mora A.	<b>PO3-144</b>	Naumkin F.	<b>PO1-240</b>
Morais S.	PO1-127	Nava P.	<b>PO2-270</b>
Moran D.	I-073	Navizet I.	<b>C-137, PO2-160</b>
Moraru I.-T.	<b>PO2-259</b>	Nazarikatouli F.	PO3-58
Mori S.	<b>C-044, PO2-23</b>	Neale S.	<b>PO2-31</b>
Moro G.J.	PO2-142	Neese F.	I-344, <b>PL-12</b> , PO1-23, PO1-245, PO1-286, PO1-46, PO2-1, PO2-170, PO2-47, PO3-225, PO3-27, PO3-288, PO3-289
Morokuma K.	C-044, PO1-143	Negri F.	<b>I-262, PO2-124</b>
Morozov D.	<b>PO1-115</b>	Nemes G.	PO2-259
Morris M.	PO1-57	Nemukhin A.	<b>I-105</b>
Morrison A.	I-335	Nenadović M.	I-412
Morshedi M.	PO2-199	Nenov A.	<b>PO3-128</b>
Moses P.G.	IN-7	Nerukh D.	<b>C-026</b>
Moskaleva L.	PO3-88	Neto A.D.M.	C-014
Moszynski R.	PO3-280	Netz P.A.	<b>PO2-61, PO1-274</b>
Mougel V.	PO2-135	Neugebauer J.	<b>PL-10</b> , PO1-153, PO1-171, PO2-37
Mráziková K.	PO3-16	Neuhauser D.	PO1-12, PO1-219
Mück-Lichtenfeld C.	<b>PO3-206</b>	Neves R.P.P.	PO1-116
Mühlbach A.	<b>PO2-272</b>	Nguyen Q.N.	<b>PO2-207</b>
Mukamel S.	<b>I-172, PO3-128</b>	Nicolini P.	PO2-130
Müller C.	<b>PO3-243</b>	Nicu P.V.	PO2-77
Müller-Plathe F.	<b>I-102</b>	Niehaus T.	PO3-101, PO3-105
Munarriz J.	<b>PO3-218</b>	Nieminen M.T.	PO1-173
Munejiri S.	PO1-307	Nikiforidis G.	PO1-11
Muñoz F.	PO3-145	Nikšić-Franjić I.	<b>PO3-179</b>
Muñoz-Muriedas J.	PO1-99, PO1-239	Ning A.	PO3-232
Muñoz-Rugeles L.	C-052	Ninkovic D.	C-112, <b>PO3-200</b>
Muñoz-Santiburcio D.	C-148, PO3-31	Nishimoto Y.	<b>PO1-26</b>
Murdachaew G.	<b>PO2-172</b>	Nishimura Y.	<b>PO1-225, PO1-305</b>
Murugan N.A.	C-138	Nisula M.	C-017
Mustalahti S.	PO1-115	Nizovtsev A.	<b>PO3-46</b>
Mutapčić I.	PO2-145	Noble B.	<b>PO3-92</b>
Muuronen M.J.	<b>PO2-308, I-301</b>	Nocton G.	PO1-259, PO2-278
Myllyperkio P.	PO1-115	Noga P.	I-412
Myllys N.	<b>PO2-300</b>	Noguchi Y.	PO1-135, <b>PO1-224</b>
<b>N</b>		Nogueira Perez J.J.	<b>PO2-95, PO2-113, PO2-140</b>
Nachtigall P.	C-168	Nooijen M.	<b>I-371</b>
Nadj A.	PO2-48	Norman P.	<b>I-401, PO3-29</b>
Nagami T.	C-091, <b>PO1-298</b>	Norrby P.-O.	C-025
Nagaoka M.	PO2-226	Novko D.	C-088
Nagase S.	PO3-87	Novoa J.J.	C-101
Nagy P.	<b>C-123</b>	Nowak W.	<b>C-058, PO1-227</b>
Najibi A.	<b>PO1-295</b>	Nyvang A.	<b>PO3-213</b>
Nakahara M.	C-085	<b>O</b>	
Nakai H.	<b>I-051, PO1-225, PO1-233, PO1-268, PO1-269, PO1-280, PO1-305, PO2-68</b>	Oakley M.	<b>PO2-59</b>
Nakakoji K.	PO1-223	Oberli S.	<b>PO2-35</b>
Nakano M.	<b>C-091, PO1-247, PO1-276, PO1-298, PO2-191, PO2-8</b>	Ochsenfeld C.	PO2-242, PO2-244, PO2-273, PO3-157, PO3-177, PO3-20, PO3-26, PO3-28
Nakano S.	PO3-53	Oda T.	PO1-223
Nakatsuji H.	<b>PL-8</b>	Odriozola-Gimeno M.	PO2-58
Namuangruk S.	PO2-223, PO2-66	Oesterling S.	PO2-157
Nandi S.	C-046	Ofial R. A.	PO2-141
Narevicius E.	PO2-177	Ohmiya H.	PO2-23
Naruse Y.	<b>PO1-3</b>	Ohno K.	PO1-223
Narva T.	PO3-131	Okiyama Y.	PO3-87
Nascimento M.	<b>I-313, PO3-61</b>	Okoshi M.	<b>PO1-233</b>
Natarajan U.	PO1-168		

## Author Index

Oláh J.	PO2-82	Pareek M.	<b>PO1-75</b>
Olenius T.	PO2-300	Pareras G.	C-162
Olinto G.	<b>PO1-92</b>	Park J.H.	PO2-190
Oliveira Jr R.R.	PO3-129	Park J.W.	<b>PO3-63</b>
Olivucci M.	PO3-215	Park J.Y.	<b>PO1-11</b>
Ollitrault P.J.	PO3-137	Parker K.	PO2-53
Olsen J.M.H.	I-014, <b>I-084</b> , PO2-22, PO2-132	Parker S.	<b>PO3-149</b>
	PO3-213, PO3-5	Parrinello M.	<b>I-211</b> , PO3-241
Olsson M.A.	I-212	Partos B.	I-295
Olszówka M.	PO3-208	Pas E.	<b>C-078</b>
O'Mara M.L.	PO1-150, PO2-199, PO3-197	Pascual M.J.	PO3-155
Ong T.-G.	PO2-218	Pasteka L.F.	<b>PO3-257</b>
Onitsuka Y.	PO1-29	Pastore M.	<b>I-263</b> , PO3-294
Ono Y.	C-042	Patel A.	PO1-1
Oostenbrink C.	PO2-62	Patel H.	PO3-245
Oppel M.	PO2-240	Pathak B.	<b>I-264</b> , PO1-134
Orian L.	PO2-78	Pathak H.	<b>PO1-90</b>
Oriana A.	PO3-128	Pathak S.	PO2-1
Ornellas F.R.	PO2-43	Pati S.K.	PO2-167
Orozco M.	<b>I-193</b> , PO2-152, PO2-164	Patkowski K.	<b>PO3-156</b>
Ortega D.E.	PO1-146	Paton R.	PO1-108
Ortega-Castro J.	C-148	Patoz A.	PO3-134
Ortí E.	PO1-53	Patschinski P.	PO2-71
Ortiz J.V.	I-381	Paukku Y.	<b>PO1-289</b>
Ortiz de Luzuriaga I.	C-018	Paulikat M.	<b>PO2-21</b>
Ortiz-Chi F.	PO1-66	Paulus B.	<b>I-233</b> , PO1-164, PO2-249, PO2-6, PO2-7
Ortu F.	PO3-219	Pavanello M.	<b>I-215</b>
Oruganti B.	C-035	Pavosevic F.	<b>PO3-27</b>
Osella S.	C-138	Pawlak M.	<b>PO2-177</b>
Osipov V.A.	C-037	Pawłowski F.	I-014
Ostermeir K.	<b>PO2-54</b>	Pearce K.C.	<b>PO3-274</b>
Osuna S.	PO2-229	Peccati F.	<b>PO1-139</b>
Ota Y.	<b>PO1-74</b>	Pecher L.	C-016, <b>PO2-238</b>
Otero de la Roza A.	PO1-211, PO2-176	Peláez D.	C-103
Ottosson H.	PO2-76, PO2-90	Peltzer R.	<b>PO3-214</b>
Overgaard J.	PO3-213	Pendás Á.M.	PO1-39
Oyama T.	PO1-268	Penfold T.J.	PO3-59
Ozmaldar A.	<b>PO2-91</b>	Peng C.	<b>PO1-52</b> , PO3-27
		Peng Q.	PO3-2
<b>P</b>		Perchik M.	<b>PO1-59</b>
Pacchioni G.	PO1-80, PO2-96	Pereira R.	PO1-242
Page A.J.	<b>C-024</b> , PO1-128, PO1-129, PO1-130, PO1-152, PO1-246, PO1-293, PO1-300, PO2-69	Peres J.	PO1-124
Pahl E.	<b>PO1-167</b> , PO2-181, PO3-296	Perez M.A.S.	PO2-277
Palacino-González E.	<b>PO3-244</b>	Pérez del Valle C.	C-148
Palikot E.	<b>PO3-262</b>	Pernal K.	<b>I-035</b>
Palsgaard M.	PO2-274	Perrier A.	<b>C-166</b> , PO2-163
Palusiak M.	C-162	Persico M.	PO1-24, PO1-260
Palyulin V.	<b>C-113</b> , PO3-93	Peschel M.	<b>PO2-15</b>
Pan X.	PO1-193	Peschina J.	<b>PO2-294</b>
Panas I.	PO3-96	Peter C.	<b>I-104</b>
Paneth P.	PO1-17	Peters L.D.M.	<b>PO3-28</b>
Pantaleone S.	PO1-139	Petersen T.	<b>PO1-162</b>
Pantazis D.A.	PO1-46, PO1-245, PO1-286	Peterson K.A.	PO2-104, PO2-181
Papadakis R.	PO2-76	Peterson L.	PO1-57, PO1-58, PO1-59, PO1-63, PO1-65
Papai M.	<b>PO3-59</b>	Petrone D.A.	C-068
Pápai I.	PO2-116, <b>PO2-3</b> , PO2-32	Petrov V.	PO2-18
Parasuk V.	<b>PO1-232</b> , PO1-40, PO2-67	Petrovic P.	C-112, PO3-200
Parasuk W.	PO1-40, <b>PO2-67</b>	Pettersson M.	PO1-115
Paredes K.	<b>PO1-291</b>	Petuker A.	PO3-239
		Pfeifer R.	<b>PO3-129</b>

## Author Index

Pham L.N.	<b>PO1-277</b>	
Phung Q.	<b>PO1-148</b>	
Piccini G.	<b>PO3-241</b>	
Piccinin S.	I-263	
Picconi D.	<b>PO2-175</b>	
Pichierri F.	<b>C-172</b>	
Pieck F.	PO2-238, <b>PO2-279</b>	
Piecuch P.	<b>I-395</b>	
Pierlout K.	PO1-148, PO1-68	
Pilmé J.	PO2-28	
Pinheiro Jr M.	<b>PO1-120</b>	
Pinski P.	<b>PO2-47</b>	
Pinto da Silva L.	<b>PO1-242</b>	
Piquemal J.-P.	<b>C-125</b> , PO2-80	
Piris M.	<b>C-071</b>	
Pisarek J.	<b>PO2-115</b>	
Pittner J.	I-083, <b>I-344</b> , PO3-225, PO3-230	
Pižl M.	<b>PO3-44</b>	
Pla P.	<b>PO1-262</b>	
Plasser F.	PO2-109, <b>PO2-140</b> , PO3-101	
Platts J.A.	PO3-180	
Ploetz E.A.	PO3-6	
Pluharova E.	<b>PO3-1</b>	
Poblador Bahamonde A.I.	<b>C-068</b>	
Podewitz M.	<b>PO2-234</b>	
Pohl M.	PO3-282	
Pohl V.	PO1-164, <b>PO2-254</b> , PO3-99	
Poier P.P.	<b>PO1-183</b>	
Poisson L.	PO3-100	
Polkehn M.	I-112	
Polly R.	<b>PO1-169</b>	
Polo V.	<b>PO2-260</b> , PO3-218	
Polozij M.	C-168	
Pomelli C.S.	<b>PO1-290</b>	
Postils V.	PO3-268	
Postils Ribó V.	<b>PO3-250</b>	
Postnikov A.	PO2-94	
Pototschnig J.V.	<b>PO1-158</b>	
Potter T.	<b>PO1-28</b>	
Prager S.	PO3-196	
Prats Garcia H.	<b>PO1-50</b>	
Prem M.	PO3-162	
Prestianni A.	PO1-14	
Price A.	<b>PO3-163</b>	
Pritchard T.E.	PO1-196	
Prlj A.	PO2-46	
Procházka K.	PO3-130	
Proppe J.	<b>PO1-177</b>	
Prosmi R.	PO1-102	
Puchta R.	<b>PO3-300</b>	
Puggina de Freitas M.	PO2-180	
Pulay P.	<b>I-092</b>	
Puripat M.	<b>PO1-40</b>	
Putau A.	PO2-105	
Puthenkalathil R.	PO3-7	
Puzzarini C.	PO3-100	
Pyykkö P.	<b>I-042</b>	
<b>Q</b>		
Qu C.	I-161	
Quanz H.	<b>PO3-246</b>	
Quapp W.	<b>C-047</b> , PO1-218	
Quinn T.	C-025	
Quiñonero D.	I-064, <b>PO1-238</b>	
<b>R</b>		
Rabani E.	PO1-12, PO1-219	
Radadiya A.	<b>PO3-245</b>	
Radchenko E.	C-113, <b>PO3-93</b>	
Radom L.	<b>I-073</b> , PO1-91	
Radon M.	<b>PO1-191</b>	
Radu L.-F.	<b>PO2-84</b>	
Raeker T.	<b>PO2-221</b>	
Ragogna P.J.	PO1-196	
Rahm M.	<b>C-104</b>	
Rajabi N.A.	<b>PO3-170</b>	
Rajagopala Reddy S.	<b>PO2-50</b>	
Rajaraman G.	<b>I-224</b>	
Ramanan R.	I-251	
Rambabu G.	PO1-206	
Ramek M.	PO2-145, PO2-34	
Ramin Moayed M.M.	PO2-280	
Ramírez Solís A.	PO3-143	
Ramos E.	PO2-65	
Ramos M.J.	PO1-116	
Ramos-Cordoba E.	C-076, PO1-44, PO1-142, <b>PO3-269</b>	
Randall S.	PO3-219	
Rao A.G.	PO3-161	
Rasmussen S.	IN-7	
Ratanasak M.	PO1-232	
Rawat K.S.	<b>PO1-134</b>	
Raybaud P.	PO2-133	
Raynaud C.	I-061	
Réal F.	PO3-188	
Reddy S.R.	PO2-4	
Rehn D.R.	<b>PO3-29</b> , PO2-162	
Reich D.	<b>PO1-200</b>	
Reidelbach M.	<b>PO3-91</b>	
Reiher M.	<b>I-243</b> , PO1-177, PO1-187, PO2-174, PO2-246, PO2-269, PO3-107, PO3-166	
Reining L.	<b>I-384</b>	
Reiter K.	<b>PO2-302</b>	
Reiter S.	<b>PO2-127</b> , PO2-201	
Rekhroukh F.	PO1-118	
Ren T.	PO3-4	
Renevey A.	<b>PO1-16</b>	
Renger T.	PO3-228	
Repisky M.	I-041, PO3-74	
Restrepo A.	<b>C-053</b> , PO1-66	
Reta D.	<b>PO3-219</b>	
Reuter K.	<b>I-261</b> , PO2-243	
Révész Á.	PO2-116	
Reynaud S.	<b>PO3-110</b>	
Řezáč J.	<b>C-077</b> , PO2-235, PO2-255	
Rhee Y.M.	<b>I-353</b> , PO2-202	
Ribas J.	<b>PO1-218</b>	
Ribas X.	PO1-208	
Ribas-Arino J.	C-047	

## Author Index

Ribeiro A.	C-094	Ruiz-Barragan S.	<b>PO3-31</b>
Ricardi N.	PO3-196	Rulišek L.	<b>C-086</b> , PO1-22, PO1-306, PO2-289
Ricci G.	PO2-124	Rungnim C.	<b>PO2-66</b>
Rice J.	<b>I-253</b> , PO1-1	Rusu T.	<b>PO1-8</b>
Richards N.	PO3-245	Ruud K.	<b>I-041</b>
Richter M.	C-032	Rybak L.	PO1-200
Rickmeyer K.	PO2-224	Rybarczyk M.	PO2-261
Riedle E.	PO2-157	Ryde U.	<b>I-212</b> , PO1-229
Riipinen I.	PO2-300	Rydzewski J.	C-058, <b>PO1-227</b>
Riniker S.	<b>I-184</b> , PO1-16, PO3-114, PO3-220	Ryu S.	PO2-182, PO2-228
Rinke P.	PO2-147, PO2-286		
Riplinger C.	<b>PO3-306</b>	<b>S</b>	
Rivera M.	PO2-119, <b>PO2-161</b>	Saalfrank P.	<b>I-174</b>
Rivera-Arrieta H.I.	<b>PO3-124</b>	Saavedra-Torres M.	PO2-194
Rivero U.	<b>PO1-122</b>	Sabolović J.	<b>PO2-34</b> , PO2-145
Rivilla I.	PO2-58	Sadeghian K.	PO3-157
Rivlin T.	PO3-22	Sagarik K.	<b>PO3-304</b>
Rizzo A.	<b>I-405</b>	Sainz-Díaz C.I.	<b>PO2-26</b> , C-148, PO2-155
Robb M.A.	C-101, PO1-126	Sairi M.	<b>PO1-33</b>
Roberts A.	PO1-239, <b>PO3-15</b>	Saita K.	<b>PO3-106</b>
Roca-Sanjuán D.	<b>C-034</b>	Saito T.	<b>PO2-288</b>
Rocca D.	I-263	Saitow M.	PO3-225
Roch L.	<b>PO3-150</b>	Sakata K.	<b>PO1-140</b>
Rocha V.	PO3-78	Sakellaris C.	<b>PO3-293</b>
Rodrigues Silva D.	PO2-179, <b>PO2-180</b>	Sakti A.W.	<b>PO1-305</b>
Rodríguez J.F.	C-068	Sakuma S.	PO1-307
Rodríguez Mayorga M.A.	<b>PO1-98</b> , C-076, PO1-44	Salama R.	PO1-38
Rodríguez Segundo R.	PO1-102	Salvador M.A.	<b>PO1-127</b>
Rodríguez-Santiago L.	PO3-35	Salvador P.	C-076, C-111, <b>PO3-268</b> , PO3-250
Rodziewicz P.	PO2-173, PO3-125	Salzner U.	<b>C-163</b>
Roemelt M.	PO3-239	Samanta P.	<b>PO1-175</b>
Roethlisberger U.	<b>PL-11</b>	Sami S.	C-132
Rogachev A.	<b>C-081</b>	Samu G.	C-123
Rogozina M.	<b>PO1-236</b>	Sánchez O.	PO3-299
Röhr M.I.S.	PO3-8	Sánchez-Navas A.	C-148
Roithova J.	C-086	Sancho-García J.C.	PO1-53
Rojas-Valencia N.	C-053	Sandberg L.	<b>PO3-139</b>
Róldan-Gómez S.	PO1-208	Sandoval A.B.	PO1-293
Romero A.	PO2-229, <b>PO2-282</b>	Sandoval-Salinas M.E.	<b>PO1-190</b> , PO1-296
Romero J.	<b>PO3-187</b>	Santa Cruz T.	<b>PO3-151</b>
Romerosa A.	PO1-155	Santiso E.	PO3-186
Rommel J.	<b>PO2-263</b>	Santos J.	PO1-92
Roos M.K.	PO2-121, <b>PO2-201</b>	Sanz F.	C-062
Rossetti G.	PO1-207	Sanz Matias A.	<b>PO3-19</b>
Rossky P.J.	C-036	Sarkar A.	<b>PO2-112</b>
Rothlisberger U.	PO1-199, PO2-277	Sarrami Foroushani F.	<b>PO1-151</b>
Rott F.	PO2-15, <b>PO2-157</b>	Sastre S.	PO3-145
Roulet J.	<b>PO3-117</b>	Sastry G.N.	<b>I-204</b>
Rovira M.	PO1-208	Satoh H.	<b>PO1-223</b>
Roy L.	<b>PO1-94</b>	Saue T.	<b>I-044</b>
Rozgonyi T.	PO3-59	Sauer J.	PO2-143, PO2-150, PO2-214
Rubes M.	<b>PO3-204</b>	Sauer S.	PO3-162
Rubez G.	PO3-113	Saura P.	<b>PO3-13</b>
Rubio A.	PO2-239	Savasci G.	<b>PO2-267</b>
Rudek B.	PO3-61	Sawamura M.	C-044, PO2-23
Rudolph J.	<b>PO1-202</b>	Sawatlon B.	<b>PO2-159</b>
Rudzinski J.	<b>PO2-206</b>	Sayós R.	PO1-50, PO3-299
Rüger R.	I-031, <b>PO1-104</b>	Scalambra F.	PO1-155
Ruipérez F.	<b>C-106</b> , PO1-136	Scalmani G.	PO3-208
Ruiz E.	C-062, <b>C-108</b>	Scarbath-Evers L.K.	<b>PO2-56</b>

## Author Index

Scemama A.	C-073	Selles P.	PO2-35
Schaefer H.F.	<b>I-093</b> , PO3-71, PO3-77, PO3-123, PO3-124	Selner E.	PO1-58, <b>PO1-65</b>
Schäfer A.	PO2-212	Sels B.	PO1-68
Schapiro I.	PO3-161, PO3-221	Sen K.	<b>PO1-204</b>
Schattenberg C.J.	<b>PO2-52</b>	Sen S.	<b>PO2-225</b> , <b>PO3-108</b>
Schatz G.	<b>I-154</b>	Senami M.	<b>PO1-228</b>
Schaub T.	PO2-212	Senjean B.	<b>PO3-32</b>
Scheffler M.	<b>I-244</b>	Serga I.	PO3-258
Scheiner S.	PO1-241	Sergentu D.-C.	PO1-288, PO2-28
Scherbinin A.	PO3-119	Serwatka T.	<b>PO2-6</b>
Scherrer C.	IN-8	Sethio D.	<b>PO1-48</b>
Schieschke N.	C-128	Sgrignani J.	<b>PO1-132</b>
Schild A.	<b>PO3-291</b>	Shagam Y.	PO2-177
Schimmenti R.	PO1-14	Shah A.	PO3-245
Schlangen M.	PL-4, PO1-10	Shah N.J.	PO1-207
Schlegel H.B.	<b>I-173</b>	Shahsavand A.	PO3-58
Schlott H.	<b>PO1-27</b>	Shaik S.	<b>I-251</b> , PL-4
Schlüns D.	PO1-171	Shalashilin D.	PO2-240
Schmid P.	PO3-199	Shalom M.	PO1-27
Schmidt A.-C.	PO2-212	Shang C.	<b>PO2-309</b>
Schmitt-Monreal D.	<b>PO1-258</b>	Shao M.	PO3-136
Schmitz G.	<b>PO2-209</b> , PO3-189	Sharapa D.	<b>PO2-306</b>
Schnabel J.	<b>PO2-24</b>	Sharma S.	PO3-202
Schnappinger T.	<b>PO1-279</b>	Shemesh D.	<b>PO1-231</b>
Schneider G.L.	PO1-22, PO1-205	Shen J.	I-395
Schnieders D.	PO1-153, <b>PO1-222</b>	Sherrill D.	<b>I-205</b>
Schnitzer T.	PO3-26	Sheu S.-Y.	<b>PO1-54</b> , PO1-55
Schoenebeck F.	PO2-284	Sheu W.-S.	<b>PO1-182</b>
Schönborn B.	I-174	Shiga M.	PO1-135, PO1-74
Schoonheydt R.	PO1-68	Shigemitsu Y.	<b>PO1-156</b>
Schooss D.	PO3-84	Shih P.	<b>PO1-166</b>
Schreckenbach G.	<b>C-011</b>	Shiozaki T.	<b>I-391</b> , PO3-63
Schreiner P.R.	<b>I-072</b> , PO1-145, PO1-299, PO3-246	Shoji Y.	PO1-269
Schröder B.	<b>PO2-261</b>	Shpiro B.	PO1-12
Schröder H.	<b>PO2-25</b>	Shuai Z.	<b>I-265</b> , PO3-2
Schulz C.	<b>PO1-46</b>	Sibaev M.	<b>PO1-294</b>
Schulz J.B.	PO1-207	Sidler D.	<b>PO3-114</b>
Schumann-Gillett A.	<b>PO1-150</b>	Siegmann M.	<b>PO2-129</b>
Schüppel F.	<b>PO2-121</b>	Siemering R.	PO1-279
Schurkus H.	<b>PO2-244</b>	Sierka M.	<b>C-013</b> , PO1-210, PO2-27, PO2-30
Schwabe T.	PO2-25	Sierraalta A.	PO2-307
Schwaninger A.	PO3-114	Silaghi-Dumitrescu R.	PO1-229
Schwarz H.	<b>PL-4</b> , PO1-10, PO1-5	Sillar K.	PO2-143
Schwarzer M.C.	<b>PO2-23</b>	Silva J.C.F.	C-014
Schweizer J.I.	PO2-48, <b>PO2-81</b>	Silvani A.	PO1-132
Schwell M.	PO3-100	Sim E.	<b>I-303</b>
Schwerdtfeger P.	<b>I-021</b> , PO1-167, PO2-181, PO3-257, PO3-296	Simm G.	<b>PO1-187</b>
Schwilk M.	I-082, PO1-195	Simmermacher M.	<b>PO3-237</b>
Scott C.J.C.	<b>PO3-65</b>	Šindelka K.	<b>PO3-130</b>
Scuderi D.	PO3-37	Singh A.	<b>PO1-105</b>
Scuseria G.	<b>I-081</b>	Sinha V.	<b>PO1-78</b>
Sebald P.	PO2-261	Sirohiwal A.	<b>PO1-245</b>
Sebastiani D.	PO2-295	Sisourat N.	PO2-35
Seebach D.	PO2-246	Sitkiewicz S.	<b>PO3-126</b>
Segarr-Marti J.	PO3-128	Sivalingam K.	PO1-23
Segatta F.	PO3-128, <b>PO3-174</b>	Skaf M.	<b>I-415</b>
Seibert J.	<b>PO2-72</b>	Skitnevskaya A.	<b>PO2-100</b>
Seino J.	PO1-268, PO1-269, PO1-280	Sklenak S.	<b>C-147</b>
		Skomorowski W.	PO1-200
		Skylaris C.-K.	PO3-273



## Author Index

Sladek V.	PO3-53	Sulzer S.	PO2-296, PO3-81
Slaviček P.	PO3-275, PO3-282	Sumiya Y.	<b>PO2-293</b>
Slipchenko L.	<b>I-323</b>	Summerfield A.	PO3-46
Smeu M.	<b>PO3-70</b>	Sun Y.	<b>PO1-19</b>
Smiatek J.	PO2-281	Sunaga A.	<b>PO3-98</b>
Smidstrup S.	PO2-275	Sundholm D.	<b>I-094</b> , PO1-137, PO3-190
Smirnova A.	PO2-18	Sunoj R.B.	<b>I-223</b>
Smith A.-S.	I-355, PO3-256	Suomivuori C.-M.	<b>PO1-137</b>
Smith D.M.	<b>I-355</b> , PO2-233, PO2-248, PO3-256	Supady A.	C-082
Smits O.	PO2-181	Suzuki K.	<b>PO1-143</b> , PO1-181
Smyrnova D.	<b>PO3-215</b>	Suzumura T.	<b>PO2-17</b>
Sobolewski A.L.	<b>C-133</b> , PO2-101	Svatek S.	PO3-46
Sochorová Vokáčová Z.	PO3-1	Svinarenko A.	PO3-259
Sodupe M.	PO1-139, PO3-35	Swang O.	<b>C-118</b>
Sokkar P.	<b>PO3-104</b>	Swart M.	<b>I-045</b> , PO2-229, PO2-256, PO2-282
Solà M.	C-162, PO2-76, PO2-90, PO2-257	Swope W.C.	PO2-123
Solans-Monfort X.	PO1-139, <b>PO3-35</b>	Sylvetsky N.	<b>PO2-104</b>
Sollogoub M.	PO2-128	Symonds C.	PO2-240
Solomon E.I.	PO1-22	Szabla R.	C-136, PO2-146, <b>PO3-224</b>
Song L.	<b>PO3-278</b>	Szalay P.G.	<b>I-295</b>
Sosa Carrizo E.D.	<b>PO1-237</b> , PO2-53	Szalay S.	I-083
Sotiropoulos J.-M.	<b>PO2-53</b>	Szalewicz K.	<b>I-234</b>
Sousa C.P.	PO1-127	Szatyłowicz H.	<b>PO1-272</b>
Sousa S.	PO1-124	Szczesniak M.	PO3-281
Souza T.	C-094	Szilvási T.	I-083
Spezia R.	PO3-37		
Sponer J.	PO3-16, PO3-224	<b>T</b>	
Springborg M.	<b>C-048</b> , PO1-172, PO2-13	Taenzler P.	<b>PO3-157</b>
Srebro-Hooper M.	<b>PO1-217</b>	Taeschler C.	<b>IN-2</b>
Srnec M.	PO1-306, PO3-223	Taft C.	PO1-92
Staemmler V.	PO1-174	Taioli S.	PO3-174
Staniszewska M.	<b>PO2-154</b>	Tajti A.	I-295
Stanke M.	PO3-262, <b>PO3-47</b>	Takagi M.	C-085, <b>PO1-159</b>
Stanton J.F.	<b>I-085</b> , I-295	Takamuku S.	<b>PO1-276</b> , PO2-191
Stasyuk A.	<b>PO2-257</b>	Takano Y.	PO2-288
Steenbergen K.G.	<b>PO3-296</b>	Takaya D.	PO3-87
Steenbock T.	<b>PO1-266</b>	Takenaka M.	C-144
Stefanovic R.	C-024, <b>PO1-128</b>	Takenaka N.	<b>PO2-226</b>
Steffen J.	<b>PO1-189</b>	Taketsugu T.	<b>C-042</b> , C-044, C-085, C-144, PO1-29, PO2-218, PO3-97
Stein C.	<b>PO2-174</b> , PO3-107	Talbot P.	C-105
Stein M.	<b>C-098</b> , PO2-118, PO2-266	Talhi F.	<b>PO1-4</b>
Steinmetzer J.	<b>PO2-216</b>	Talotta F.	<b>PO2-45</b>
Stemmle C.	<b>PO2-7</b>	Tamayo T.	<b>PO3-146</b>
Štěpánek M.	PO3-130	Tamm T.	<b>PO3-131</b>
Stepic R.	I-355, <b>PO3-256</b>	Tamura H.	I-112
Stirling A.	<b>C-173</b>	Tan Y.S.	<b>PO1-192</b> , C-078
Stojanovic L.	<b>PO3-101</b>	Tannor D.J.	<b>I-144</b> , PO2-38
Stokbro K.	PO2-274, PO2-275	Tanriver G.	<b>PO2-296</b> , PO3-81
Stopkowicz S.	<b>C-141</b>	Tapavicza E.	<b>PO3-154</b>
Stradi D.	PO2-275	Tarumi M.	<b>PO1-181</b>
Straka M.	<b>C-064</b>	Tashiro M.	PO3-54
Strange R.W.	PO1-204	Tavşanlı A.	<b>PO2-73</b>
Stroet M.	<b>PO2-92</b>	Tavares da Costa L.	PO3-226
Suarez D.	<b>PO1-20</b> , PO1-32	Tavernelli I.	<b>I-114</b>
Subotnik J.	<b>I-155</b>	Tecmer P.	PO1-133
Sugimoto M.	<b>C-041</b>	Teixeira Mancini D.	PO3-226
Sugino O.	PO1-135, PO1-224, PO2-10, PO2-29, PO2-83	Tejero T.	<b>PO3-79</b>
Suksumolrat N.	PO2-67	Tellgren E.	PO3-108
Sullivan M.B.	PO1-76	Ten-no S.	<b>I-142</b> , PO2-208
Sulskus J.	<b>PO2-168</b>		

## Author Index

Tennyson J.	I-165, PO3-22
Teodoro T.	<b>PO2-77</b>
Teramae H.	<b>PO1-141</b>
Ternovsky E.	<b>PO3-259</b>
Ternovsky V.	<b>PO3-258</b>
Teusch T.	<b>PO1-161</b>
Teuteberg T.	<b>PO2-74</b>
Tew D.P.	<b>I-392</b> , C-075
Teze D.	PO1-288
Thallmair S.	PO2-15, <b>PO3-6</b>
Thiel W.	<b>I-131</b> , PO2-193, PO2-85, PO3-62
Thom A.J.W.	PO3-65
Thomas M.	PO2-11, <b>PO2-199</b>
Thompson T.H.	<b>PO3-177</b>
Thomsen M.	PO3-213
Þórhallsson A.	C-158
Thoss M.	PO2-4, PO2-50
Titov E.	I-174
Todorova T.K.	<b>PO2-135</b>
Tokiwa H.	PO3-53
Toldo J.M.	<b>PO2-117</b>
Tomaschun G.	<b>PO1-7</b>
Tomza M.	PO2-247
Tonner R.	<b>C-016</b> , PO2-238, PO2-279
Töpfer K.	<b>PO2-93</b>
Toro-Labbé A.	PO1-146, PO1-178, PO3-182, PO3-271
Torrent Sucarrat M.	<b>PO2-58</b>
Tosoni S.	PO1-80, <b>PO2-96</b>
Tóth G.	PO2-82
Tóth Z.	<b>PO3-75</b>
Toulouse J.	<b>I-273</b>
Tozer D.	<b>I-271</b>
Traber P.	<b>PO2-42</b>
Tran D.H.	<b>PO3-173</b> , C-078
Tremblay J.C.	<b>C-088</b> , PO1-164, PO2-254, PO2-6, PO2-93, PO3-99
Trindle C.	PO1-114, PO1-71
Trnka T.	PO3-133
Trofimov A.	PO2-100
Truhlar D.	<b>I-201</b> , PO1-289
Tsatsoulis T.	<b>PO1-163</b>
Tsuchimochi T.	<b>PO2-208</b>
Tsutsumi T.	C-042
Tucholska A.	<b>PO3-280</b>
Tuczek F.	PO1-82
Tuna D.	<b>PO2-193</b>
Tuñón I.	PO3-160
Tuononen H.M.	PO1-196
Turi L.	<b>C-036</b>
Turner M.	<b>PO3-180</b>
Turney J.M.	PO3-124
Turupcu A.	<b>PO2-62</b>
Tuvi-Arad I.	<b>PO3-185</b>
Tvaroška I.	PO3-133

### U

Ueno-Noto K.	<b>PO2-185</b>
Uhlig F.	<b>PO2-281</b>
Unnikrishnan A.	<b>PO1-70</b>

Uno T.	PO1-223
Unsleber J.	<b>PO1-153</b>
Uosaki K.	PO3-97
Uranga J.	<b>PO1-45</b>
Uranga O.	<b>PO3-122</b>
Urban M.	<b>I-412</b>
Urbanek P.	PO1-281
Uta M.-M.	<b>PO2-107</b>
Uusitalo J.J.	PO3-167

### V

Vacher M.	I-152, <b>PO1-126</b>
Vaiana A.C.	I-195
Vala H.	PO3-245
Valeev E.F.	<b>PL-5</b> , PO1-23, PO3-27, PO3-57, PO3-229
Valjus J.	<b>PO1-196</b>
Vallejo W.	<b>PO1-213</b>
Vallet V.	PO3-188
Valsson O.	<b>PO2-227</b>
Van de Sanden M.C.M.	PO1-6
Van Dijk M.	PO2-303
Van Gastel M.	PO3-239
Van Lenthe E.	PO1-104
Van Neck D.	PO1-39, PO2-230
Van Niekerk D.	<b>PO2-108</b>
Van Niekerk D.M.E.	C-177
Van Sittert C.G.C.E.	PO1-95
Van Wüllen C.	PO2-169
Vanelderden P.	PO1-68
Vaniček J.	PO3-110, , PO3-116 PO3-117, PO3-134, PO3-235
Vankó G.	PO3-59
Varella M.T.d.N.	PO2-292
Varga S.	PO2-116
Varga Z.	PO1-289
Vargas A.	<b>PO1-66</b>
Varner M.E.	PO1-302
Vaucher A.	<b>PO3-166</b>
Vecharynski E.	PO3-136
Vehkamäki H.	PO2-300
Vehtari A.	PO3-164
Veiros L.F.	PO3-292
Veis L.	I-083, I-344, <b>PO3-230</b>
Vej-Hansen U.G.	<b>PO2-274</b> , PO2-275
Vercauteren D.P.	C-027
Verdonk M.	<b>IN-4</b>
Verstraete F.	I-083
Very T.	C-038
Via Nadal M.	<b>PO1-44</b> , C-076
Vícha J.	C-064, <b>PO1-273</b>
Vidal-Daza I.	C-148
Vieira T.F.	<b>PO1-124</b>
Vila Verde A.	PO3-217
Vilhena F.D.S.	<b>PO1-84</b>
Villegas-Escobar N.	<b>PO1-146</b>
Viseras C.	PO2-155
Visscher K.M.	<b>PO2-303</b> , PO2-123
Visscher L.	<b>I-031</b> , PO1-104, PO2-225, PO2-77, PO3-74
Vlček Jr. A.	PO3-44

## Author Index

Vogler S.	<b>PO2-242</b>
Vöhringer-Martinez E.	PO1-125
Voigt A.	PO1-207
Voigt B.A.	<b>PO2-237</b>
Volkenandt S.	C-057
Von Looz M.	PO1-123
Vondung L.	<b>PO1-64</b>
Voora V.K.	I-301
Voronina E.	<b>PO2-271</b>
Voth G.	<b>I-245</b>
Vucemilovic-Alagic N.	I-355
Vyboishchikov S.	<b>C-153</b>

### W

Waigel W.	PO3-199
Waite S.	<b>PO1-246</b>
Waite C.	C-074
Waldt E.	PO3-84
Wales D.J.	PO3-65
Waller M.	<b>C-043</b>
Walsh J.P.S.	PO3-213
Wan S.	PO1-36
Wang C.-Y.	PO1-35
Wang D.	PO3-10
Wang F.	<b>C-156</b>
Wang G.	PO1-96
Wang H.	PO3-242
Wang J.	C-035
Wang K.	I-161
Wang Q.	<b>PO1-269</b>
Wang T.	<b>PO3-201</b>
Wang W.	PO2-188
Wang X.	<b>PO1-193, PO3-57</b>
Wang Y.	I-161, PO1-262, <b>PO1-96</b>
Wang Z.	C-156
Wanless E.	PO2-69
Warnau J.	<b>PO1-283</b>
Wasif Baig M.	<b>PO3-30</b>
Watanabe C.	<b>PO3-87</b>
Watanabe H.	PO3-87
Watanabe K.	C-091, PO1-298
Watanabe Y.	PO3-53
Webb A.	PO1-239
Webber G.B.	PO1-128, PO1-130, PO2-69
Weber F.	C-103
Weber M.	PO3-91
Wei Z.	<b>PO3-141</b>
Weidman J.	<b>PO3-77</b>
Weigend F.	PO2-302
Weinstein J.	PO3-216
Weiske T.	PL-4
Wellendorff J.	PO2-274, <b>PO2-275</b>
Weller A.S.	PO2-144, PO3-52
Wells B.	<b>PO2-192</b>
Welz E.	<b>PO3-263</b>
Wender J.H.	<b>PO2-241</b>
Wennemers H.	PO3-26
Werner H.-J.	<b>I-082</b> , PO1-195, PO1-270, PO1-284, PO3-205
Werner M.	<b>PO1-271</b>

Wesolowski T.A.	PO3-196
Weßing J.	PO1-51
White N.G.	PO2-199
Whitfield J.H.	PO3-197
Wibowo M.	<b>PO1-24</b>
Wick C.	I-355, <b>PO2-233</b>
Wiebeler C.	<b>PO3-161</b>
Wiebeler H.	<b>PO3-66</b>
Wiest O.	<b>C-025</b>
Wilcken R.	PO2-157
Willitsch S.	PO1-122
Wilson D.	<b>C-176</b>
Wilson M.	PO1-28
Winpenny R.E.P.	PO3-219
Wipff G.	PO3-279
Wirsing S.	PO3-162
Witasek R.	PO3-60
Witek H.A.	PO1-201
Witek J.	<b>PO2-114</b>
Wodrich M.D.	I-252, PO2-159
Wolff W.	PO3-61
Wolter M.	<b>PO1-123</b>
Womack J.C.	PO3-273
Won J.S.	<b>PO2-190</b>
Wong M.W.	PO1-76
Wood B.	PO1-248
Wood G.	<b>PO3-186</b>
Woody A.	PO1-57
Worth G.A.	<b>I-115</b> , PO2-240, PO2-287
Wouters S.	PO1-148
Wright D.W.	PO1-36
Wu H.-N.	<b>PO3-209</b>
Wu J.	PO1-190
Wu X.	<b>PO2-101, PO2-85</b>
Wu Y.-D.	C-067, PO3-209
Wuttke A.	<b>PO2-231</b>
Wylie L.	C-078

### X

Xantheas S.	<b>I-065</b>
Xavier N.	<b>PO3-80</b>
Xie W.	<b>PO1-30</b>
Xiong X.-G.	I-231
Xu L.	C-067
Xu X.	<b>PO3-132</b>
Xu Z.-H.	<b>PO1-251</b>

### Y

Yamada D.	PO1-249
Yamada S.	PO3-53
Yamamoto Y.	<b>PO2-10, PO3-53</b>
Yamane M.	C-091, PO1-298
Yamasaki M.	<b>PO1-307</b>
Yamashita M.	PO2-8
Yamazaki K.	<b>PO1-29</b>
Yanai T.	<b>I-231</b>
Yáñez M.	<b>I-292</b>
Yang C.	PO1-11, PO3-136
Yang D.-Y.	PO1-54, <b>PO1-55</b>
Yang K.	<b>PO2-184</b>



## Author Index

Yang T.	<b>PO1-87</b>
Yang W.	<b>I-091</b>
Yang Y.	PO1-164
Yates B.	<b>C-083</b>
Yavuz I.	<b>PO3-302</b>
Ye J.	C-068
Yepes D.	PO1-146, <b>PO3-283</b>
Yimieraishan M.	<b>PO1-89</b>
Yönder Ö.	<b>PO1-198</b>
Yong C.W.	PO1-204
Yoshimura T.	C-044
Yoshino T.	PO1-140
Yu C.	<b>PO1-214</b>
Yu H.	PO1-193, <b>PO3-10</b>
Yu J.-S.K.	<b>PO1-9</b>
Yu Q.	I-161
Yuan Y.Y.	<b>PO1-121</b>
Yudanov V.	<b>PO3-270</b>
Yung M.-H.	C-126
Yurchenko S.	<b>I-165</b>

## Z

Zacharias M.	PO2-264
Zaichenko A.	<b>PO2-215</b>
Zakay I.	<b>PO1-302</b>
Záliš S.	PO3-44
Zanotto M.	C-094, <b>PO1-107</b> , PO2-55
Žari S.	PO2-111
Zaric S.	<b>C-112</b> , PO3-200
Zauleck J.P.P.	PO1-279, PO2-15
Zech A.	<b>PO3-196</b>
Zefirov N.	C-113, PO3-93
Zeman J.	PO2-281
Zeng J.	PO1-52
Zeng Y.	PO2-186, <b>PO2-205</b>
Zettergren H.	PO3-103
Zgid D.	<b>I-382</b>
Zhang H.	<b>PO1-230</b>
Zhang H.-X.	<b>C-164</b>
Zhang J.	I-352
Zhang W.H.	PO3-197
Zhang X.	C-067, <b>PO1-108</b> , <b>PO1-6</b> , <b>PO3-2</b>
Zhang X.-J.	PO2-309
Zhang Y.	PO2-42
Zhang Z.	C-056
Zhao L.	<b>PO1-47</b> , <b>PO3-4</b>
Zhao Q.	C-072
Zheng C.	PO3-120
Zhong R.	PO3-4
Zhou J.-K.	PO1-54
Zhou M.	PO2-13
Zhou Q.	<b>PO1-110</b>
Zhou S.	PL-4, <b>PO1-10</b>
Zhu J.	<b>PO1-49</b>
Ziebarth B.	IN-10
Zins E.-L.	PO1-49
Zipse H.	PO2-141, PO2-71
Zlatař M.	<b>PO2-217</b>
Zobel P.	<b>PO2-113</b>
Zöllner M.S.	PO2-251, <b>PO2-280</b>

Żuchowski P.	PO1-133
--------------	---------



Landsberger Strasse 155 | 80687 Munich | Germany