



# PLENARY TALKS



## Ground and Excited State Dynamics on Graphical Processing Units

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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**

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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].

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## Quantum Chemistry in Magnetic Fields

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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].

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

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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]<sup>•</sup> 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].

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

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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.

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

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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

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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.

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

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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.

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## Multireference Coupled Cluster Theory, Infinities, and Renormalization

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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.

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

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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.

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## 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>**

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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

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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.

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# INVITED TALKS



## Strong correlation in electron gases.

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

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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.

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

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

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

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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

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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**

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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.

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

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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>.

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## Graphene nanoribbon based electronics and spintronics

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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.

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

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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

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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.

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

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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].

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

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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.

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

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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

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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.

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

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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].

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

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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.

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## 4-component relativistic calculations with periodic boundary conditions

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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.

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

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### 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*.

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## New Scenarios for Strongly Correlated Electrons

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**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].

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## Variational perturbation theory in geochemistry

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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 ?

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

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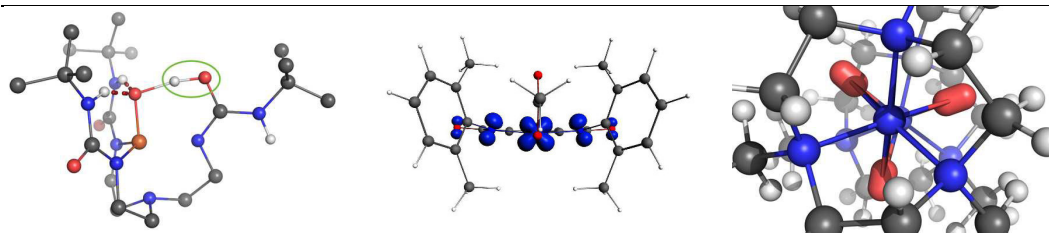
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Oxidation processes of hydrocarbons in a selective, efficient and environment-friendly manner remains one of the major challenges at present today.[1] The majority of these studies is based on experiment, and computational chemistry plays sometimes 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.



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

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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.

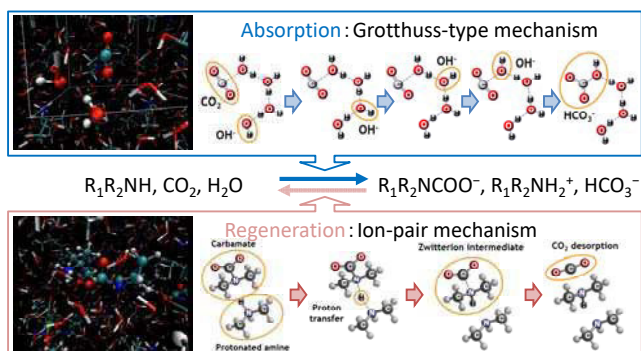


Fig. 1. Reaction mechanisms for CO<sub>2</sub> absorption and regeneration processes proposed by the DC-DFTB-MD simulations.

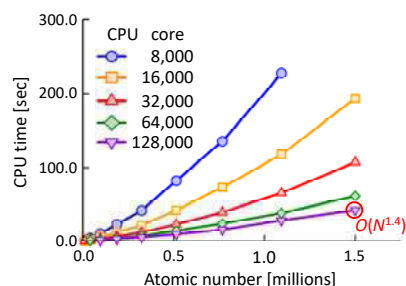


Fig. 2. CPU times for DC-DFTB energy calculations of water clusters.

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

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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**

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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.

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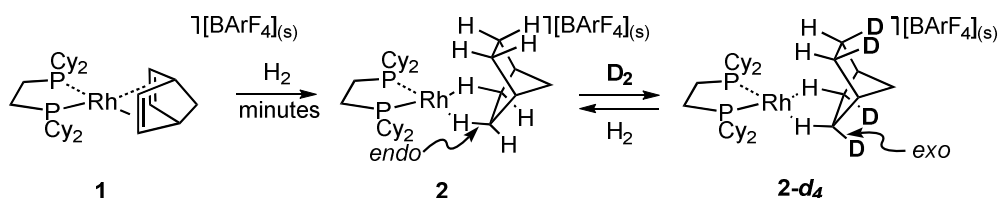
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## Modelling Alkane $\sigma$ -Complexes in the Solid State

Tobias Krämer and Stuart A. Macgregor

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$\sigma$ -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]

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## Directionality and the Role of Polarization in Electrostatic Catalysis

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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.

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

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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.

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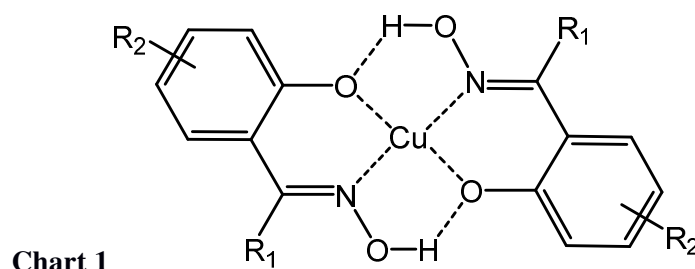
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## Exploring NMR properties of paramagnetic Cu phenolic oxime complexes.

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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>



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

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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.

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

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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).

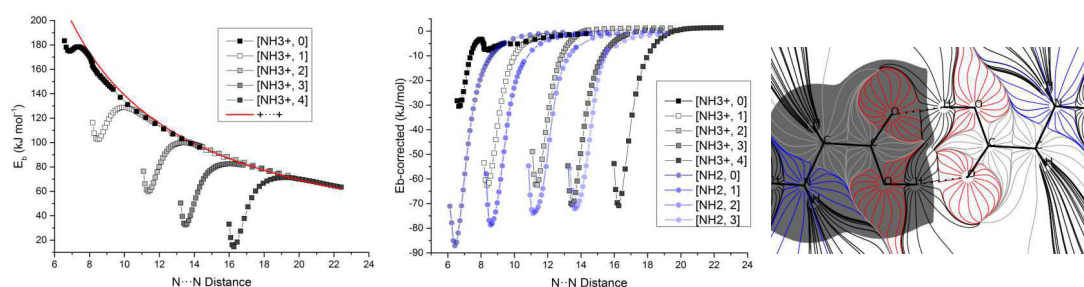


Fig. 1. (a) Dissociation profile versus the N...N intermolecular distance. (b) Coulombic repulsion removed from the profile. (c) Electric field in the dimer of the protonated glycine.

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

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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.

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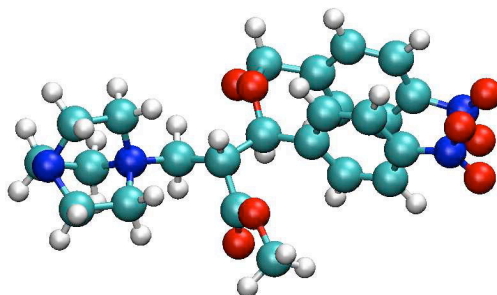


## Modelling Reaction Mechanisms and Kinetics in Homogeneous Catalysis: Challenges and Progress

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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.

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## London Dispersion Effects in Molecular Chemistry

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

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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”.

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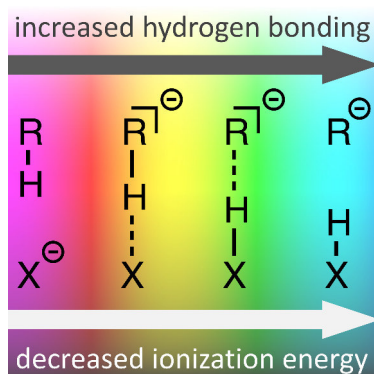
## Impact of Hydrogen Bonding on the Susceptibility of Peptides to Oxidation

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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**

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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 ( $RR'C=SiR^-$ ) 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.

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## **Dynamics of Pericyclic Reactions**

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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  
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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

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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).

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

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F. Verstraete<sup>4</sup>, C. Krumnow<sup>5</sup>, J. Eisert<sup>5</sup>

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<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.

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## Wave Functions with Several Sets of Optimized Orbitals

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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>**

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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.

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

**Weitao Yang**

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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.

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

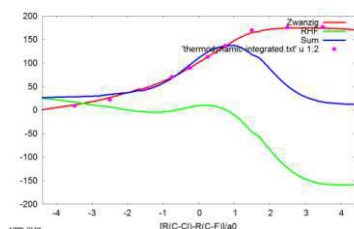
Krzysztof Wolinski,<sup>1</sup> Géza Fogarasi<sup>2</sup>, Peter Pulay<sup>3</sup>

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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].

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**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>**

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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

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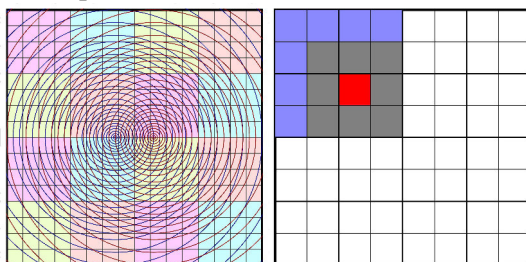
## Numerical Electronic Structure Theory Methods for Massively Parallel Computations on Molecules

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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.

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

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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)

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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

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

**Florian Müller-Plathe**

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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]

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

**Christoph Dellago**

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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>**

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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.

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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,

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

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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.

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

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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.

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

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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

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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.

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

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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 an 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].

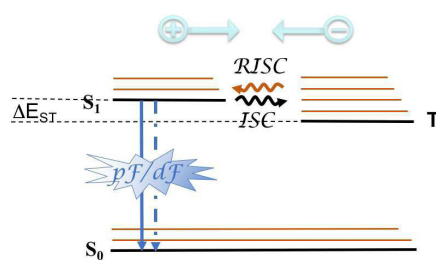
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## TADF efficiencies in coinage-metal coordination complexes and metal-free donor–acceptor systems

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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.



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

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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

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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.

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

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### 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.

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1. “Crossing conditions in coupled cluster theory”, Eirik F. Kjørstad, 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. Kjørstad and Henrik Koch (submitted - <https://arxiv.org/abs/1708.01269>)

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

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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].

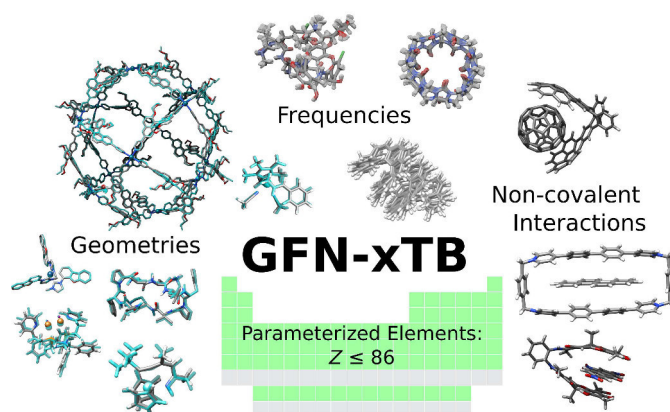
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## Applications of the Extended Tight Binding Method (GFN-xTB)

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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.



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## Developing Improved Force Fields.

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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].

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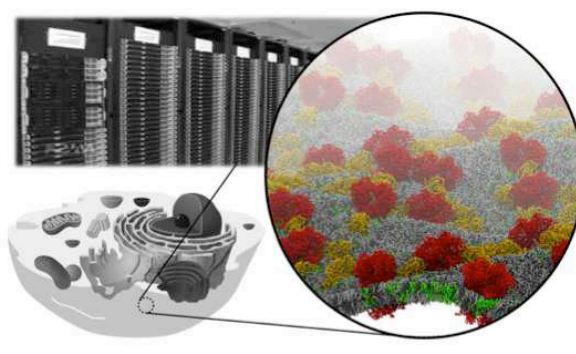
## Computational microscopy of (bio)molecular processes

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].



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

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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

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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].

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## Stochastic Orbitals for Electronic Structure and Quantum Chemistry

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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.

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

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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.

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

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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**

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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].

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## **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>**

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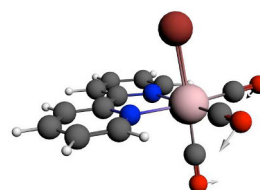
That the origin of chemi- and bioluminescence is a non-adiabatic process originating from the breakage of a peroxide bond is well understood. However, some details in the mechanisms of chemi- and bioluminescence are not well understood. In this lecture we will unravel one of these lesser understood experimental 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**

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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.

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

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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

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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**

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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

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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.

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

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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.**

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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

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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.

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## Attochemistry: imaging and controlling electron dynamics in molecules

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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].

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

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### 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.

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**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

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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].

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

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Boyke Schönborn<sup>1</sup>, Evgenii Titov<sup>1</sup>

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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].

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## On the Perturbative Computation of Ionization Energies

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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.

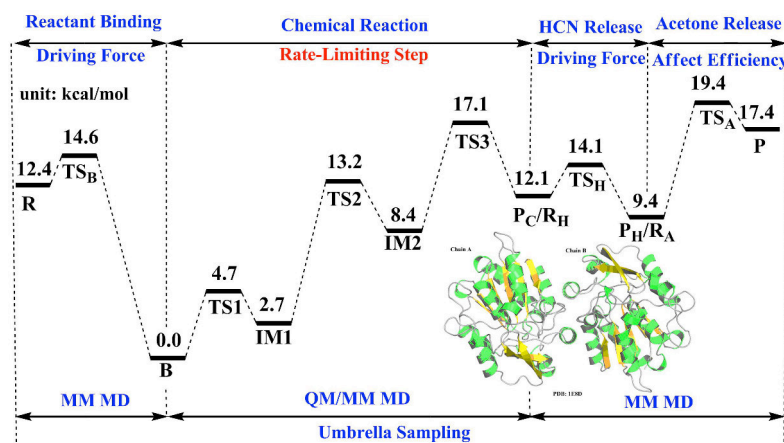
## Global Simulation of Cyanohydrin Cleavage by Hydroxynitrile Lyases

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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*.



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## Metadynamics Simulations of G-Protein Coupled Receptors

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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]

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## Quantitative Atomistic Simulations for Chemical and Biological Applications

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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

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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.

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

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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**

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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.

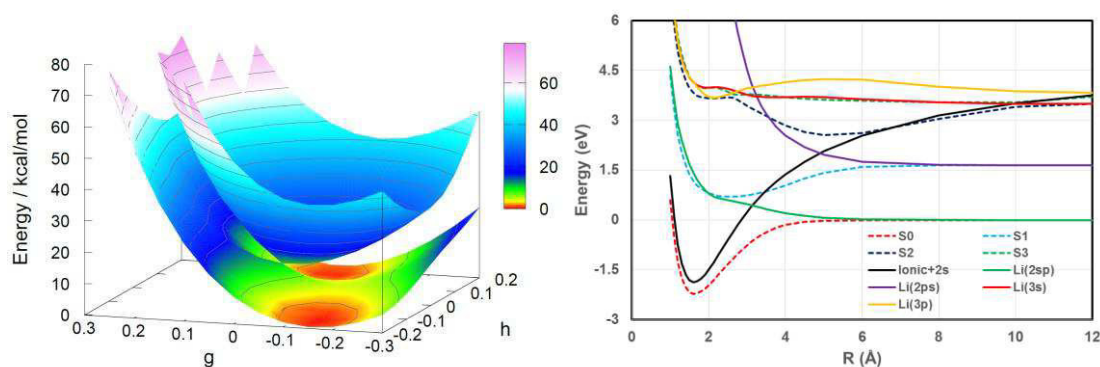
## Methods and applications of multistate density functional theory (MSDFT)

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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.



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## 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.

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

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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.

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

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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**

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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.

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

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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].

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# Reliable DFT results for spin-crossover complexes

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## 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

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**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.

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## Large Datasets for Benchmarking Noncovalent Interactions

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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.

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## Enhanced sampling for chemistry

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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

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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.

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

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<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.

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

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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.

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

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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.

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

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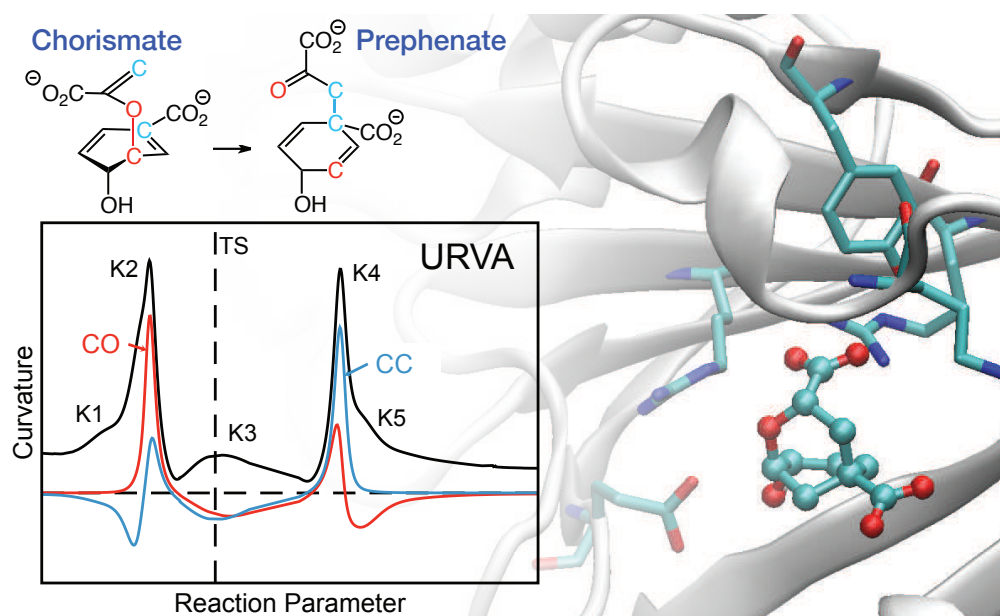
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<sup>†</sup> In Memoriam

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

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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

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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.

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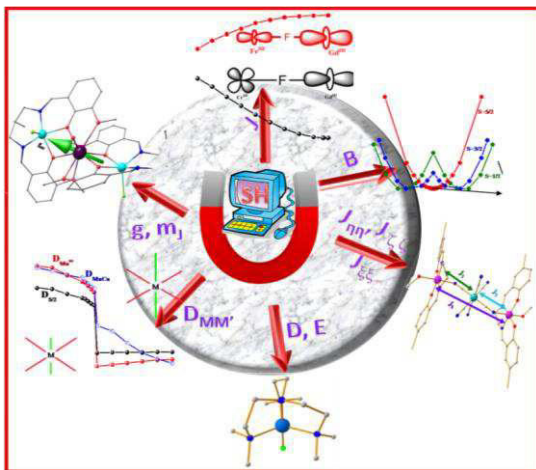
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## Are Single Molecule Magnets Predictable? Learning from Ab initio Calculations on Lanthanide and Transition Metal Molecular Magnets

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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>



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

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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.

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

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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

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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].

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## The method of increments applied to weakly bound systems

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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].

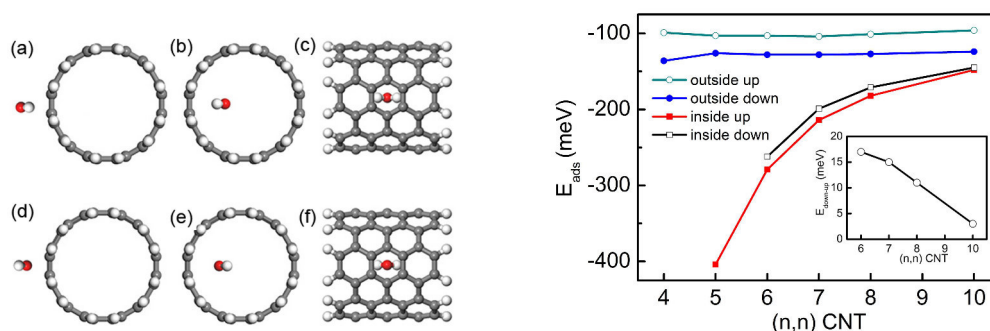


Figure 1: Curvature dependence of the adsorption energy of water inside and outside an arm-chair carbon nanotube, calculated at the LCCSD(T) level.

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## Physics-based intermolecular potentials for material design

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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.

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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].

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# 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>,  
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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.

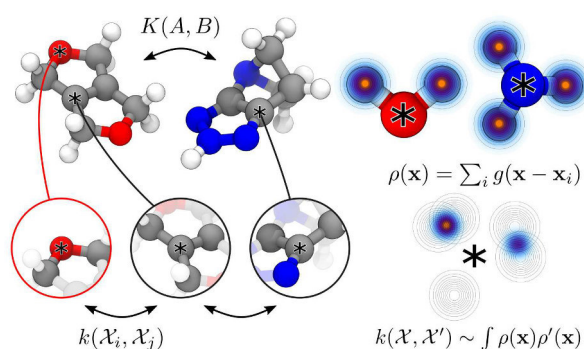


Figure 1: Machine-learning based on a mathematically-sound representation of chemical environments provides the basis for an universally-applicable framework to predict the properties of materials and molecules

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**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

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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.

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(\*) 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

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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.

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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!

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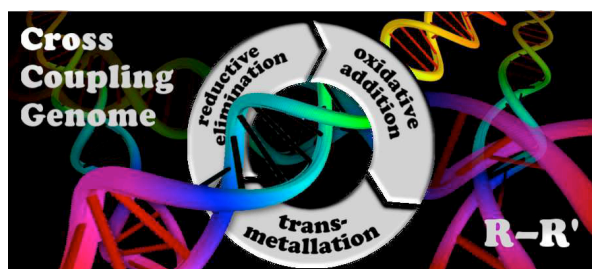
## Bringing Volcano Plots as a Tool to Understand and Predict Homogenous Catalysts

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

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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.



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## **"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>**

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**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.

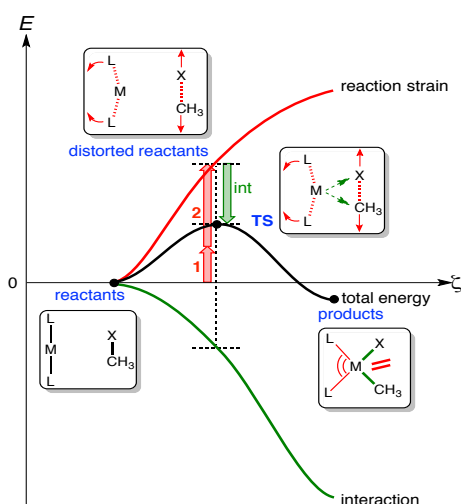
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## Rational Design of Chemical Reactions

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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.

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## Development and Applications of Direct Dynamics Simulations

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<sup>1</sup>*Department of Chemistry and Biochemistry, Texas Tech University,  
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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.

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## Refining First-Principles Photo-Electrocatalysis

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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

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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.

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

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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.

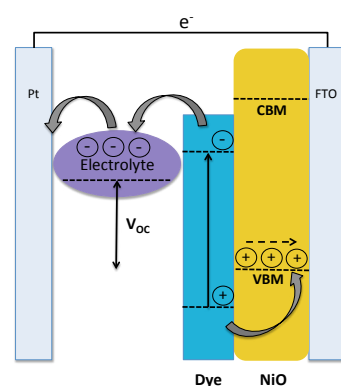


Figure 1. Operational mechanism of a p-type DSC

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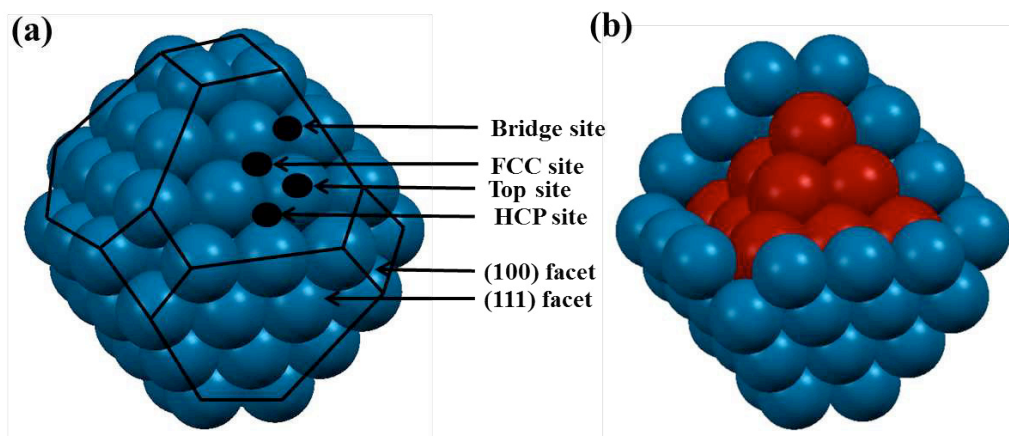
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## Atomistic Modeling of Nanocluster Based Electrodes for Fuel Cell Applications

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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.



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## Understanding Intramolecular Singlet Fission Process in D-A Polymer From Correlated Wavefunction Perspective

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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. Targeting 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.

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## Exchange-correlation functionals from density scaling

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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.

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## Self-interaction Corrected Energy Functional Applied to Molecules and Solids

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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.

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## Combining density-functional theory and many-body methods

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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].

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## Dispersion interactions from the exchange-hole dipole moment

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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

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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.

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## Multi-scale methods for electron and exciton transfer in biological and organic materials

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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

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## **Solvation and solvent-mediated driving forces: Spatially resolved information from detailed atomistic trajectories**

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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

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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.

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## Efficient approximation of configurational entropy changes upon binding to biomolecules

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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.

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## Theoretical determination of properties of helium for new temperature and pressure standards

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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.

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## Spontaneous generation of radicals and design of anion sponges through Beryllium bonds

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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.

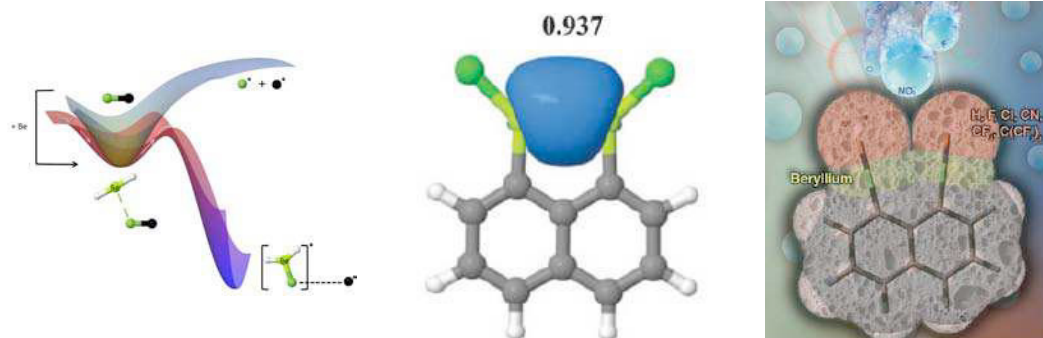


Figure 1. (a) Potential energy curves associated to the exergonic formation of radicals from  $\text{BeH}_2\text{FR}$  complexes. (b) one-electron localized MO and its population for 1,8-diBeCl-naphthalene radical anion. (c) 1,8-diBeX-naphthalene derivatives acting as anion sponges.

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## Improvements of Instanton Theory to Simulate Atom Tunneling in Astrochemical Reactions

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Jan Meisner<sup>1</sup>, Andreas Löhle<sup>1</sup>, April M. Cooper<sup>1</sup>, Alexander Denzel<sup>1</sup>,  
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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.

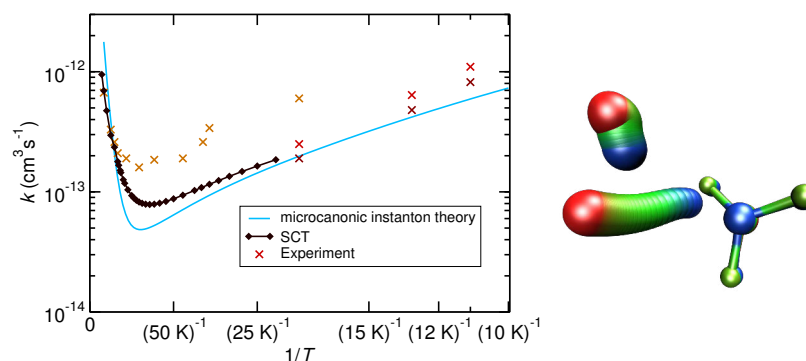


Fig.: Rate constants and instanton path for the reaction  $\text{NH}_3^+ + \text{H}_2 \rightarrow \text{NH}_4^+ + \text{H}$  [5].

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## Borophenes, Borospherenes, Boranes, 3D-Boron Allotropes and Boron-Rich Solids.

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**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.

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## On the accuracy of Coupled-Cluster-type methods describing excited states

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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.

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## 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.

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## Reliable DFT results with density correction

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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]

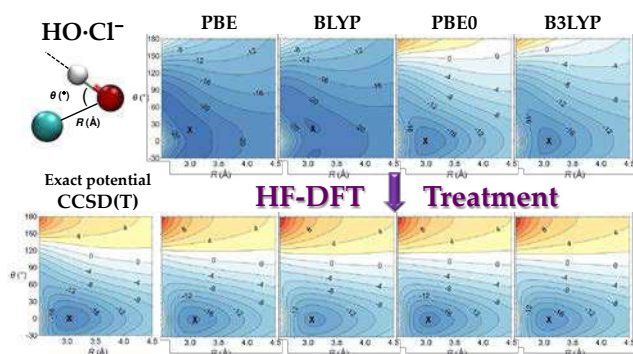


Fig. 1 Improvement using HF-DFT: Potential Energy Surface of HOCl-.

(top panel) self-consistent DFT results and (bottom panel) exact and HF-DFT results

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## Density-functional methods with the accuracy and wide applicability of high-level multireference approaches

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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.

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## Variational Principle for Partitioning Molecules into Atomic Contributions

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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

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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

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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

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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).

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**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*

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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.

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**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].

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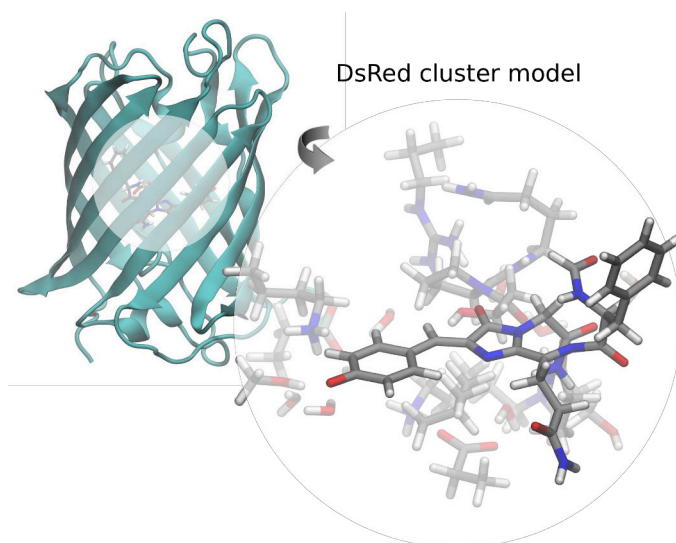
## Excited States in Complex Systems through Polarizable (Density) Embedding

**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.

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- [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>

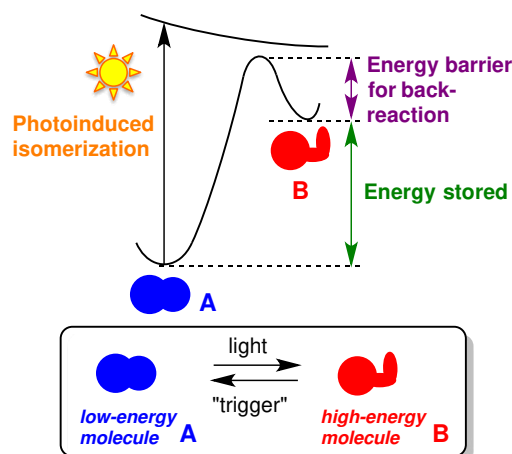
**A) Department of Chemistry, University of Copenhagen, Copenhagen, Denmark**

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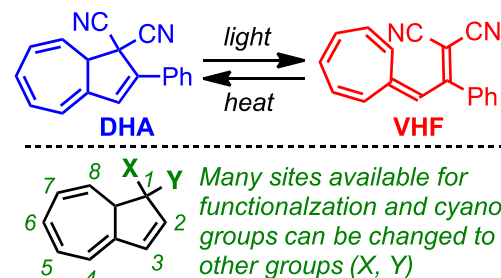
## Purpose of the Project

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**

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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

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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.

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## **The Algebraic Diagrammatic Construction - a versatile approach to excited electronic states, ionization potentials and electron affinities**

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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

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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.

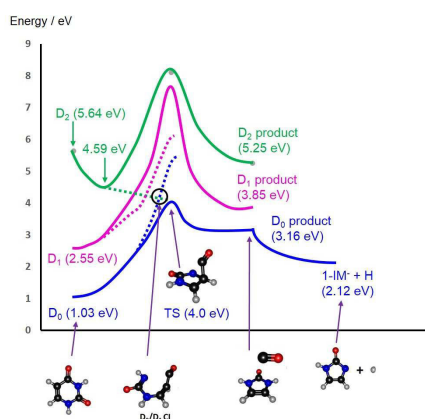


Figure 1: Schematic representation of the overall reaction paths showing the sequential elimination of CO and H from uracil<sup>-</sup> when LEE with energies around 5-6 eV attach to uracil.

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## First-Principles Exciton Models, with Application to Singlet Fission

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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].

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**Quantitative Molecular Orbital Theory**

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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.

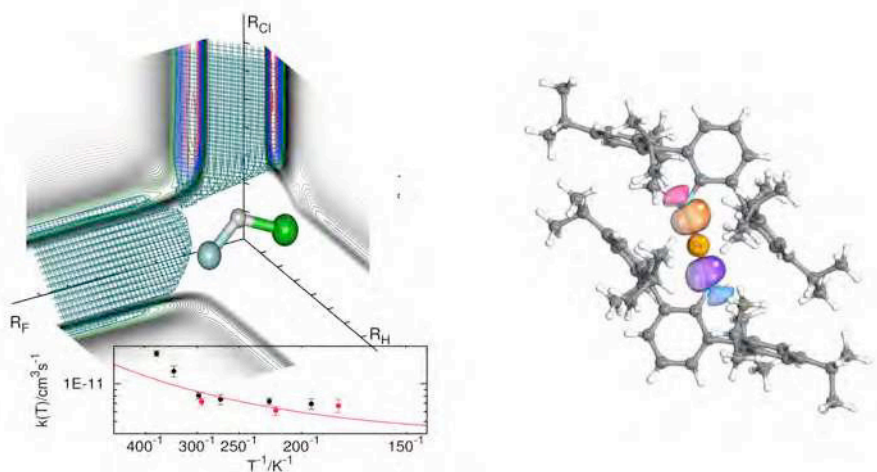
## Applications of internally contracted multireference coupled-cluster theory

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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.



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## Advances in Electronic Structure Methods for Strongly Correlated Systems and Condensed Phase Systems

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**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>

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## DMRG-externally-corrected local pair natural orbital based coupled cluster method

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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.

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## Tensor decomposition and coupled cluster theory

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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]

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## Nanosecond-Timescale Conformational Dynamics of Enzymes, and its Impact on Reaction Rates

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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:

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## Computer simulations of chemical reactions in solution

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### 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

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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.

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## How Native and Alien Metal Cations Bind ATP

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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].

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## A Multiscale Computational Investigation of SILP Catalysis: The Water-Gas Shift Reaction

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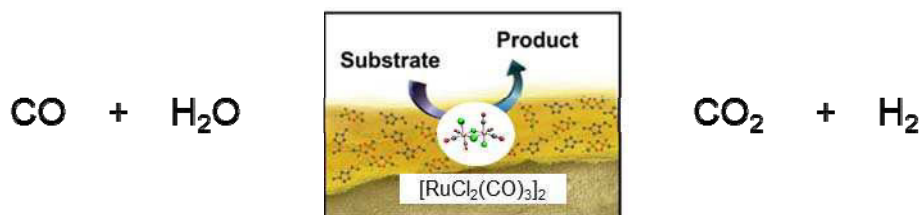
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The Water Gas-Shift reaction (WGSR) is a process which results in the conversion of CO and H<sub>2</sub>O into H<sub>2</sub> and CO<sub>2</sub>, usually in presence of a catalytic material. The abundance of water, the toxicity of carbon monoxide and 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.

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## Theory for the Entropy of Liquid Mixtures of Flexible Molecules

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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.

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## Entropy and enzyme catalysis

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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

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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].

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## Cell Penetration and Membrane Fusion: Two Sides of the Same Coin

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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

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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].

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## **Towards a Local Coupled Cluster Theory for Solids.**

**Marcel Nooijen, Mike Lecours<sup>1</sup> and Ondrej Demel<sup>2</sup>**

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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

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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].

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## Electronic Structure Calculations for Correlated Electron Materials: a Dynamical Mean Field Perspective

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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].

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## Affordable High Numerical Accuracy for Large Molecules and Materials from Numeric Atom-Centered Basis Functions

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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.

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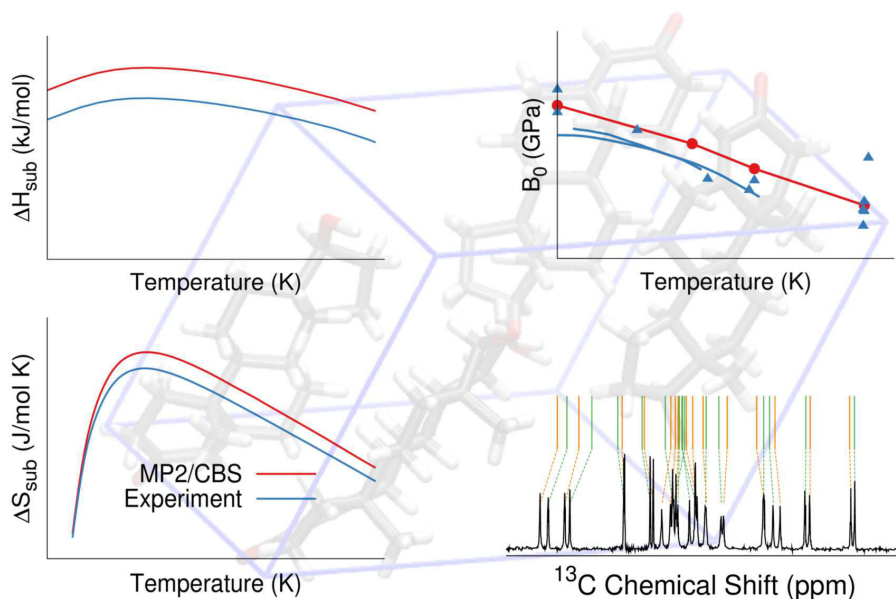


## *Ab initio* Molecular Crystallography: Aiding and Abetting Experiment

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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.



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# Many-body Green's function theory: Algebraic recursions, linked- and irreducible-diagram theorems, and general-order algorithms

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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 ( $\Delta MPn$ ,  $\lambda$ -variation, diagrammatic, the three recursions) are implemented, all giving the same results except one ( $\Delta MPn$ ). 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  $\Delta MPn$  and MBGF. We quantify the impact of the diagonal, frequency-independent, perturbation, and  $\Delta MPn$  approximations on the self-energy.

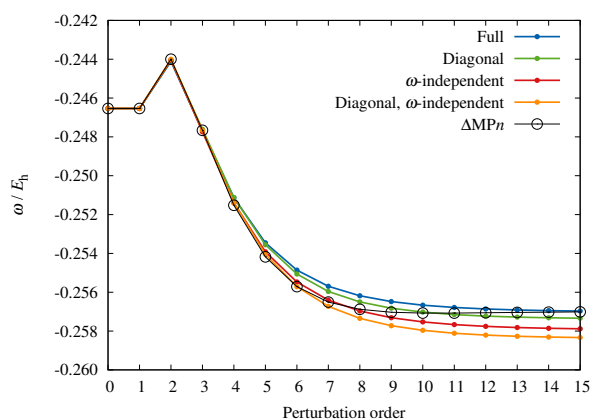


Figure 1: Convergence of the self-energy of HOMO of BH.

## 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>,  
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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?

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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.

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## Quasi-particles and satellites from a direct approach to the calculation of many-body Green's functions

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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.

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## Using the *GW* and Bethe-Salpeter Methods in Molecular Quantum Chemistry

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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.

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## **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

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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.

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***Ab initio* modeling of inter-molecular electronic transition processes  
in molecular aggregates**

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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.

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## Open-shell MC-srDFT -

**a new way to describe high-spin, low-spin, intermediate spin states and more**

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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.

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## Stochastic CC( $P;Q$ ) Theory: Converging High-Level Coupled-Cluster Energetics by Monte Carlo Sampling and Moment Expansions

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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.

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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.

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## Streamlining Coupled Cluster Response Theory

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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.

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## Towards investigating the optical properties of molecular and ionic crystals using multi-scale approaches

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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].

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## Developing Theoretical “Beamlines” for Modern Experiments

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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].

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**Electronic nonlinear spectroscopies:  
recent contributions of theory and computational science.**

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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.

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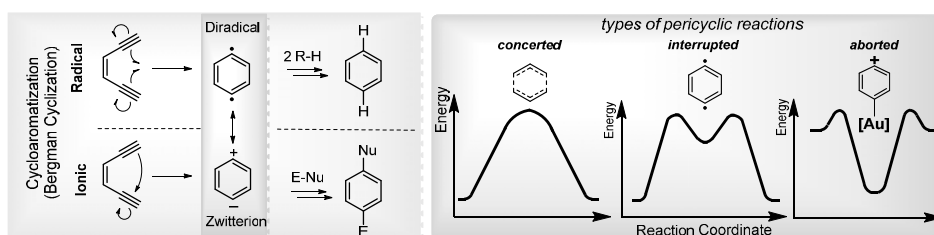


## Reinventing cycloaromatization reactions: the diradical /zwitterion dichotomy.

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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.

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## DFT study of the Au-C bond formation in gold implanted polyethylene.

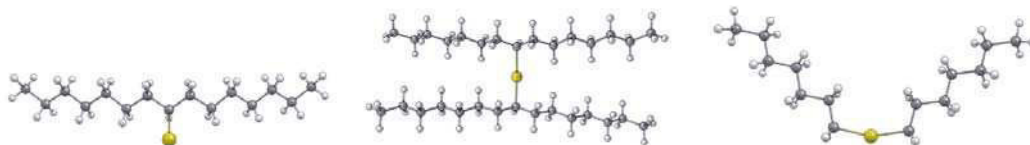
**Andrej Antušek<sup>1</sup>, Martin Blaško<sup>2</sup>, Miroslav Urban<sup>2</sup>, Pavol Noga<sup>1</sup>, Miloš Nenadovič<sup>3</sup>**

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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 Au<sup>+</sup>, Au and AuH with PE. Based on CCSD(T) benchmarks and previous studies on small Au<sub>n</sub> – 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 cm<sup>-1</sup>, (difficult to measure experimentally) and a broad 1000 - 1300 cm<sup>-1</sup> 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.

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## Astructural Molecules

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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.

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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].

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## Thermodynamic forces between plant cell wall constituents

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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.

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# INDUSTRY SYMPOSIUM



## **The Challenge of Chemical Thermodynamics and Kinetics for Real World Problems**

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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

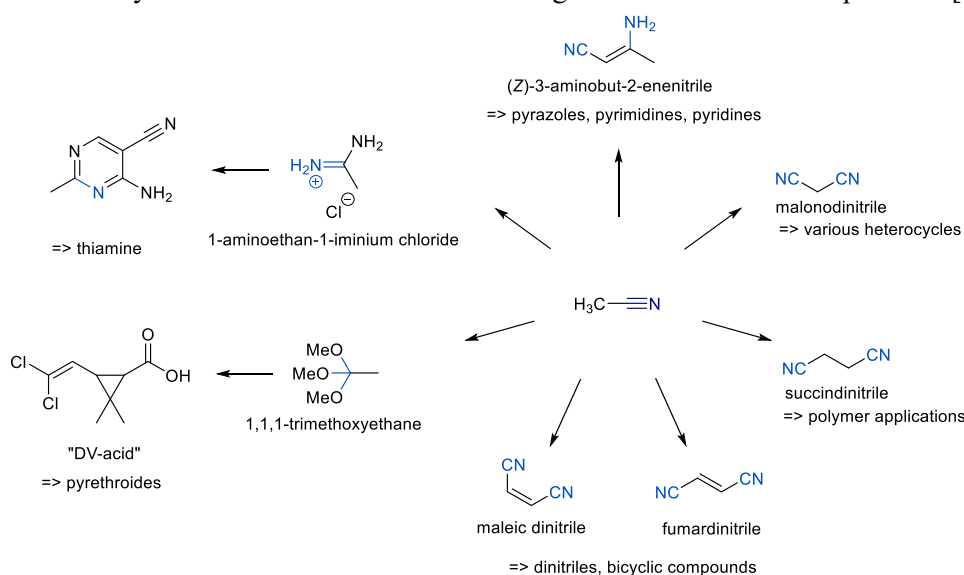
Hanns Jörg Freund<sup>2</sup>, Wolfgang Hieringer<sup>2</sup>, Nichola McCann<sup>1</sup>

Christoph Taeschler<sup>1</sup>, Peter Wasserscheid<sup>2</sup>, Gizem Zoludomir<sup>2</sup>

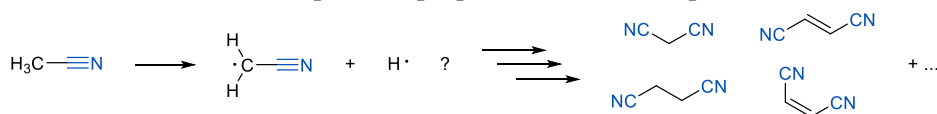
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Nitriles are essential intermediates used in the pharma, food and agrochemical industry as well as in material sciences. Acetonitrile is one basic example of this class of compounds that can not only serve as solvent but also as starting material for 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.



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## **Digging deep into binding modes in protein-ligand-complexes by quantum chemistry**

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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).  
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## **The use of scoring functions for structure-based drug discovery.**

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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

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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

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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.

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## **A Complete Reaction Mechanism for Standard and Fast Selective Catalytic Reduction of Nitrogen Oxides on low coverage VOx/TiO<sub>2</sub>(001) catalysts**

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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?”

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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.

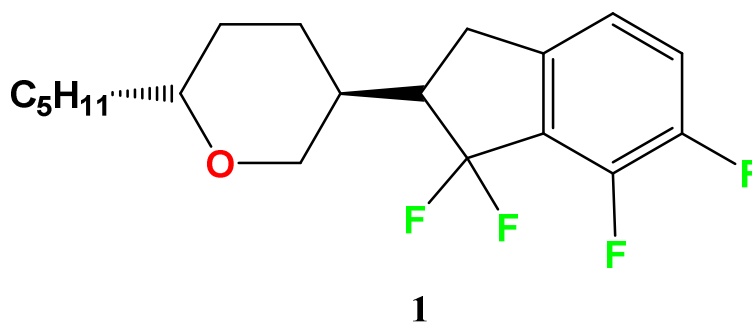
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## Increasing the Polarity of Liquid Crystals – Synthesis and Computations

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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**

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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.