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Modeling of Two-Dimensional (2D) Materials: Influence of Chemical Modifications

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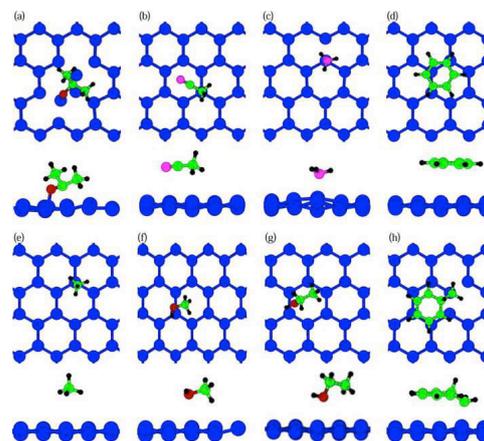
Quantum chemistry methods has reached maturity for a number of applications, allowing the non-specialist to use its tools in a productive manner, while being very much frontier areas with active research and development in other aspects. Amongst the latter is the computational **modeling of materials**. Materials modeling is a frontier area chiefly because of the *complexity* involved that is generally much higher than for more traditional studies on isolated molecules. Thus, it becomes essential to choose computational models that capture the essence of the physics and chemistry of the system of interest, yet remain tractable at an appropriate computational level.

The novel class of **2-dimensional (2D) materials** is placed at the interface of physics, chemistry and materials science. In order to fully exploit these unique materials, it is desirable to be able to *tune their properties*, such as the band gap. Chemistry plays a unique role in this respect, in that *chemical modifications* allow for the desired versatility in modifying properties. [1]

For a variety of 2D materials (silicene, germanene, stanene etc.) the influence on structure and electronic structure/ band structure of the choice of material, electric fields, and chemical substitutions (small organic molecules and heavy metals) have been studied. Both, **periodic boundary conditions** and **cluster models** have been applied. These types of computational models are complementary; each approach has its own unique advantages in characterizing materials.

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Organic molecules adsorbed onto silicene, top and side views. (Optimized structures; periodic calculations.) [2]

Local Correlation for Crystalline Solids: Dual Basis Sets by Projection in the Reciprocal Space.

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In the quantum-chemical treatment of crystalline solids, methods based on local atom-centered (gaussian) functions have certain advantages with respect to the plane wave approach, such as a more efficient screening of exchange integrals and consequently faster code for Hartree-Fock and hybrid functionals.

However, the problem of choosing a basis set is a major one, as: (i) molecular basis sets cannot be adopted as such, since they can give rise to linear dependencies and severe numerical instabilities in the infinite Ewald summations; (ii) standardized basis sets for solids do not exist, also because of the difficulty posed by the many different chemical situations possible in solids, as the same atomic species can be involved in ionic, covalent or metallic bonding situations. Such problems become even more severe when electron correlation methods are to be used, as large basis sets with diffuse functions are required.

In this contribution I will present a newly developed dual basis set scheme which allows to handle basis sets up to augmented quintuple-zeta at the post-HF level for crystalline solids. The approach is based on the extension to periodic systems of the dual basis set approach of Liang and Head-Gordon[1]. In essence, the SCF and localization are performed in a small basis and then the result is projected in a larger basis, where the correlation calculation is performed. The small basis is not required to be a subset of the large one, and no diagonalization of the Fock matrix in the large basis is needed. The only constraint is that the small basis is good enough (*e.g.* triple-zeta) to represent the occupied manifold. The method has been implemented in the CRYSCOR[2,3] program, which enables local correlation methods [4] for nonconducting crystalline solids.[5]

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Density functional theory for periodic systems using density fitting and continuous fast multipole method.

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An implementation of Kohn–Sham density functional theory using Gaussian-type orbitals as basis functions is reported that treats molecular and periodic systems of any dimensionality on an equal footing. Its key component is a combination of density fitting/resolution of identity (DF) approximation and continuous fast multipole method (CFMM) applied for the electronic Coulomb term [1,2]. The inherent limitations of DF, i.e., significant memory demand and $O(N^3)$ scaling with the system size are circumvented using a low-memory iterative density fitting (LMIDF) method [3]. It is based on a combination of CFMM and a preconditioned conjugate gradient solver applied for an iterative solution of the DF problem. Computational efficiency and favorable scaling behavior of our implementation approaching $O(N)$ for the formation of the Kohn–Sham matrix and calculation of energy gradients is demonstrated for various molecular and periodic systems, with the largest one containing several thousands of atoms.

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Adsorption of Glycerol and Dihydroxyacetone on CaO and MgO Surfaces
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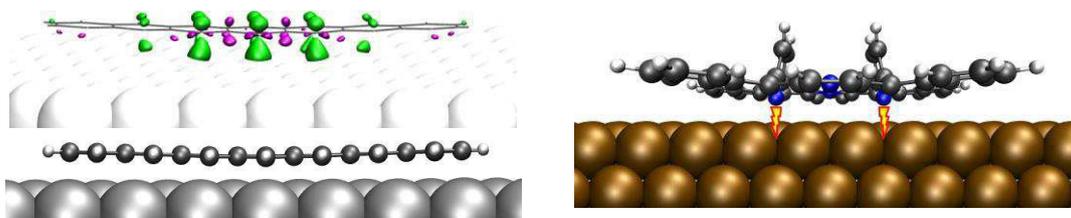
Glycerol, propanetriol, is one of the byproducts of biodiesel production. Due to the production of this polyalcohol exceeds its demand, strategies and alternatives of use of glycerol have been studied. Among these alternatives is the reform of glycerol with water vapor. Ab initio calculations of large cluster models have been performed in order to study glycerol and dihydroxyacetone adsorption at the three-fold coordinated adsorption site on pure MgO(001) and CaO surfaces. The geometric parameters of the adsorbed glycerol and dihydroxyacetone molecules were optimized to analyze binding energies, charge transfer, and the geometry through bonding distances, angles and dihedral. We have used Mulliken population analysis, electrostatic and natural atomic charge methods in order to evaluate charge distribution and transfer. The descriptors used are the electron populations of different types, and the number of the unpaired electrons of atom in ground state. The investigations on the model systems, for the adsorption of glycerol on MgO surface, showed that the striking directionality and affinity toward electron density donors. An NBO analysis indicates that the second-order orbital interaction plays an important role in stabilizing the directional bond.

Electronic Structure of Molecules at Metal Surfaces: Recent Results on Adsorbed Organic Molecules and Coordination Compounds

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Molecules adsorbed on atomically well-defined single-crystal metal surfaces are important building blocks for the bottom-up fabrication of functional nanostructures. In particular, adsorbed transition metal coordination compounds can exhibit interesting electronic properties at metal substrates. We use quantum chemical methods to analyze the electronic structure and spectroscopic properties of “large” organic molecules as well as coordination compounds on metal surfaces. In this contribution, we discuss recent examples of large oligophenylene rings [1] and acenes [2,3] as well as porphyrins [4,5] that are demonstrated to undergo unexpected electronic interactions with metal substrates.



In particular, we show that dispersion-corrected density functional theory calculations predict an unprecedented “inverted” structure of free-base porphyrin on a copper surface that is stabilized by a combination of electronic and van der Waals dispersion effects. [5] The metal surface is also shown to have a pronounced effect on the reactivity of the central metal in related coordination compounds.

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Explaining organic chemistry at surfaces with energy decomposition analysis

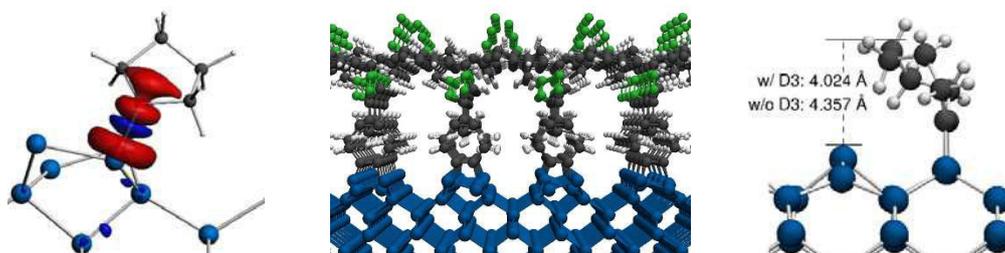
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Hybrid organic-inorganic interfaces are of current interest to the scientific community due to their large application range (e.g. OLEDs) but also for the unsolved questions regarding the details of charge transfer processes. An accurate description of interface structure, energetics and reactivity in the construction of these materials is therefore required.[1] Selected challenges for theory in this field are the understanding of (i) adsorption dynamics, (ii) surface bonding and (iii) on-surface reactivity of organic molecules.

We transferred the well-established energy decomposition analysis (EDA) method[2] from molecular systems to extended systems in the framework of density functional theory (pEDA)[3] to address these questions for organic functionalization of silicon surfaces.

By exploiting the advantages of both plane wave based approaches and local basis sets, we could shed light on the questions outlined above. The pEDA could resolve the question regarding the balance in surface bonding (physisorption/chemisorption) for the precursor state of ethene on Si(001), which is a prototype system for unsaturated organic adsorbates.[4] This investigation helped us to reveal the adsorption dynamics of cyclooctyne - a highly relevant interface building block where accurate description of dispersion interactions is required to explain the experimental observations.[5] The understanding for the on-surface reactivity of tetrahydrofuran, a model system for functionalized interface building blocks, could then ultimately be found in textbook organic chemistry after careful pEDA analysis.[6]



Surface bonding (left) and dispersion-induced bending (right) as two approaches to understand hybrid organic-inorganic interfaces (middle).

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Crystal structure prediction of inorganic-organic coordination polymers

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Atomic/molecular layer deposition (ALD/MLD) offers a highly controllable way to synthesize crystalline inorganic-organic coordination polymer (CP) thin films.[1] The fabricated materials could also be considered as metal-organic framework (MOF) thin films and they show a layered structure with inorganic-organic interfaces. We have recently investigated lithium aryloxide CP thin films fabricated by ALD/MLD (dilithium 1,4-benzenediolate, $\text{Li}_2[\text{p-C}_6\text{H}_4\text{O}_2]$).[2] The atomic-level structure of the CP thin films was solved by combining X-Ray diffraction and infrared spectroscopic studies with Density Functional Theory (DFT) calculations. In this case, a related bulk crystal structure facilitated the structure solution of the CP thin film. Using 2-aminoterephthalic acid (TPA-NH₂) as the organic building block also results in a crystalline CP thin film. However, no previous structural information from related bulk materials is available and the structure must be solved from scratch. We used the USPEX evolutionary crystal prediction approach together with DFT calculations to predict the atomic-level structure.[3] When we define the inorganic-organic CP as a pseudo-molecular structure with rigid building blocks, the USPEX structure search works in a highly efficient manner.

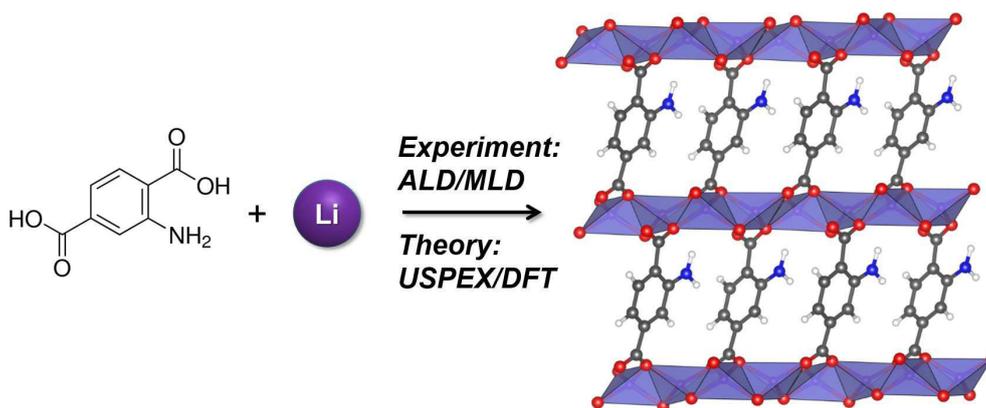


Figure 1: The predicted structure of $\text{Li}_2\text{-TP-NH}_2$ coordination polymer (USPEX/DFT)

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Transition Metal Doped Magnetic Zn₁₂S₁₂ Nanoparticles

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Nanoparticles of semiconducting materials are gaining attention due to their electronic, optical and catalytic properties. In this work, we focus on small hollow ZnS nanoclusters, concretely, on Zn₁₂S₁₂, characterized previously both theoretically [1] and experimentally [2]. The cavity inside the structure allows for the design of endohedral compounds resembling those of C₆₀. Transition metal doped compounds are very sound compounds due to their magnetic properties. However, previous studies [3, 4] predicted that the first-row TM@Zn₁₂S₁₂ endohedral compounds were unstable compared to the surface compounds, where the TM atom was located at the surface of the compound. The transition states connecting both structure families were calculated, and the estimated half-life of these compounds were seen to be very small for experimental detection.

However, in the mentioned previous works dispersion effects were not taken into account. In order to check for the influence of dispersion, several functionals were tested and compared to MP2, which is known to account for these effects. All these calculations were carried out using the def2-TZVPP basis set and a smaller DZP quality basis set combined with the SKBJ core potentials. PBE functional, using the empirical D3BJ term for dispersion, combined with the small basis set, compared pretty good with MP2/def2-TZVPP results, and were further used in this study. We recalculated the relative stability of the endohedral compounds vs the surface ones, and recalculated the barriers separating both minima, using the new methodology. Surprisingly, dispersion plays a very important role for such metals with the 4s3d shell half-filled or completely filled. From the magnetic point of view, the endohedral Cr(⁷S)@Zn₁₂S₁₂ compound was the most interesting case, since the endohedral compound was predicted to be the most stable one with a barrier towards the surface compound of roughly 20 kcal/mol. Further Ab Initio Born-Oppenheimer Molecular Dynamics simulations at 300K confirmed this stability. According to these results, we believe that these materials could be experimentally detectable, and would be very interesting compounds for applications such as spintronics.

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The name is bond - Hydrogen bond

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A new energy decomposition analysis method for periodic systems based on absolutely localized molecular orbitals is presented [1, 2]. In combination with an accurate and efficient technique to compute nuclear quantum effects and the previously developed second generation Car-Parrinello molecular dynamics approach [3, 4, 5], this not only allows for quantum molecular dynamics simulations on previously inaccessible time and length scales, but also provide unprecedented insights into the nature of hydrogen bonding between water molecules. The effectiveness of this new combined approach is demonstrated on liquid water, ice and the water/air interface [6]. Our simulations reveal that although a water molecule forms, on average, two strong donor and two strong acceptor bonds, there is a significant asymmetry in the energy of these contacts. We demonstrate that this asymmetry is a result of small instantaneous distortions of hydrogen bonds and show that the distinct features of vibrational and X-ray absorption spectra originate from molecules with high instantaneous asymmetry [7, 8]. Moreover, we found a striking correlation between the covalency of a hydrogen bond and the anisotropy of the proton magnetic shielding tensor, which enables to experimentally determine the strength and charge transfer of hydrogen bonding by NMR [9].

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High-throughput screening of drug-membrane thermodynamics

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The partitioning of small molecules in cell membranes—a key parameter for pharmaceutical applications—typically relies on experimentally-available bulk partitioning coefficients. Computer simulations provide a structural resolution of the insertion thermodynamics via the potential of mean force, but require significant sampling at the atomistic level. Here, we introduce high-throughput coarse-grained molecular dynamics simulations to screen thermodynamic properties. This application of physics-based models in a large-scale study of small molecules establishes linear relationships between partitioning coefficients and key features of the potential of mean force. This allows us to predict the structure of the insertion from bulk experimental measurements for more than 400,000 compounds. The potential of mean force hereby becomes an easily accessible quantity—already recognized for its high predictability of certain properties, e.g., passive permeation. Further, we demonstrate how coarse graining helps reduce the size of chemical space, enabling a hierarchical approach to screening small molecules.

New insights into nitrogenase: QM/MM broken-symmetry DFT studies of FeMoco and model compounds

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Nitrogenase is one of the most fascinating enzymes in Nature, being responsible for all biological nitrogen reduction. Despite decades of research it remains the enzyme in bioinorganic chemistry whose mechanism is the most poorly understood. The MoFe protein of nitrogenase contains 2 metal-sulfur clusters: the P-cluster that receives electrons from the Fe protein and shuttles them to FeMoco, an iron-molybdenum-sulfur cluster where N₂ reduction takes place. The resting state of FeMoco (E₀) has been characterized by crystallography, multiple spectroscopic techniques (XAS, Mössbauer, EPR) and theory (BS-DFT) and its molecular structure can be considered complete while the complex electronic structure, involving 8-metal spin coupling, delocalized electrons and weak metal-metal bonding, is not completely understood yet[1, 2, 3]. Much less is known about the other redox states (E₁-E₇) where no crystal structure is available and only limited spectroscopic data but hydrides have been proposed to be present in the early redox states. Theory can contribute a lot to this field although it is vital to compare computations to experimental data, given the imperfect theoretical tools being used and new experimental data on this system is greatly needed.

We have recently created QM/MM models of FeMoco and the P-cluster within a local version of Chemshell in order to go beyond the standard cluster modelling and properly incorporate protein environmental effects. The CHARMM36 forcefield has been used to describe the MM region while broken-symmetry DFT calculations using the TPSSh functional are used to describe the QM region using ORCA. The QM region has been systematically expanded and the convergence of the FeMoco geometry and redox potentials has been analyzed. Analysis of the resting state geometry of the FeMoco cluster reveals how it changes with different spin isomers that leads us to suggest one spin isomer is favored over others: an unusual case of spin coupling being observed in the molecular structure. Additionally we have taken first steps towards characterization of the E₁ and E₂ states and put forward new models for these states that are in agreement with the experimental data available.

Finally we present reaction mechanisms of structural model compounds of FeMoco that show catalysis of many of the same substrates as nitrogenase. The insight gained into these substrates may have relevance for the yet unknown mechanism of nitrogenase [2].

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Quantum Chemical Insights into Polymer Solvation and Hofmeister Effects in Aqueous and Non-Aqueous Environments

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We present quantum chemical simulations showing how inorganic salts influence the structure and solvation of polymers in ionic liquids (ILs) and water. Such specific ion or “Hofmeister” effects were established in the 1880s. Despite intense research, our understanding of their origins remains poor. We provide fundamental insights into the origins of specific ion effects, for both aqueous and non-aqueous solvents. We discuss two specific cases:

(1) **Poly(N-isopropylacrylamide) (PNIPAM) in water/salt mixtures.**

We show that the well-known “Hofmeister series” correlates with the relative strengths of the polymer-ion and ion-solvent interactions, and depend primarily on polarization effects (Figure 1a). We also show that trends in specific ion effects are observed without any solvent whatsoever.

(2) **Polyethylene oxide (PEO) in IL/salt mixtures.**

ILs such as propylammonium nitrate are “nanostructured” – the bulk structure features well-defined polar and non-polar domains that arise from the segregation of the ionic and neutral components of the constituent ions (Figure 1b). We show how added salts lead to a change in bulk IL nanostructure, and how, in turn, this change in solvent nanostructure influences the IL-polymer interactions and dissolved polymer structure [1-2].

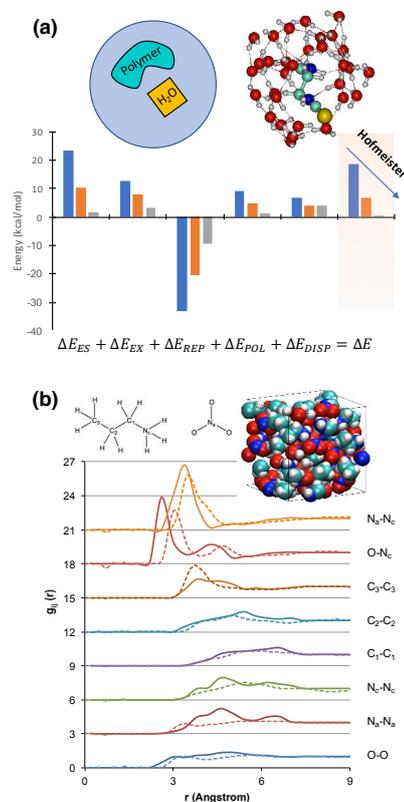


Figure 1. (a) LMOEDA analysis (M06-2X/aug-cc-pVTZ) reveals energetic origins of Hofmeister effects in water. (b) DFTB3-D/MD simulations show nanostructure in ILs and influence of dissolved salts.

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The Past, Present, and Future of Q2MM

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The further develop of the Quantum Guided Molecular Mechanics (Q2MM) method [1] is presented. Q2MM allows the rapid parameterization of accurate and reaction specific transition state force fields (TSFF) using the approach shown in Fig. 1, left. These TSFFs can be used for fast virtual screening of ligands in enantioselective catalysis (Fig 1, right). The Q2MM and virtual screening codes as well as the TSFFs are available to the community free of charge at github.com/q2mm

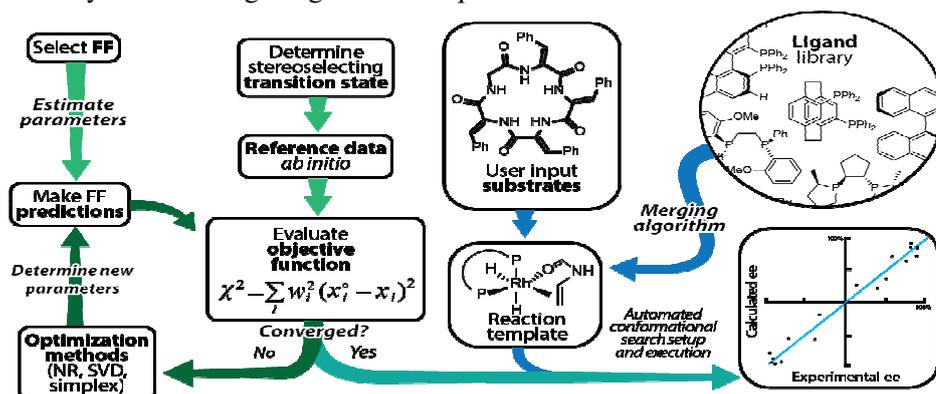
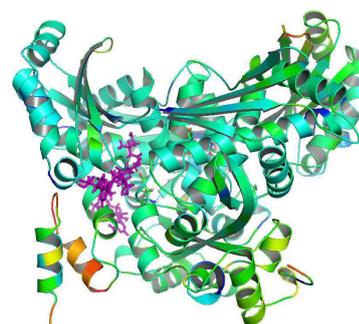


Figure 1: Flow scheme for generation of TSFF by Q2MM and application to virtual screening of ligands for enantioselective catalysis.

Application of Q2MM to biomolecular systems such as HMG CoA Reductase (HMGR, Fig 2) is an attractive alternative to QM/MM approaches because it enables long time scale simulations at the transition state, allowing the protein to sample the conformational space and providing insights into the large-scale protein movement that contribute to catalysis



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Figure 2: 20 μ s simulation of hydride transfer TS of HMGR

Hybrid Molecular Dynamics - hydrodynamics modelling of liquid solutions: whole virus at atomistic resolution

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Our novel methodology for modelling liquid molecular systems at very different space and time scales simultaneously with consistent transition between the scales is described. Regions of atomistic representation of the liquid of arbitrary shape and time evolution coexist with fluctuating hydrodynamics environment which in turn is coupled to macroscopic hydrodynamics at larger scales. In the model, the hydrodynamics description is used as an effective boundary condition to close the molecular dynamics solution without resorting to standard periodic boundary conditions. A nominally two-phase liquid model is considered as a representation of the same chemical substance. The ‘phases’ are immersed into each other as ‘fine grains’, the surface tension effects are irrelevant, and both ‘phases’ simultaneously occupy the same control volume. The partial concentrations of the MD ‘phase’ and the hydrodynamics ‘phase’ are equal to s and $1-s$, respectively, where s is a parameter of the model $0 \leq s \leq 1$. s is a user-defined function of space and time which controls how much atomistic information is required in a particular region of the simulation domain. The approach is implemented in a popular Molecular Dynamics package GROMACS.

As an example, a virus PCV2 is modelled at all-atom resolution for the protein shell of the virus, surrounded by a layer of atomistic water (any model of water such as TIP3P, SPC, etc can be used) that gradually changes to hydrodynamic continuum away from the virus. We analyse the connection between the number of ions inside an empty capsid of PCV2 virus and its stability. We compare the crystallographic structures of the capsids with unresolved N-termini and without them at physiological conditions and show that the structure is preserved. We find that the chloride ions play a key role in the stability of the capsid. A low number of chloride ions results in loss of the native icosahedral symmetry, while an optimal number of chloride ions creates a neutralising layer next to the positively charged inner surface of the capsid. Understanding the dependence of the capsid stability on the distribution of the ions will help clarify the details of the viral life cycle that is ultimately connected to the role of packaged viral genome inside the capsid.

Reduced point charge models of proteins - Influence of protein-solvent interactions

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We investigate the influence of various solvent models on the structural stability and the protein-water interface of three Ubiquitin complexes (PDB access codes: 1Q0W, 2MBB, 2G3Q) modelled using Amber99sb with two different point charge distributions. A previously developed reduced point charge model (RPCM) [1], where each amino acid residue is described by a limited number of point charges, is tested and compared to its all-atom (AA) version. The complexes are solvated in TIP4P-Ew or TIP3P water molecules, involving either a correction of the Lennard-Jones protein- O_{water} interaction parameters [2] or the coarse-grain SIRAH water description [3]. Molecular Dynamics (MD) simulation conditions are first refined for complex 1Q0W, whose ligand is a single helix structure that has the ability to bend due to a low α -propensity region occurring in its amino acid sequence. Results are further confirmed by MD simulations carried out on complexes 2MBB and 2G3Q.

MD results show that the best agreements between the RPCM and AA models are obtained when using (i) the TIP4P-Ew water force field (FF) with a correction factor $\gamma = 0.7$ or (ii) the hybrid TIP3P/SIRAH FF with a sufficiently large box size and a molecule/bead ratio of 1.2 to 1.4. At the RPCM level, a decrease in γ or the inclusion of SIRAH particles allows to weaken the protein-solvent interactions. It results in a slight collapse of the protein structure and a less dense hydration shell, thus involving a decrease in the protein-water and water-water H-bonds. The dynamics of the surface protein atoms and of the water shell molecules is also slightly refrained, thus allowing to generate stable RPCM trajectories, at a reduced computational cost. Conversely, solvation conditions such as the uncorrected TIP4P-Ew FF and the TIP3P FF at $\gamma = 1.1$ proposed by Best *et al.* [2] favor the unfolding of protein RPCMs.

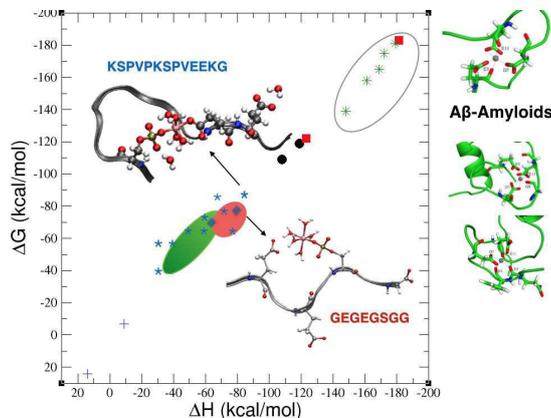
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Insights into the Structural Toxicity of Aluminum with Biomolecules, using a Computational Approach

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The increased bioavailability of aluminum due to human intervention, raises concerns on the toxic effects that this so far "excluded from biology" metal might have on living organisms. Consequently, the bioinorganic chemistry of aluminum has emerged as a very active field of research. However, the experimental determination of structure and affinities of Aluminum-Bioligand complexes is not without difficulties and theoretical methods have emerged as a fundamental tool to unveil aluminum biochemistry. In the present talk I will review some of the recent advances made by our group on this field. We will show how computational methods (DFT, QM/MM and classical molecular dynamic simulations) can be combined to determine the relative affinity of aluminum towards potential biological chelators. This can shed light on the type of biological compounds responsible for the so-called structural toxicity mechanism of aluminium.



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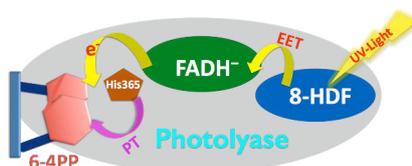
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Utilizing light for repair of light-induced DNA damages: the clever mode of action of DNA photolyases

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UV radiation triggers various chemical reactions in DNA such as intra-strand cross-linking between adjacent pyrimidines, causing genetic mutations. In fact, pyrimidine dimers are supposed to be the major players in the formation of skin cancer. DNA photolyases are enzymes initiating cleavage of mutagenic pyrimidine (6-4) pyrimidone photolesions by a photo-induced electron transfer from flavin adenine dinucleotide to the lesion.



Using hybrid quantum mechanical/molecular mechanical (QM/MM) dynamics, we have carried out series of simulations to completely map out the entire evolution of functional processes involved in the molecular mechanism of this important biological system. We have demonstrated that the electron catalyzing the repair is generated via an intermolecular Coulombic decay (ICD) process [1]. In fact, this is the first example for ICD as operating mechanism in a real biological system. We have presented the most energetically feasible electron-induced splitting mechanism in which the initial step is electron-coupled proton transfer from the protonated Histidine to the lesion, which proceeds simultaneously with intramolecular OH transfer along an oxetane-like transition state [2]. Our theoretical findings are in agreement with experimental time-resolved measurements [3]. The experimental spectroscopic signature of the detected 6-4PP intermediate is assigned theoretically to a specific molecular structure determining the operating molecular mechanism of the electron-induced restoration of (6-4) photolesions. Thereby, all pieces of the (6-4) photolesion repair puzzle are finally put together [4].

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Numerical exact MACGIC-QUAPI simulations of electron transfer dynamics in *Drosophila* cryptochrome (dCRY).

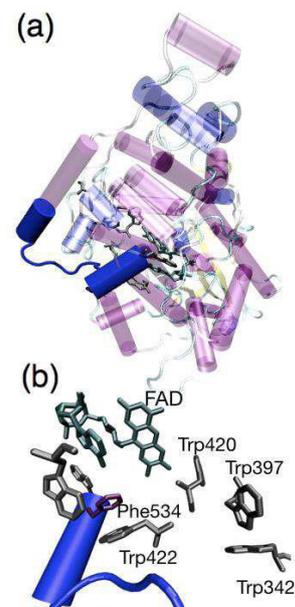
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The description of dissipative quantum dynamics subject to non-Markovian system-bath memory poses persistent challenges that arise in particular for systems of biological relevance, composed of multiple exciton states coupled to charge transfer states. Moreover the ‘sluggish’ protein environment imposes system-bath memory times of substantial length. The quasi-adiabatic propagator path integral (QUAPI) method [1] in principle allows for the numerical exact solution of such quantum dissipative dynamics but is limited by exponential scaling with growing memory time and system size.

We present a novel method, termed mask assisted coarse graining of influence coefficients (MACGIC)-QUAPI [2], that offers appealing computational savings due to an intermediate coarse grained representation of Feynman- Vernon influence coefficients, exploiting physical properties of system decoherence. The MACGIC-QUAPI method allows access to the regime of biological significant long-time system-bath memory (~100 propagation time steps) while retaining rapid convergence to exact QUAPI results.

Performance of the method is demonstrated for microscopically derived model Hamiltonians of multi-step electron transfer dynamics in dCRY, a flavoprotein that undergoes ultrafast charge separation upon electronic excitation (cf. Figure inlay). Site energies, inter-chromophore couplings and fluctuation dynamics were parametrized by first principles QM/MM (TD-DFT(BNL)/amber *ff14SB*) trajectory simulations. The simulated transfer dynamics is characterized by sub-picosecond initial charge separation that renders perturbative approaches inaccurate. Key protein residues responsible for an electrostatic control of active electron transfer pathways are identified and their influence on transfer dynamics will be discussed.



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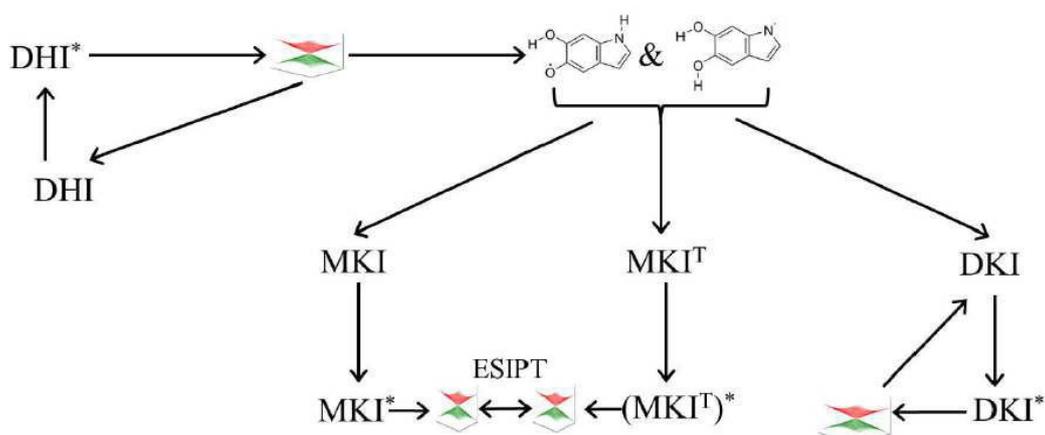
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Photoprotection Mechanism in Eumelanin

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Eumelanin, the functional polymer in human skin, forms a heterogeneous layered structure intrinsic to its broadband monotonic spectra. The inherent structural heterogeneity of eumelanin makes the photoprocesses very complex and diverse in nature. In this study, we re-create the potential energy surfaces of the low-lying excited states of the multiple monomeric forms of eumelanin constituents that play a prominent role in either photoprotection or photo-damage pathways.[1] Our results indicate a diverse set of pathways for the photoexcited species to relax back to the ground state, which depends on the specific monomeric form. Furthermore, the excited state reaction channels show the scope of extensive interconversion between the different monomers and therefore, we propose that the heterogeneity of eumelanin is key to its photoprotection capability.[2] In this talk, I will describe the photoprotection channels and the novel role of heterogeneity in the channels.



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Chemically-induced excited-state chemistry

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Excited-state chemistry is often initiated by irradiating with light (photo-chemistry) a molecular system. By this means, chemical processes that are not typical of ground-state chemistry can then take place. In addition to photons, a chemical reaction can also induce excited-state processes [1,2,3]. Wonderful examples in Nature are worms, bugs, and deep-sea creatures, which produce bioluminescence for several purposes such as communication, mating, or to escape from predators [1]. Furthermore, “dark” photoproducts, such as E/Z isomers or cyclobutane dimers can be produced via chemical reactions without light [2]. All these phenomena are based on internal conversions and inter-system crossings, which require multiconfigurational methods for an accurate description [4]. In this contribution, we will discuss in detail the mechanisms of chemically-induced excited-state chemistry and their relevance in biology, medicine, and nanotechnology.

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Exploiting excited-state aromaticity for the design of efficient light-driven rotary molecular motors

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The most developed class of synthetic rotary molecular motors available today are the overcrowded alkenes introduced by Chemistry Nobel Laureate Ben Feringa in 1999. For example, owing to a concerted experimental effort in the subsequent years [1] and complementary insights from in silico modeling [2–4], a variety of ways have been found to drastically reduce the free-energy barriers of the critical thermal steps that, at first, severely restricted the performance of these motors. Unfortunately, however, there has not been a similar progress in improving the rather low (20–30%) quantum yields (QYs) of the photoisomerizations that actually power the rotary motion of overcrowded-alkene motors. In this light, we and other research groups have recently shown by means of non-adiabatic molecular dynamics (NAMD) simulations that motors containing a protonated or alkylated Schiff base constitute a viable alternative to overcrowded-alkene motors [5–7], at least as far as the efficiency of the photochemical steps goes.

In this presentation, a new motor design that – in contrast to Schiff-base motors – lacks a cationic nitrogen center but instead features a moiety that becomes aromatic in the photoactive excited state is proposed and evaluated based on NAMD simulations within the framework of multiconfigurational quantum chemistry. Remarkably, it is found that this design exhibits not only very high (~75%) quantum yields for the olefinic-bond *Z/E* photoisomerizations of one isomer into the other, but also a clear ~60% tendency for two consecutive photoisomerizations to produce a full 360° rotation. Such a tendency is a hallmark of a true rotary molecular motor. Furthermore, the two photoisomerizations are very fast, with associated excited-state lifetimes of about 200 fs only. Altogether, these results highlight the enormous but hitherto unexplored potential of exploiting excited-state aromaticity in the design of efficient light-driven rotary molecular motors.

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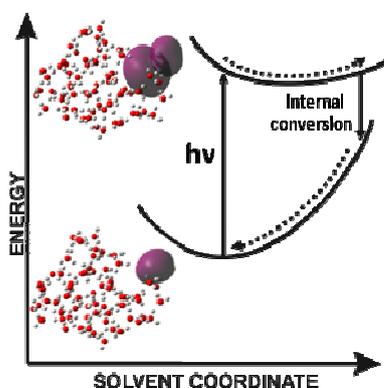
Electronic Excited State Lifetimes of Anionic Water Clusters: A Quantized Time Correlation Function Approach.

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Despite numerous studies of negatively charged water clusters, a controversy remains regarding the electron-binding motif, whether the excess charge center is localized at the cluster surface or within the interior. Here, we address this via interpretation of recent experimental time-resolved photoelectron imaging data obtained for relatively warm clusters [1]. Mixed quantum-classical dynamics simulations and subsequent analysis of the solvent and electronic relaxation phenomena is reported for a wide range of cluster sizes

(up to $n = 1000$) at $T \sim 200\text{K}$ [2]. The calculated excited state lifetimes for surface state clusters are in nearly quantitative agreement with the reported experimental results ($n \leq 200$). A minimum is predicted for $n \sim 150\text{-}200$, with an increase for larger clusters, approaching bulk state values from below. This implies that the electron resides in a surface-localized motif in all of these measured clusters, dominating at least up to a cluster size of 200.

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How to Control the Absorption Wavelength of Light Harvesting Complexes

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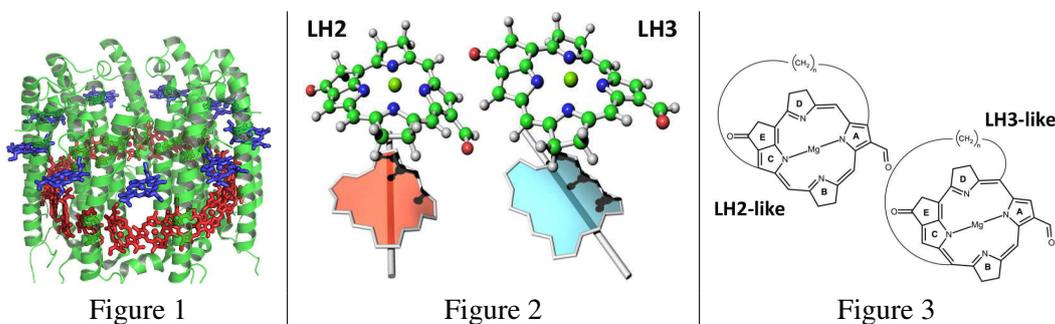
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Light-harvesting systems 2 and 3 (LH2 and LH3) protein–chromophores complexes from the purple bacterium *Rhodoblastus acidophilus* have identical overall arrangements of bacteriochlorophyll *a* (BChl) chromophores (Figure 1), while the proteins differ in their primary structures. The 18 BChls ring (shown in red in Figure 1) absorbs at 850 and 820 nm in LH2 and LH3, respectively.[1] While previously suggested that such difference is due to a rotation of the BChl acetyl moiety,[2] we recently found that such changes cannot be responsible for a 30 nm blue shift.[3] In this work, we use our previously established methodology [3, 4] to analyze BChls from crystal structures of LH2 and LH3, and uncover which feature is the real cause of the blue shift. Thus, we employ state-of-the-art MS-RASPT2//RASSCF and TD-DFT/PBE0 technologies to follow changes in excitation energies, and subsequently translate them into changes in simulated absorption spectra of the whole complex. We find that the absorption wavelength is controlled, largely, by the curvature of the BChl macrocycle ring (Figure 2). Therefore, the protein scaffolding is responsible, primarily, for setting up such curvature, thus controlling the absorption wavelength, and only secondarily for fine tuning it, through the acetyl moiety torsion. Such idea can also be applied to future synthetic chromophores (Figure 3).



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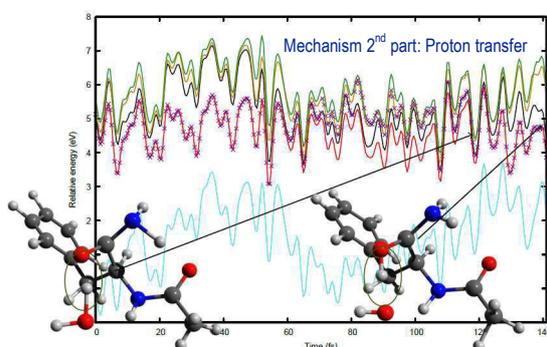
**Excited states deactivation in model proteins chains:
Nonadiabatic dynamics simulations and *ab initio* methods.**

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Abstract: Following UV absorption, many **biomolecular systems** are endowed with mechanisms of **excited-states deactivation** that ensure their **photochemical stability**. One of the major goals of our research is to investigate conformer-selective dynamics of biologically relevant molecular systems by an original innovative computational strategy in order to document the **basic physical phenomena** controlling the **lifetime** of excited states, highlighting the **link between electronic dynamics and structure**. This **innovative**



multi-step computational strategy allows to both characterize the first excited states of bio-relevant systems and model efficiently their potential energy surfaces, using, first, **nonadiabatic dynamics simulations** based on TDDFT (NA-TDDFT) to provide hints about the critical motions that drive the deactivation, which will then be **investigated at a better level** with two families of methods: i) the **standard approximate coupled cluster** singles and doubles method

(CC2) and ii) and **multireference (MRCI)** methods. **Developed** on small capped peptide models and always backed up by **key conformation-selective gas phase experiments** carried out in our team at several timescales,^{1,2} this innovative strategy is now applied to monohydrated capped peptides as well as capped dipeptides. We will present here the last results obtained on these systems. In addition, **benchmark of the CC2 method** on a set of model peptide chains (structure, energetic and vibrational frequencies of the first $\pi\pi^*$ excited state)^{3,4} as well as **assessment of the CC2 method validity** from comparison with **MRCI methods**⁵ will be also reported.

Keywords: Excited states computations, Photochemistry of biomolecules, Nonadiabatic dynamics, Size-extensive CC and MRCI linear scaling methods, TDDFT.

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First-Principles Molecular Dynamics Simulations on Ammonia Synthesis and Decomposition

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We report the first-principles molecular dynamics calculations on catalytic reactions of (i) ammonia formation from nitrogen and hydrogen gas mixtures and (ii) ammonia decomposition to hydrogen and nitrogen molecules. As a catalyst, we focus on Ru/MgO catalysts. We aim at revealing important reaction sites on Ru nano particles in the supported catalyst, the reaction mechanism, and a role of the catalyst support. The calculations were carried out using the density functional theory with the periodic boundary condition at finite temperature. The two types of chemical reactions were successfully carried out in several simulations. Figure 1 indicates a snap shot of one of simulations of ammonia formation. In the lecture, we will mainly discuss on surface topology playing an important role in each elementary reaction.

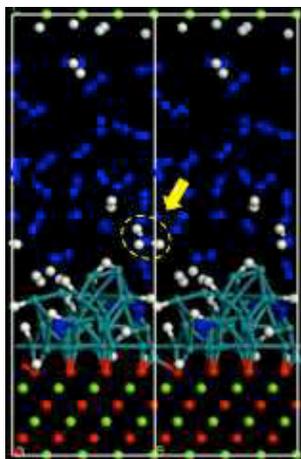


Figure: A snap shot of the ammonia formation simulation using the first-principles molecular dynamics method

Reaction-Path Bifurcation Analyses based on Valley-Ridge Transition and Global Reaction Route Mapping

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In theoretical chemistry, the "reaction path" concept has been utilized as a basic tool to provide an intuitive picture of the structural change as the reaction proceeds. The intrinsic reaction coordinate (IRC), defined as the minimum energy path connecting two minima and one transition state on the potential energy surface (PES) in mass-weighted coordinates, has been accepted as the reference reaction pathway for elementary reaction processes, and is used to discuss the reaction mechanism. It is known that the IRC sometimes becomes unstable with respect to a vibrational coordinate orthogonal to the IRC through valley-ridge inflection (VRI) or valley-ridge transition (VRT). The VRI or VRT causes a branching of the reaction pathways, and its dynamical aspect has been discussed in applications to some organic reactions. The reaction-path bifurcation has been studied from various viewpoints, i.e., a second-order Jahn-Teller effect [1], an attempt to define a bifurcating pathway [2,3], isotope effects [4,5], totally-symmetric VRT [6], trifurcation [7,8], and bifurcation analyses on a global reaction route map [9,10]. In this presentation, I will discuss the significant roles of the totally-symmetric VRT [6], and introduce new analyses of the reaction-path bifurcation based on a global reaction route mapping [9,10].

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Retrosynthesis and Reaction Prediction with Deep Neural Networks

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In the recent years, Deep Learning with neural networks has transformed computer vision, speech processing (built in in all modern smartphones), and many other pattern recognition tasks. Earlier last year, a system based on neural networks has even beaten the world champion in Go, a strategic game far more complex than chess. Remarkably however, smart assistants are basically absent from the chemical lab.

In our work, we combine Deep Learning with the core concept of named reactions, or more generally, reaction types. Our model can learn overnight which are the most likely reactions to make a molecule for retrosynthesis, or under which reaction type the starting materials will likely react (Forward Reaction Prediction). The key point is that we train the machine with essentially the complete published knowledge of organic chemistry (>3.5 million reactions acquired from the Reaxys database). This allows our model to learn reactivity conflicts and the selectivity of transformations from data with an unprecedented precision. Before, this information had to be laboriously encoded by hand.

In the largest scale comparison of reaction prediction systems ever conducted, we show that our approach has a higher than 95% accuracy when allowed to suggest up to 10 different routes for a target molecule on a test set of around 1 million reactions. Furthermore, preliminary studies indicate that coupling the neural networks with modern tree search techniques, it outperforms traditional computational synthesis planning with handcoded heuristics.

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**Graph Theory Approach in Exploration of Reaction Path Networks:
Rh(I)BINAP-Catalyzed Isomerization of Allylic Amines**

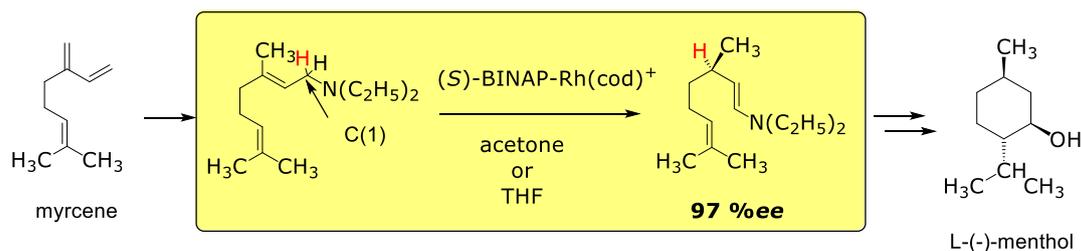
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Quantum chemical methods are very useful to analyze the reaction mechanisms for design and develop a new catalysis. Cationic Rh(I)-BINAP complex is used for asymmetric isomerization of allylic amines to enamines, which reaction is very important not only in organic synthesis but also in industry.¹ This catalyst is also used in hydrogenation of enamides. Our group previously reported the origin of excellent enantioselectivity by using QM/MM calculations for Rh(I)-BINAP catalyzed hydrogenation of enamides.² Whereas there are numerous reports to explain the enantioselectivity of the Rh(I)-catalyzed asymmetric hydrogenation reactions of enamides, only a few reports exist for the asymmetric isomerization of allylic amine. In this study, we explored the associative (with additional amine coordinate Rh-complex) and dissociative pathways by using Artificial Force Induced Reaction (AFIR) and ONIOM methods³ followed by Prim's method based on graph theory. Prim's algorithm is deterministic to select and visualize the most economical reaction pathways from the complicated reaction path network. The procedure and the results presented in this manuscript will provide a good example of a comprehensive reaction path search using the AFIR method combined with graph theory.⁴



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Automated searching method for reaction paths using molecular graphs and chemical reaction network

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Reaction intermediates including reactants and products are local minima composed of a reaction path, but their brute-force sampling is too demanding because of their large degrees of freedom. A stochastic sampling method inherently requires many trials no matter how effective it is, because it cannot guarantee 100% probability of finding a designated target structure within a finite number of samplings [1]. Therefore, a deterministic sampling method would be desirable. We are developing such a deterministic method based on molecular graphs [2]. Combinatorial sampling of molecular graphs gives a number of possible reaction intermediates. A chemical reaction network can be made by connecting the resultant molecules, followed by the kinetic analysis. Our method quickly estimates the activation energy of each elementary reaction with a reasonable accuracy based on molecular graph analysis. Therefore, very efficient searching for reaction paths is feasible as compared to other approaches resorting to transition state calculations. Our method predicts favorable reaction paths just from reactants and products in a fully automated fashion within a few hours on a single workstation. In this talk, we show the recent progress in this project with several examples that include famous organic reactions, complicated unimolecular reactions, and organometallic reactions.

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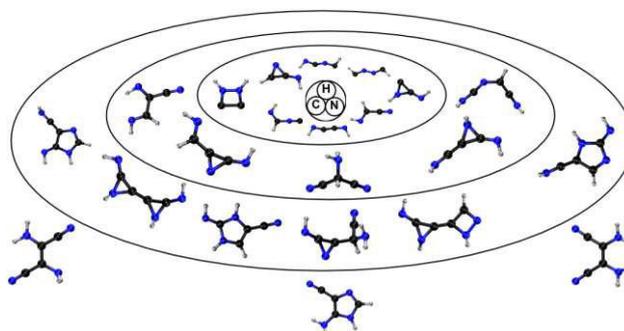
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Exploring Chemical Evolution using Tabu-Search Based Automated Reaction Finding Algorithm

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Understanding the chemical origin of life is an evergreen scientific interest. Oligomerization of hydrogen cyanide is proposed as one of the important pathways towards the prebiotic synthesis of elementary biomolecules. Theoretical and experimental studies suggest that HCN is a precursor to the formation of purines[1][2][3][4][5]. We used our Tabu-Search based automated reaction finding algorithm, implemented in PyAR software, [6] to explore the reaction pathways for the sequential addition of HCN or HNC to form the tetramer ($\text{H}_4\text{C}_4\text{N}_4$). We calculated the minimum energy path (MEP) connecting the minima using nudged elastic band (NEB) method for a selected set of products and optimized the TS. Our study led to several possible oligomers of HCN, some of the previously reported ones and many new geometries. We were able to explore the vast and complicated reaction network in the chemical space of HCN oligomerization process.



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Patterns of Moving Saddle Points in Catalysis and Mechanochemistry

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The description of a chemical process under mechanical stress or catalytic enhancement is performed by the generation of an effective potential energy surface (PES). Changes for minima and saddle points by the stress are described by Newton trajectories (NTs) on the original PES [1, 2]. Families of NTs define pulling corridors. If there are different exit saddles then there can exist saddles of index two, at least, in between. Then the case that a full pulling corridor crosses a saddle of index two, is the normal case. It leads to an intrinsic hysteresis of such pullings for the forward or the backward reaction, see Figure 1. Assuming such relations we can explain strange results in the literature, as well as the existence of roundabout corridors which can switch between different saddle points by a reversion of the direction. The findings concern the mechanochemistry of molecular systems under a mechanical load as well as the electrostatic force and can be extended to catalytic and enzymatic accelerated reactions. The ansatz includes both kinds of forces in a natural way without an extra modification.

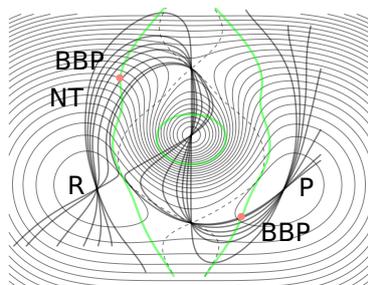


Figure 1: Bold NTs are good directions for a pulling force for successful pulling scenarios. An asymmetric chemical corridor by Newton trajectories (NT) from left to right minimum (R→P). The red points are the optimal barrier breakdown points (BBP).

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On the Theoretical Optimization of Properties.

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During the last few decades, theoretical calculations have become of increasing importance in providing supporting and complementary information to what is provided by experiment. On the one side, such studies can help in the interpretation of experimental results and, on the other side, through such calculations a first screening of systems can be carried through, ultimately allowing for reducing the synthetic work in the lab. In all those cases, the conventional approach is to start with a realistic structure for the system of interest whose stoichiometry is known, subsequently let the system relax to a close structure of a local total-energy minimum, and finally for this calculate the properties of interest.

The situation is different when essentially nothing is known about the structure of the system of interest. This is, e.g., the case for clusters and nanoparticles. For such systems, specialized theoretical methods that aim at identifying the global total-energy minima have to be applied. Another challenge is to identify molecular systems with optimal properties without specifying the stoichiometry.

In the present contribution we shall at first demonstrate how methods based on genetic algorithms can be used in optimizing the structure of nanoparticles. Subsequently, related methods will be used in identifying molecular systems with optimal properties, whereby, as a playground system, mixed Ge-Si clusters with optimal properties in solar-energy harvesting shall be identified. The purpose of this method, PooMa, is to provide useful information for experiments about interesting systems with predefined properties. It is based on many approximations and is not aimed at providing exact information on any detail. PooMa is developed as a simple, efficient method that does not rely on heavy computations or results from, e.g., high-throughput studies.



PooMa: M. Springborg, S. Kohaut, Y. Dong, and K. Huwig: *Mixed Si-Ge clusters, solar-energy harvesting, and inverse-design methods*, Comp. Theo. Chem. 1107 (2017) 14-22.

Carbon nanotubes immersed in superfluid helium: An incomplete flooding due to quantum effects

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Carbon-based nanoporous materials have attracted much attention due to their outstanding adsorption capabilities with potential applications for gas storage and separation. Among them, single-walled nanotubes stand out because of their one-dimensional flow channels, which can be adjusted in terms of helicity, channel length and diameter. A recent experiment of Ohba [1] of gas adsorption on single-walled carbon nanotubes at temperatures between 2 and 5 K reported a quenched propagation of helium through carbon nanotubes with diameters below 7 Å despite the small kinetic diameter of helium atoms. This unexpected outcome caught our interest and triggered a series of computational studies on the interaction of helium with carbon-based structures at ultracold temperatures. [2, 3]

After assessing the performance of a potential model for the He-nanotube interaction via *ab initio* calculations with DFT-based symmetry adapted perturbation theory, we apply orbital-free helium density functional theory to show that the counterintuitive experimental result is a consequence of the exceptional high zero-point energy of helium in comparison to the dwell-depth of the He-He interaction potential, and the tendency to form spatially separated layers of helium upon adsorption at lowest temperatures. We attribute this unusual finding to an even increased zero-point energy for helium atoms inside the nanotube due to the confinement, paired with the tendency to keep the overall helium distribution minimally distorted. This is particularly evident for nanotubes with helicity (8,8), which show an axial cavity even after full submersion into the He droplet. Helium filling factors are derived for a series of carbon nanotubes and compared to the available experimental data. Moreover, we propose a new additive pairwise potential model for the interaction of atoms and molecules to carbon materials. The performance of our model is demonstrated for the interaction of a single He atom or molecule of N₂ with carbon nanotubes [3].

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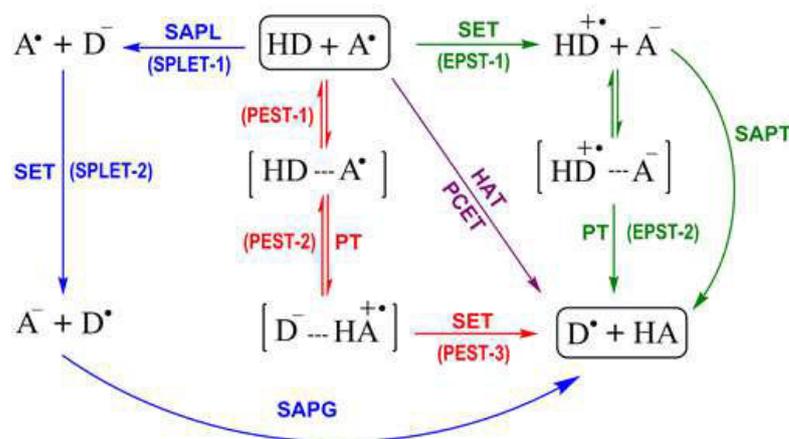
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The Role of Acid-Base Equilibria in Formal Hydrogen Transfer Reactions: Uric Acid with tryptophanyl radical

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The results presented in this work demonstrate the high complexity of chemical reactions involving species with multiple acid-base equilibria. For the study case investigated here, it was necessary to consider two radical species for tryptophan and the three fractions of uric acid¹ (all of them formed via acid-base equilibria) in order to properly reproduce the experimental results. At pH = 7.4, two main reaction mechanisms were identified: Proton-Electron Sequential Transfer (PEST)² and Sequential Proton Gain-Electron Transfer (SPGET). They –combined– account for more than 99 % of the overall reaction despite they involve minor species, i.e., H₃Ur and Trp⁺, respectively. The excellent agreement between the calculated overall rate constant and the experimental value seems to support this proposal. In addition, if only the dominant species at pH = 7.4 (H₂Ur⁻ and Trp_(-H)[•]) were considered, there would be a large discrepancy with the experimental value (about 4 orders of magnitude). This result also supports the finding that the key species in this case are not the most abundant ones. The influence of the pH on the kinetics of the investigated reaction was explored.

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Thermodynamics of the partition of Ibuprofen in a lipid bilayer

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Sodium ibuprofen, a Nonsteroidal Anti-Inflammatory Drug (NSAID) has been extensively used for decades as pain-killer, and reduction of fever and swelling. However, despite its therapeutic effects, there are several indications that ibuprofen has serious gastrolesive properties [1]. Diverse experimental and computational studies suggest that side effects produced by ibuprofen could be related to the interaction between the drug and the phospholipids that make up the cell membrane [1-3]. Nonetheless, the mechanism involved in the changes occurring at the membrane is not well understood.

In this work, we carry out a classical molecular dynamics simulation coupled to umbrella sampling to investigate, from the molecular perspective, how the cell membrane environment is affected when the NSAID is present. A model system was built. This includes one anionic ibuprofen molecule and a hydrated phospholipid bilayer, constituted by dimyristoylphosphatidylcholine (DMPC) and water molecules. The system was simulated using the CHARMM36 force field that considers all atoms. Our results suggest that ibuprofen prefers to reside at the interface between the lipid's polar head group and the hydrocarbon region and that entropy is the driving factor behind structural preferences.

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Automatization of the Nwat-MMGBSA method to rescore docking results in medium-throughput virtual screening applications

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Nwat-MMGBSA is a variant of MM-PB/GBSA based on the inclusion of a number of explicit water molecules that are the closest to the ligand in each frame of a molecular dynamics trajectory.[1] This method can increase the correlation between predicted and experimental binding energies in both ligand-receptor and protein-protein complexes,[2] compared to standard MM-GBSA. The protocol for molecular dynamic (MD) simulations, preparatory to subsequent Nwat-MMGBSA calculations, has now been optimized to maximize efficacy and efficiency, thus making the calculations practical in low-to-medium throughput virtual screenings. Three systems, penicillopepsin, HIV1-protease and BCL-XL, have been used as test cases. Calculations have been performed in triplicates on both classic HPC environments as well as on workstations equipped by GPU cards, evidencing no statistical differences in the results, but a dramatic decrease of the “cost per nanosecond” for the latter systems. With the optimized protocol, the whole calculation, from equilibration to production MD and subsequent Nwat-MMGBSA rescoring, averagely took about one hour per ligand using a single GPU.

A set of scripts for automatic structure based virtual screening, from library setup to docking and rescoring, has also been designed and tested within a retrospective virtual screening for inhibitors of the Rac1-Tiam1 protein-protein interaction. The screening library has been built using compounds experimentally tested, with a ratio between actives

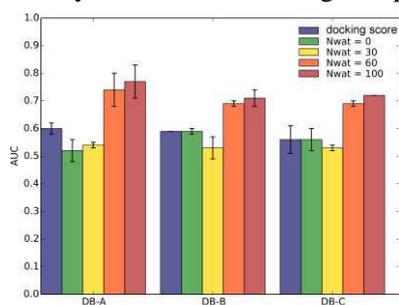


Figure 1

and real inactives of 1 to 10, and different protocols were used to process the library prior to docking (DB-A, DB-B and DB-C, Figure 1).

The results, summarized in Figure 1, confirmed the benefit of including explicit water molecules MM-GBSA calculation and the validity of Nwat-MMGBSA to rescore virtual screening results.

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Stressed Disulfide Bonds in Alkaline solution.

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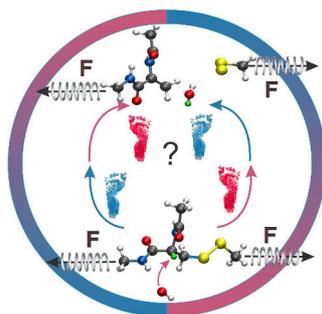
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Research on the impact of tensile forces on the disulfide bond reductions is crucial in order to understand the mechanisms by which disulfide switches regulate the activity of certain proteins.

By using *ab initio* molecular dynamics and metadynamics simulations in the condensed phase, we investigate the response of the β -elimination channel [1] of a disulfide bond reduction [2] in alkaline solution to mechanical stress. Our simulations reveal that the rate-determining first step of the reaction, which is the abstraction of a proton of the disulfide by an hydroxide ion, is not accelerated by external tensile forces. Even more interestingly, forces larger than ca. 1 nN are able to revert the order in which the steps of the β -elimination mechanism take place.



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Wetting Behavior of a Surface Decorated with Periodic Pillars

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Using Monte Carlo (MC) and molecular dynamics (MD) simulations, we examined the phase behavior of water confined between hydrophobic pillars by varying the size and shape of pillar and the inter-pillar spacing. The drying transition of water with decreasing the inter-pillar spacing is related to the Wenzel (WZ) to Cassie-Baxter (CB) transition of droplet. A continuum theory is developed for the inter-pillar spacing and pressure at which the CB to WZ transition occurs for a droplet deposited on a periodic array of pillars. With increasing interpillar spacing or pressure, the liquid on top of the domed pillars penetrated smoothly down into the gap between the pillars [1]. This wetting transition contrasts with that observed for the gap between rectangular or cylindrical pillars, where a liquid abruptly fills in the interpillar gap at a critical interpillar spacing or pressure. The gap between the domed pillars was more susceptible to the intrusion of the bulk liquid on top of the pillars, due to the open geometry of the gap between the domed pillars. Also, the liquid penetrating into the gap between the domed pillars was locally more fluctuating in density and compressible than that penetrating into the gap between square or cylindrical pillars. Simple analytic expressions of the critical spacing and pressure at which the wetting transition occurs for the domed pillars were derived using continuum theory. These continuum results agreed reasonably well with the present molecular simulations, even for pillars as small as a few nanometers in width. We also replot a large scale MD simulation study of the wettability of a gold surface engraved with (hemi)spherical cavities [2]. By increasing the depth of cavities, the contact angle (CA) of a water droplet on the surface was varied from a hydrophilic (69°) to a hydrophobic value ($>109^\circ$). The nonmonotonic behavior of the CA vs the depth of the cavities was consistent with the Cassie–Baxter theory, as found in the experiment by Abdelsalam et al. [3]. Depending on the depth of cavities, however, the droplet existed not only in the CB state, but also in the WZ or an intermediate state, where the cavities were penetrated partially by the droplet.

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Communication in proteins and protein-substrate complexes.

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Cellular function often need to be controlled at the molecular level, between molecules as well as within the same molecule or molecular complex. In allosteric processes information, i.e. a ligand binding, a reaction step, or a conformational change, taking place in one part of a molecule is propagated to another, distant part of the molecule, causing a response effect at that ('allo-steric') 'other-space'. Often, allosteric proteins are homo-oligomers where e.g. co-operative effects are due to substrate binding manifested in major conformational transitions between apo form, intermediate, and bound states. Communication within a protein is also observed to signal more local changes such as the protonation of a residue via e.g. re-wiring hydrogen-bonded networks, to sites distant from the protonation site. We use molecular dynamics simulations of proteins in different states of substrate binding or a reaction and analyse the communication between different parts of the protein-substrate complexes so as to reveal optimal communication paths. By employing different metrics for communication, we show that not only the strength and pathways of communication can be altered upon substrate binding but also the optimal means of communication.

include figures the usual way:



Figure 1: Optimal communication path between two residues in protein Cytocrome c Oxidase

Camphore's and Huperzine's adventures in Proteinland

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Biologically relevant ligands often migrate between solvent environments and enzymatic active sites to complete their physiological missions. Theoretical prediction of such transport paths is a challenging task [1,2]. Recently, we have developed an advanced computational scheme, based on memetic sampling (MS) during molecular dynamics simulations [3]. MS effectively predicts pathways of medium-size (27 – 36 atoms) ligands within crowded protein matrices. After dimensionality reduction of ligand-protein conformational space and calculating reaction coordinates [4], we selected ligand exit paths in two enzymatic systems: cytochrome P450cam-camphor and acetylcholine esterase-huperzine A. For these paths comprehensive metadynamics simulations [5 ,6] revealed free-energy barriers encountered by both ligands during the unbinding from their enzymatic active sites. Chemical nature of these rate-limiting regions was determined. Based on our thermodynamical data for wild type proteins, possible biological roles of selected point mutations are discussed.

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Conductance Switching in Expanded Porphyrins through Aromaticity and Topology Changes

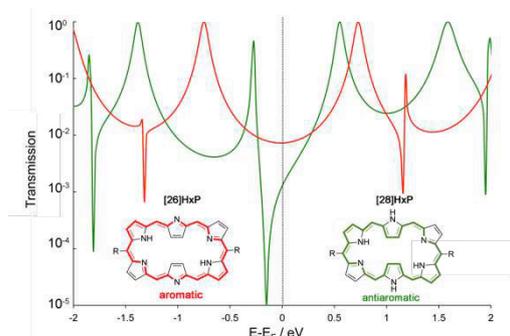
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Expanded porphyrins are flexible enough to switch between different π -conjugation topologies (Möbius, Hückel and twisted-Hückel) encoding distinct electronic properties and aromaticity.[1] Since the topological/aromaticity switch can be induced by different external stimuli, expanded porphyrins represent a promising platform to develop a novel type of molecular switches for molecular electronic devices.[2] In recent years, aromaticity emerged as the key concept determining the electronic, magnetic and photophysical properties of expanded porphyrins and accordingly, we proposed different methods to quantify the Hückel and Möbius aromaticity.[2,3]

In this work, we assess computationally the feasibility of conductance switches based on expanded porphyrins for the first time. Thus, the electron transport properties of single thiol-terminated expanded porphyrins bound to gold electrodes with different π -conjugation topologies and aromaticity were investigated using DFT methods and Green's function formalism. This study is particularly relevant since the link between transmission and key concepts in chemistry, such as aromaticity and polarizability, is

established allowing a chemical understanding of conductance.[4] Our results highlight the importance of the macrocyclic aromaticity on determining the transmission functions of the different states. Finally, we provide a set of qualitative rules to predict the presence of a quantum interference close to the Fermi level based on a simple model for Hückel and Möbius systems.



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Spin-dependent transport and magnetoresistance in metalloporphyrin-based supramolecular wires at room temperature

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Paramagnetic coordination compounds are appealing candidates for the design of single molecule devices if their spin degrees of freedom can be controlled by external stimuli (such as magnetic or electric fields). Complexes with two or more accessible and readable states can be envisioned as switches, which could be integrated to form more complex devices, as molecular transistors. Electronic conductance is a technologically convenient way to distinguish between binary states (“read”). Thus, magnetoresistance phenomena in molecular systems is a desired property to design molecular devices.

Recently, we observed huge magnetoresistance effects at room temperature in STM molecular junctions incorporating octahedral M^{II} complexes ($M = \text{Mn, Fe, Co, Ni}$).^[1,2] Electronic structure calculations clarified the role of electronic configuration of the transition metal in the observed behavior. These studies were extended for a family of metalloporphyrin molecular wires with M^{II} ($M : \text{Co, Ni, Cu and Zn}$) cations and the 5,15-diphenylporphyrin ligand (DPP). Co and Cu complexes exhibit magnetoresistance effects, independent of the current direction. Non-equilibrium Green Functions (NEGF) + DFT calculations [3] reproduce the experimental trend and help to assign the alpha channel as the responsible for electron transport.

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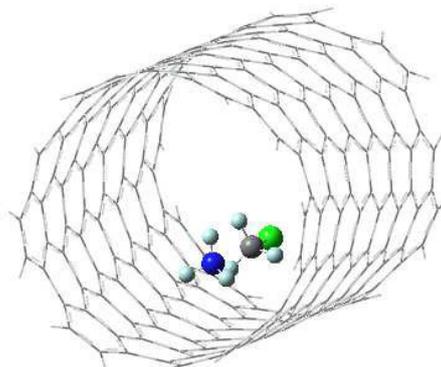
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Catalyzing chemical reactions inside carbon nanotubes

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Kinetic and thermodynamic properties of chemical reactions might be highly dependent on the surrounding medium. Recently, computational studies have shown that some S_N2 reactions suffer a significant increase in their rates when they occur inside single-walled carbon nanotubes (SWNTs) as compared to gas-phase.[1,2]



The present work is a systematic quantum mechanical DFT study of the effect of SWNT structure on the kinetics and thermodynamics of reacting systems. In particular, this work analyzes the impact of different types of SWNTs, namely *armchair*(n,n), *zigzag*(n,0) and *chiral*(n,m), on the Menshutkin S_N2 reaction between ammonia and chloromethane. Calculations have been performed with flexible and finite SWNT models at the M06-2X/6-31++G(d,p)/3-21G level.

All SWNTs considered in this work reduce significantly the activation energy, E_a , and the endothermicity, ΔH , of the reaction when compared to the gas-phase [3]. As nanotubes become wider, they all converge to the values 28 kcal.mol⁻¹ and 21 kcal.mol⁻¹, respectively for E_a and ΔH , which correspond to the reaction occurring near a graphene surface. On the other hand, as diameters decrease, a differentiation of the nanotubes is observed and each type of SWNT shows a different potential well, with chiral (6,4) SWNT (diameter 6.8 Å) exhibiting the lowest energy barrier, $E_a = 17.9$ kcal.mol⁻¹.

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Theoretical Calculations of Endohedral Fullerenes: From Chemical Bonding to Single-Molecule Switches

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Endohedral fullerenes have attracted wide interest due to their potential applications in science and technology, e.g. as MRI contrast agents, sensors, or molecular switches. We will present some of our recent findings in the area of **endohedral actinide fullerenes**, particularly the phenomenon of *unwilling* actinide-actinide bonding along $An_2@C_{80}$ ($An=Th-Cm$) series^[1] and theoretical investigations of the only Th fullerene, $Th@C_{84}$ (Figure 1).^[2]

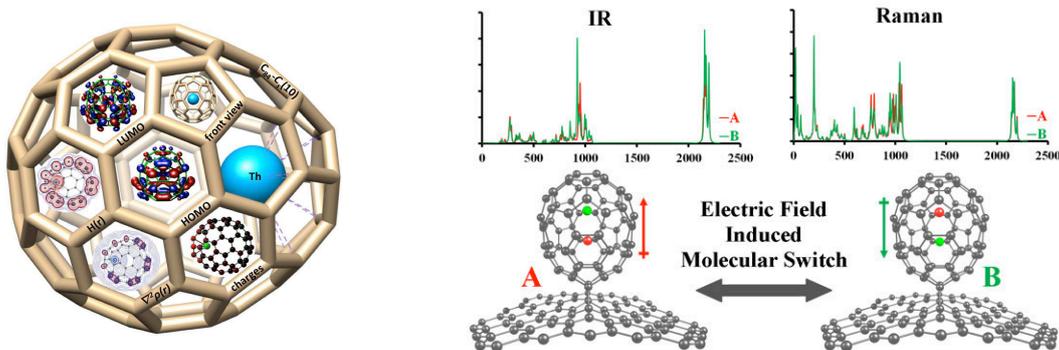


Figure 1: $Th@C_{84}$ (left) and model of endohedral single-molecule switch(right)

The proposal of a **two-state electric field-driven room-temperature single-molecule switch**^[3] based on a dipolar molecule enclosed inside ellipsoidal fullerene C_{70} (Figure 1) will be presented. We have shown that the two low-energy minima of the molecular dipole inside the C_{70} cage provide distinguishable molecular states of the system that can be switched by application of an external electric field. Such systems may provide base for high-density memory materials.

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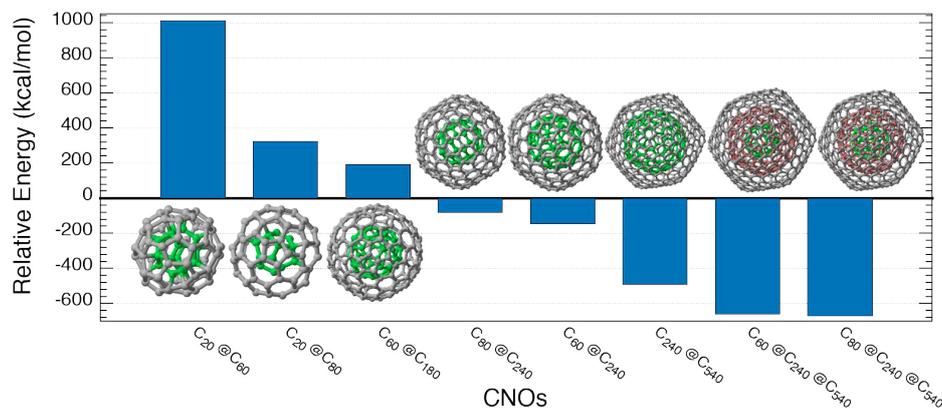
Structural and Electronic Properties of Carbon Nano-Onions

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We have investigated the double-layered carbon nano-onions (CNOs) $C_{20}@C_{60}$, $C_{20}@C_{80}$, $C_{60}@C_{180}$, $C_{60}@C_{240}$, $C_{80}@C_{240}$, and $C_{240}@C_{540}$ as well as their triple-layered analogues $C_{60}@C_{240}@C_{540}$, and $C_{80}@C_{240}@C_{540}$ with high-level electronic structure calculations. We were able to confirm earlier work that showed the free rotation of the inner Fullerene inside a CNO against the outer shell. However, we also show that this behaviour is an exception that only applies to the innermost Fullerene, and only in the case of good size-matching with the second shell of a CNO. We predict that strong dispersion interactions between individual layers of CNOs prevent this behaviour for all other shells. We show that the likely reason for this is the superadditivity of the interaction energies between individual shells; *i.e.* the total interaction energy of all shells is larger than the sum of all individual interaction energies between pairs of shells. We conjecture that this is also the reason for the experimentally observed growth of CNOs with many layers. We also show how the electronic states of individual Fullerenes are polarised, but essentially preserved in CNOs and how charge-transfer excitations between layers arise.



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Nickel effect on the spacing of 002 plane in a graphite-like structure

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Metal catalysts are commonly used for the growth of multi-walled carbon nanotubes (MWCNT). Some metal nanoparticles of the catalyst remain encapsulated in the MWCNT while other metal nanoparticles may be attached to the external wall of the MWCNT as an inorganic functionalization. Additionally, for some specific applications the presence metal nanoparticles with the MWCNT is desired. Either case, the interaction with metal nanoparticles affects the physicochemical properties of the nanotubes. For instance, it has been reported by using high-resolution transmission electron microscopy (HR-TEM) that the intershell spacing in MWCNT changes by the interaction with the metal [1]. The study of this interaction is important for improving our understanding of the system. The use of computational methods gives information at atomic and electronic level that is useful for explaining the phenomena that is involved. Therefore, as a first approximation to study the effect of nickel nanoparticles on the geometry of MWCNT, we evaluated the effect of a nickel surface on the spacing of graphene multilayers since similar interactions are expected for metal-MWCNT and it will give us a qualitative description of the interactions in this system. For this study we carried out DFT calculations using the SIESTA *ab initio* package [2]. A Ni(111) surface was used to simulate the interaction with graphene layers (from 1 to 5) in order to obtain information about the changes in the graphene spacing compared to the graphite spacing.

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Mechanistic investigation on the Pd-Catalyzed Hydrogenation of 1,6-Enynes: A DFT Approach.

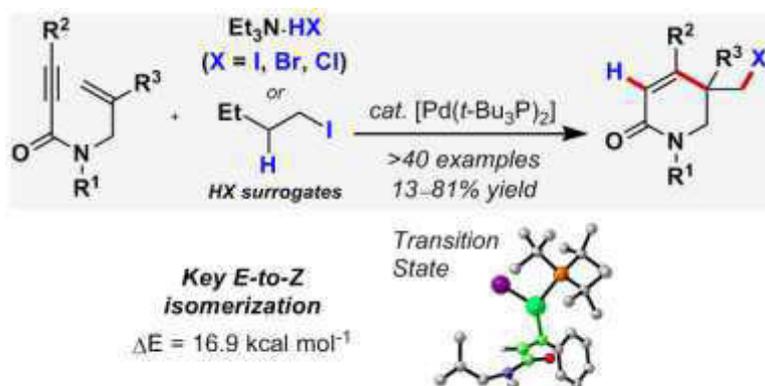
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Handling small molecules as H₂ or CO in metal catalyzed process is not trivial. The use of convenient hydrogen halide sources facilitates its use in the laboratory minimizing safety issues. Despite of these developments, their application on transition metal catalysis remains challenging [1]. Recent results on the group of Professor Mark Lautens accomplish Pd-catalyzed hydrogenation of enynes thanks to the use of ammonium halides salts as HX surrogates [2].

Herein, we present a comprehensive mechanistic investigation of this reaction by the use of Density Functional Theory (DFT). The initial alkyne insertion into the [Pd-H] species describes the observed selectivity while an unusual *E* to *Z* isomerization and the final halogen bond-forming reductive elimination steps reveal to be key processes and, therefore they will be discussed in detail.



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NOF-MP2: A global method for the electron correlation**Mario Piris^{1,2,3}**¹*Donostia International Physics Center (DIPC), 20018 Donostia, Spain*²*Euskal Herriko Unibertsitatea (UPV/EHU), P.K. 1072, 20080 Donostia, Spain*³*IKERBASQUE, Basque Foundation for Science, 48013 Bilbao, Spain*

In electronic structure theory, accurate solutions require a balanced treatment of both static (non-dynamic) and dynamic correlation. Nowadays, it is necessary to resort to multi-reference methods for correctly handling both types of correlation, however, these techniques are often expensive and demand prior knowledge of the system. On the other hand, single-reference correlation methods are well-established for dynamic correlation, but are unsatisfactory for systems with static correlation. In this presentation, a single-reference method is proposed capable of achieving both dynamic and static correlation even for those difficult cases in which both types of correlation are equally present.

The starting-point is a determinant wavefunction formed with natural orbitals obtained from a new interacting-pair model. The latter leads to a natural orbital functional (NOF) [1, 2] named PNOF7 capable of recovering the complete intra-pair, but only the static inter-pair correlation. Using the solution of the NOF, two new energy functionals are defined for both dynamic (E^{dyn}) and static (E^{sta}) correlation. E^{dyn} is derived from a modified second-order Møller-Plesset perturbation theory (MP2) [3], while E^{sta} is obtained from the static component of the PNOF7. Double counting is avoided by introducing the amount of static and dynamic correlation in each orbital as a function of its occupation. The total energy is represented by the sum $\tilde{E}_{hf} + E^{dyn} + E^{sta}$, where \tilde{E}_{hf} is the Hartree-Fock energy obtained with natural orbitals. The resulting working formulas allow for static and dynamic correlation to be achieved in one shot, as is the case in the standard single-reference perturbation theory.

The new procedure called NOF-MP2 is extraordinarily simple, has fifth order formal scaling of computational cost, and the property of size-consistency, essential for applying the method to extended systems. It is applied successfully to the homolytic dissociation of a selected set of diatomic molecules that encompass very dissimilar interactions ranging from weak to strong bonds, thus sweeping a wide range of interelectronic interactions and correlation regimes. The values obtained are in outstanding agreement with the experimental data.

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Recovering the flat plane condition in electronic structure theory at semi-local density functional theory cost

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Abstract: Piecewise linearity of the energy with respect to fractional electron removal or addition is a requirement of an electronic structure method that necessitates the presence of a derivative discontinuity at integer electron occupation. Semi-local density functional theory (DFT) exhibits instead convex behavior with electron removal or addition that has in recent years been corrected through incorporation of Hartree-Fock exchange either globally, in range-separated hybrids, or with Hubbard model corrections[1,2]. The additional requirement that the energy is invariant with respect to the spin of an electron in isoenergetic orbitals produces a tighter constraint known as the flat plane condition, wherein two linear planes meet at a fractional spin line seam. All approaches that have aimed to correct deviations from piecewise linearity in semi-local DFT are known to worsen already concave behavior on the fractional spin line, increasing static correlation error. We return to the original functional form of semi-local DFT errors along the flat plane and quantify the convexity along the fractional charge line and concavity along the fractional spin line. Analysis of the functional form of this error enables identification of the first no-computational-overhead corrections that can recover the flat plane condition within semi-local DFT. We compare these functional forms to more established approaches, including range-separated hybrid functionals and our earlier observations on how Hubbard model functionals[2] recover the derivative discontinuity. Finally, we conclude with some observations[3] on how recovery of the flat plane also impacts density properties and magnetic moments with respect to accurate correlated wavefunction theory references.

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Dressing the CI matrix with explicit correlation

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One of the most fundamental problem of conventional electronic structure methods is their slow energy convergence with respect to the size of the one-electron basis set. As pioneered by Kutzelnigg [1], one way to speed up the convergence of such methods is to introduce explicitly the correlation between electrons via a correlation factor f_{12} , leading to a prominent improvement of the energy convergence from $O(L^{-3})$ to $O(L^{-7})$ (where L is the maximum angular momentum of the one-electron basis). This gave birth to the so-called explicitly-correlated F12 methods which can achieve chemical accuracy for small organic molecules with relatively small Gaussian basis sets [2, 3].

In this talk, following Kutzelnigg's seminal idea, we propose to show that one can introduce the explicit correlation between electrons within the configuration interaction (CI) method via a dressing of the CI matrix [4]. This method, involving effective Hamiltonian theory, has been shown to be also successful in other scenario [5]. Compared to other explicitly-correlated methods, this dressing strategy has the advantage of introducing the explicit correlation at a low computational cost. The present idea is completely general and can be applied to any type of truncated, full, or even selected CI method [6]. Illustrative examples will be given on atomic and molecular systems.

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Performance of the Random Phase Approximation for first-row transition metal catalysis

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This presentation will give an overview of the performance of the (direct) random phase approximation method (RPA) for first-row transition metal catalysis. The random phase approximation gained considerable interest in recent years as an efficient method to obtain ground state correlation energies, particularly because of its seamless inclusion of non-covalent interactions. For main-group chemistry, its performance is similar to commonly used hybrid functionals with a Grimme-type dispersion correction [1]. RPA presents itself as a cost-efficient alternative to Møller-Plesset second order perturbation theory (MP2) for transition metal chemistry, an area where MP2 often fails and density functionals can produce mixed results. In this work, direct RPA based on a Kohn-Sham reference is benchmarked for a variety of properties of (mainly) first-row transition metal complexes, such as binding energies, reaction energies, and structural parameters [2]. High-level theory and experimental data are used as reference for the benchmark. Comparison is made to MP2 and several density functionals. Preliminary results are presented on C-CN bond activation through Nickel catalysis and Copper catalyzed trifluoromethylation of boronic acids. Overall, RPA outperforms MP2 and give results of the same quality as the best-performing commonly used density functionals. RPA is thus a strong alternative method for the study of transition metal chemistry.

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Highly accurate binding energies from the random phase approximation with singles corrections

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To make reliable predictions of physical and chemical properties of materials using theoretical methods, accurate schemes need to be used. The random phase approximation (RPA) to the correlation energy has emerged as a promising tool for this task. However, a general tendency to underbind has been observed for systems such as molecular solids or for adsorption. One of the ways that have been proposed to improve the accuracy of RPA are the so-called singles corrections, originally developed by Ren and coworkers [1] and later modified to improve their accuracy for systems with delocalised electrons [2]. Here we give a brief overview of this scheme and show the results of two applications to systems of wide interest. First, we present the results obtained for lattice energies of molecular solids [3]. The differences from the reference data are only about 4%. This makes RPA with singles currently the best scheme for the calculation of lattice energies within periodic boundary conditions. Moreover, the differences are similar or even lower than the errors of the reference data themselves. Second, we show the results for adsorption of small molecules in zeolites, which is another difficult test case for current density functional theory functionals. Here RPA with singles yields adsorption energies in a very good agreement with adsorption energies obtained with MP2 for most of the systems. However, for molecules with unsaturated bonds, the results of MP2 and RPA with singles differ. Reference quality CCSD(T) calculations on finite clusters show that in such cases it is RPA with singles that produces more accurate results. Together with the only cubic scaling of the RPA with singles, this makes it an extremely promising tool for the studies of extended systems, from molecular and atomic solids, over liquids, to interfaces.

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Separation of dynamic and nondynamic correlation

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The account of electron correlation and its efficient separation into dynamic and nondynamic parts plays a key role in the development of computational methods such as hybrid, range-separated[1] or local methods[2]. In this work we split the correlated part of the pair density into two correlation functions that account for nondynamic and dynamic correlation effects[3]. These functions are used in a two-electron model, giving rise to dynamic and nondynamic correlation functions that (i) depend only on natural orbitals and their occupancies, (ii) can be straightforwardly decomposed into orbital contributions, and (iii) admit a local form[4] (see Fig. 1). Finally, using the same strategy we present a separation of the Coulomb Hole into dynamic and nondynamic correlation. The long-range part of the dynamic-correlation hole can be used to identify dispersion interactions[5]. These expressions can aid in the development of density matrix functional theory (DMFT), density functional theory (DFT) and the development of local hybrid methods.

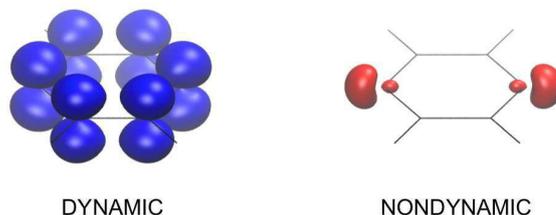


Figure 1: A real-space picture of electron correlation in *para*-benzyne.

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Describing non-covalent interactions in semiempirical QM methods: state of the art and future.

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Recent improvements in the description of noncovalent interactions in semiempirical quantum-mechanical methods (SQM, also comprising the density-functional tight-binding method, DFTB) enabled their application to large, complex systems including biomolecules. While this field is still dominated by molecular mechanics, SQM methods provide several advantages. Not only can they describe a wide range of effects of quantum-mechanical origin that are difficult to capture in classical forcefields, but they are also more practical because they do not require any system-specific parameterization. One of the successful applications of modern SQM methods is computer-aided drug design, where they may be used for large-scale calculations of protein--ligand interactions.[1]

The approximations involved in all the SQM methods lead to a rather poor description of non-covalent interactions. This can be addressed by specific corrections. The missing London dispersion can be added rather easily as a pairwise correction. The next most important issue is hydrogen bonding; here, we developed a series of corrections among which the latest version, D3H4 corrections for both PM6 and DFTB, became very successful.[2,3]

Nevertheless, these *a posteriori* corrections independent of the electronic structure have reached their limits and can hardly be improved. Careful analysis of the nature and origins of the errors in the description of hydrogen bonds[3] led us to a development of next generation of corrections for DFTB, named D3H5,[4] where the correction is integrated into the method and acts at the appropriate place, it is in the treatment of electrostatics. The D3H5 corrections improve over the previous versions not only in overall accuracy, but they also properly describe many-body effects that become extremely important in larger systems. With the latest corrections, the accuracy of the SQM methods becomes limited by other issues – I will also outline the steps needed to improve the methodology further.

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A new Spin Ratio Scaled MP2 (SRS-MP2) method for the prediction of intermolecular interactions

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Accurate prediction of intermolecular interactions is essential in understanding physicochemical properties of condensed systems such as molecular crystals as well as biological systems such as DNA and polymers. Intermolecular interactions vary in nature and strength from weak van der Waals interactions to strong hydrogen bonding. For a wavefunction-based method or a density function theory (DFT) functional method to be reliable, its accuracy needs to be within chemical accuracy for all types of interactions. Recent developments in DFT and Møller-Plesset (MP) perturbation theory have identified the importance of treating dispersion interactions accurately in order to achieve chemical accuracy.^{1,2} Recently we have shown that the original modification of the second order Møller-Plesset (MP) perturbation theory by scaling the opposite-spin (OS) and same-spin (SS) components of correlation energy can be successfully extended to studying intermolecular complexes.³ We have identified that the ratio of the opposite spin component to same-spin component when applied to correlation interaction energy, $\epsilon_{\Delta s}$, falls into a narrow range of 0.1 to 1.6, thus requiring the separation of intermolecular complexes into two groups: 1) $\epsilon_{\Delta s} < 1$ and 2) $\epsilon_{\Delta s} \geq 1$. A separate set of scaling coefficients, c_{OS} and c_{SS} , were obtained for both groups and accounted for basis set superposition error.⁴ The coefficients were initially fitted to intermolecular complexes of the well-known S22,⁵ S66⁶ and IL174⁷ databases consisting of both ionic and neutral complexes. The newly developed method, termed spin ratio scaled MP2 (SRS-MP2), shows remarkable accuracy with a relatively small basis set, cc-pVTZ, with maximum errors falling well within chemical accuracy. Recently we have applied the SRS-MP2 method for the prediction of interaction energies for a variety of intermolecular complexes ranging from radicals interacting with ionic liquids to strong hydrogen-bonded complexes and weak halogen-halogen interactions. Again, the method has achieved outstanding accuracy *for all types of intermolecular interactions, with an average error falling within 2 kJ mol⁻¹.*

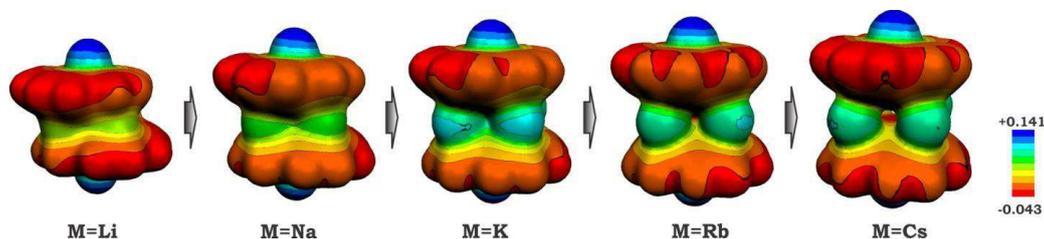
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Trianionic Corannulene: Tuning Stability of Supramolecular Aggregates with Alkali Metal Size

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Experimental achievements in chemistry of reduced corannulene ($C_{20}H_{10}$, the smallest bucky bowl) revealed a tendency of highly reduced curved polyaromatic molecules to form sandwich-like aggregates.¹ Recently, it was found that these supramolecular aggregates can be efficiently used for stabilization and isolation of highly unstable transient species such as polyaromatic trianions.² In this study, the strategy of manipulating of stability of these supramolecular traps by changing size of alkali metals in positively charged belt between two negatively charged bowl fragments was investigated in detail.³ The whole series of alkali metals, from Li to Cs, was considered. The electronic structure of suggested new sandwich-like systems was studied with help of tools of modern theoretical chemistry, including highly-accurate multi-reference perturbation theory of the second order (in XMCQDPT2 variant). Importantly, the magnetic coupling between curved polyaromatic radicals was also found to be the function of alkali metal size. Theoretical results are in perfect agreement with subsequent experimental observations.



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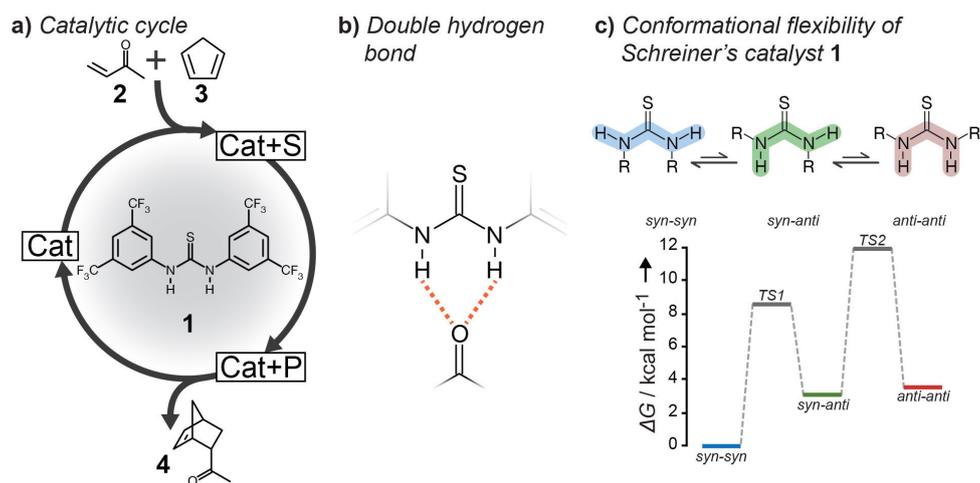
About underappreciated, yet active conformations of thiourea organocatalysts

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Catalysts speed-up reactions by binding substrates and transition states, thereby lowering reaction barriers. Noncovalent organocatalysts represent a highly selective and sustainable design alternative to conventional metal based catalysts, e.g. by utilizing a combination of hydrogen bonding with entropic and enthalpic effects to accelerate reactions. An example is illustrated below in panel **a**: Schreiner's catalyst **1** catalyzes the Diels-Alder reaction of the dienophile methyl vinyl ketone (**2**) with cyclopentadiene (**3**) to the *endo* product **4**. The established mechanism exploits the capability of NH protons in the *anti-anti* conformation of the central thiourea moiety to form a double hydrogen bond to the keto-group of **2** (see panel **b**). Organocatalysts such as **1** are flexible compounds with rich structural dynamics and their activity may be regulated via their conformational dynamics. Consequently, we performed first-principles structure searches and finally estimated Gibbs energies in dichloromethane. The global minimum structure is associated with the *syn-syn* conformation of the thiourea moiety, followed by the 3.1 kcal mol⁻¹ less stable *syn-anti* conformer (panel **c**). The *anti-anti* conformation, capable of forming the double hydrogen bond depicted in panel **b**, is energetically disfavored and 3.5 kcal mol⁻¹ less stable than the *syn-syn* conformer. Conformational changes between the minima involve barriers that are low enough to be overcome at room temperature. Starting from this, we investigate populations of the different conformers of **1** in presence of substrates. Our *ab initio* study reveals that substrate binding prefers *syn-anti* conformations of **1**. Furthermore, we find a new catalytic mechanism for Schreiner's catalyst featuring π stacking interactions. Our work highlights the need for extensive structure searches for flexible molecules, especially when aiming for structure-based design of catalytic activity.



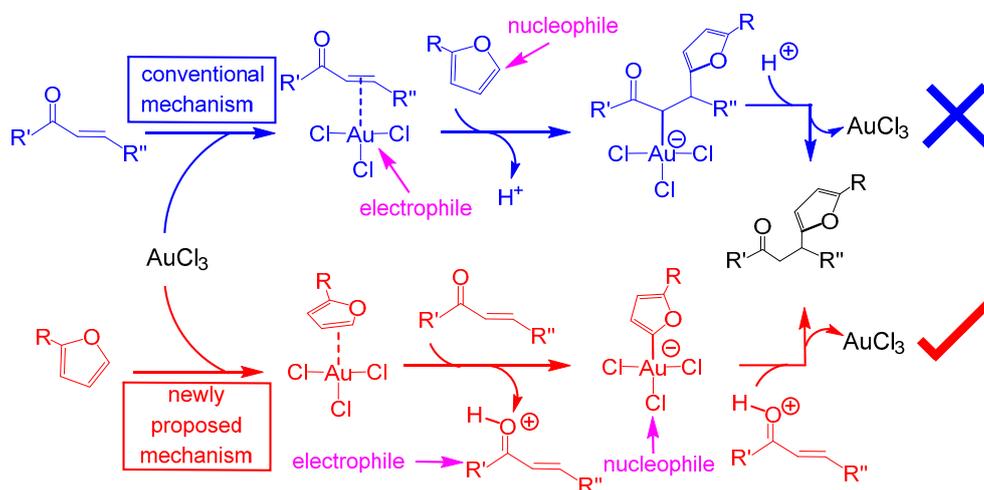
A New Mechanism for Gold Catalysis

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Gold complexes have attracted broad attention from the research community as efficient catalysts for the synthesis of many pharmaceutical drugs and natural products. A well-accepted role for the gold centre in catalysis is to activate unsaturated bonds as electrophiles, facilitating the attack of nucleophiles (Nu-H) on the gold-activated unsaturated bonds. We have used density functional theory to show that this picture is not always true and the gold centre sometimes plays a different role and serves as a proton producer via coordination to Nu-H to give Nu-Au and H⁺. The in-situ generated proton then serves as a strong electrophile and accelerates nucleophilic attack of Nu-Au on the unsaturated bonds through proton-activation. In this unprecedented mechanism, the nucleophile consists of the gold centre while in the traditional one the gold centre plays a reverse role. We investigated hydrofurylation of allenyl ketone, vinyl ketone, ketone and alcohol substrates catalysed by AuCl₃ and found that the corresponding functionalisations are best rationalised in terms of this novel mechanism [1]. This new reaction pathway is expected to receive greater consideration in other reactions catalysed by gold in future work.



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Magnetic coupling between f magnetic centers.

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The field of molecular magnetism explores more and more molecules containing lanthanide or actinide atoms. The large spin-orbit coupling and the semi-core character of the 4f and 5f orbitals confer to these molecules novel magnetic properties. Since a decade, there has been a large investigation of complexes with one magnetic center and first principles calculations have become an essential tool to interpret the experimental data, providing the nature of the ground state, the energy of exciting states and the corresponding directions of the magnetic moments.

The next experimental challenge is to gather several magnetic centers in a rational way in order to get a synergetic building of the local bricks. To achieve that, a fine knowledge of the magnetic interaction between centers is necessary. Due the semi-core character of the magnetic orbitals, the magnetic coupling between two f centers is very small, and the mechanism is still in question. The aim of this presentation is to show that quantum chemistry brings physical insights for the analysis of this magnetic coupling.

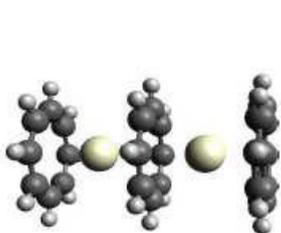


Fig. 1: $[\text{Ce}(\text{COT})_3]^{2-}$

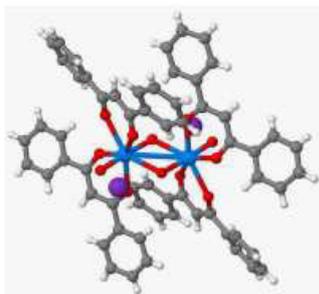


Fig. 2: $[(\text{UO}_2)\text{dbm}_2 \cdot \text{K}]_2$

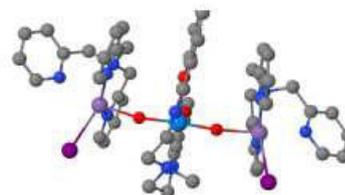


Fig. 3: $[(\text{Mn}(\text{TPA})\text{I})_2\text{UO}_2(\text{Mesalden})]^+$

I will present our results on a 4f-4f dimer of Cerium(III) (Fig. 1), a 5f-5f dimer of Uranium(V) (Fig. 2) and a 3d-5f-3d trimer of Mn(V)-U(V)-Mn(V) (Fig. 3). These molecules are described using correlated wave functions based theory. The analysis of these calculations permits to determine i) the nature and magnetic properties of the local magnetic centers ii) the coupling between these centers which in each case is strongly anisotropic. In order to recover the experimental coupling, highly correlated CI methods have to be used. All calculations are simulated using Spin Hamiltonians.

Study on Metal Nanocluster Catalysts Based on Quantum Chemical Calculation and Informatics

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The combination of the quantum chemical calculations with the informatics technologies has recently been attracted considerable attention as a candidate for predictive computational chemistry. In this study, we analyzed the results of the quantum chemical calculations of metal nanoclusters using the informatics technologies. The metal nanoclusters consisting of tens or less atoms show catalytic activity depending on many factors such as the size, composition, and shape [1]. As the first example, we focused on the catalytic activity of Cu₁₃ cluster for the NO dissociation reaction in this study. To extract the key factors for the catalytic activity, we utilized the regularized regression as typified by LASSO [2] and MC+ [3], where the regression coefficients for most of descriptors can be zero. Namely, the transition-state energy for the NO dissociation on Cu cluster is predicted from a few numbers of important descriptors obtained from the quantum chemical calculations of the adsorption states.

We next focused on the Au nanocluster (Au_n) catalysts supported by hexagonal boron nitride (h-BN)/Au surface. Although the h-BN and Au surfaces themselves are inactive, the combined h-BN/Au surface shows catalytic activity. Furthermore, Au_n/h-BN/Au shows higher activity for the oxygen reduction reaction [4]. The number of adsorption structures of Au_n/h-BN/Au grows drastically as *n* increases. To prescreen the adsorption structures before the quantum chemical calculation, we utilized the non-linear regression method for predicting the adsorption energy from the graph structure of the Au nanocluster.

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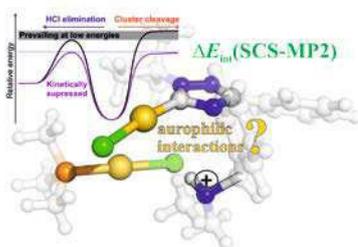
Calibrating Auophilic Interactions in Weakly Bound [L Au X]...[L' Au X] Dimers by Experiment and Theory

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Attractive metallophilic (auophilic, argentophilic, cuprophilic, ...) interactions play an important role in arrangement and stabilization of oligonuclear metal ion complexes.[1] We report a combined experimental and theoretical assessment of auophilic interactions in closed-shell gold(I) dimers. The experimental binding energies in [(LH)AuX]⁺...[(L')AuX] dimers (where X = Cl and L is a ligand derived from phosphine or N-heterocyclic carbene) charged by protonation of a remote amine group at the ligand L were determined by collision induced dissociation of mass-selected dimers in the gas phase. The results were used for benchmarking correlated quantum chemical calculations (obtained by employing the CCSD(T)-calibrated SCS-MP2 method), which were then also applied for neutral [(L)AuX]...[(L')AuX] dimers (X = Cl, Br, I). Experiments and theory have shown that the overall attractive interactions between monomeric units of the gold(I) dimers are in the order of 100–165 kJ mol⁻¹ in the charged dimers and 70–105 kJ mol⁻¹ in the corresponding neutral dimers. By comparison with smaller model systems, we demonstrate that pure auophilic interactions account for 35–40 kJ mol⁻¹ of the overall interaction energy (40–50 %). The dipole dipole interaction term contributes by approximately the same amount of energy (20–40 kJ mol⁻¹) whereas the L...L' “inter-ligand” dispersion interactions are smaller (< 10 kJ.mol⁻¹). Our experimental and theoretical findings confirm the overall importance of auophilic interactions – comparable or even stronger than very strong hydrogen bonds – but at the same time suggest that they may not always be the primary determinants of the complex molecular structures of polynuclear gold(I) complexes. [2]

Acknowledgments: Czech Science Foundation (No. 17-24155S)



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Surface-Enhanced Raman Spectroscopy Due to Charge-Transfer Chemical Mechanism: Effect of Surface and Electric Field

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Surface-enhanced Raman scattering (SERS) is one of the most sensitive spectroscopic techniques for a wide range of applications. The charge-transfer SERS as the resonance chemical mechanism is an important phenomenon and a topic of great studies. The electronic transition from filled metal orbitals (near the Fermi level) to unfilled orbitals in the molecule is usually the source of the resonance Raman CT enhancement, and it is important as represents the properties of combined system. The recognition of CT resonance selection rules is a difficult task due to the various factors that affect this process. It is known that the energies and electronic structure properties of CT-states can be influenced by the chemical nature of the surface and also the electronic potential of the interface. The quantum mechanical calculations can help to get an insight into the mechanism of CT and the source of each factor that controls this process. In our studies the calculations have been done by means of an excited-state gradient approximation for a pyridine molecule interacting with a silver cluster,¹ and the effect of electrode potential on the SERS-CT spectra has been modelled theoretically by applying an external electric field and provided a satisfactory agreement with the experimental studies.² Moreover, the effect of chemical nature of the surface on the pattern of SERS-CT spectra has been investigated for pyridine interacted with pure and bimetallic silver and gold clusters.³ The relative intensities of simulated spectra match well with the available experimental results and suggest that changing the surface, which reveals the trend by applying negative potential on a given surface, could be explained by variation of the effective charge of the cluster. These calculations also show the importance of variation of the excited-state vector gradient and dimensionless displacement by changing the surfaces and electric field and also their effects on the selection rules.

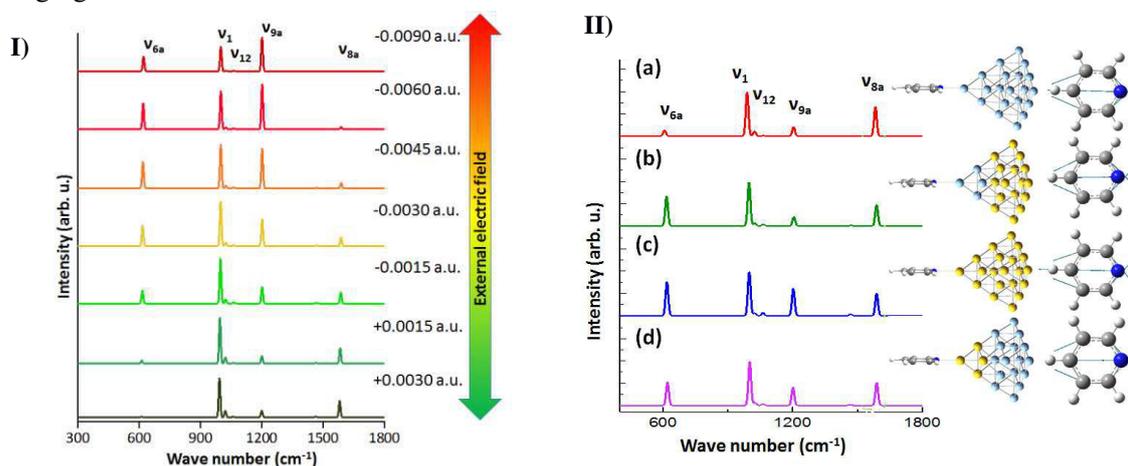


Figure 1. Calculated SERS-CT spectra of (I) pyridine with silver cluster under an applied external electric field (II) different clusters.

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Irreversible Tautomerization in Porphycene on Cu(111) Induced by Scanning Tunnelling Microscopy

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Scanning tunnelling microscopy (STM) is a widely appreciated characterization technique in surface science. The applications range from imagery to catalysis and nanoelectronics, to name but a few. In recent experiments, STM was further used to selectively induce reactions in the vicinity of metallic surfaces. It is well-known that non-adiabatic coupling to hot electrons impinging from the STM tip can play an important role in such phenomena (see Refs. [1,2] and references therein). To demonstrate their dynamical effect, we will investigate the irreversible tautomerization in porphycene on a Cu(111) surface induced by hot electrons injected by a neighbouring STM tip [3]. We demonstrate that the reaction can be understood as a quasi-thermal hydrogen migration mechanism and rationalized in terms of non-adiabatic coupling and intramolecular vibrational energy redistribution: hot electrons from the STM-tip excite a large number of skeletal vibrations of the molecule, which distorts the potential energy landscape along the hydrogen transfer coordinate [4].

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Quantum Master Equation Approach to Singlet Fission Dynamics in Molecular Aggregates

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Singlet fission (SF), which is a photophysical process with splitting a singlet exciton generated by light irradiation into two triplet excitons, has attracted much attention both experimentally and theoretically due to its potential of improving photoelectric conversion efficiency through multi-exciton generation in organic solar cells [1]. The study of SF is composed of three steps: (i) energy level matching at single molecular level, (ii) electronic coupling at molecular aggregate level, and (iii) exciton dynamics including exciton-phonon (vibronic) couplings [2]. In this study, first, the SF dynamics of realistic/artificial pentacene dimer models is investigated using the quantum master equation method in order to obtain new insight into the SF dynamics. We clarify the effects of the energy offsets of diabatic Frenkel exciton (FE) and charge transfer (CT) exciton states to the double-triplet (TT) exciton state, excitonic couplings, and state-dependent vibronic couplings on the exciton population dynamics using relative relaxation factors (RRFs) between the adiabatic exciton states [3]. Second, for multimers beyond dimer, we derive the quantum master equation and investigate the aggregate-size dependence of the SF rate and TT yield. On the basis of these results, we discuss the structure-property relationships for SF dynamics in various molecular aggregate models.

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Pathways in molecular conductance and spin coupling

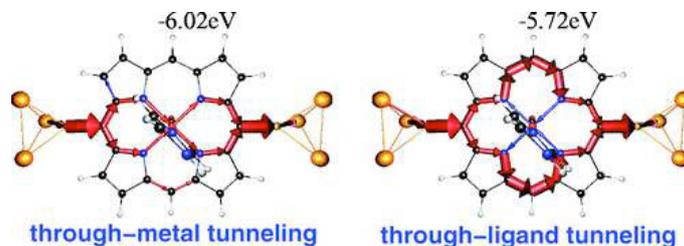
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For understanding spin-polarized electron transport through molecular bridges and (exchange) spin coupling between local spin centers within in a molecule, it is interesting to know which parts of the molecule are responsible for mediating transport or spin interactions.

In the case of spin coupling, ferro- and antiferromagnetic pathways may add up or partially cancel, which is hidden if only the total spin coupling is considered. A new approach to decomposing spin coupling based on Green's functions [1] allows not only identifying which molecular parts are responsible for spin coupling in isolated molecules, but may also allow for distinguishing, e.g., between intramolecular and through-surface contributions [2].

In electron transport through molecular junctions, local decomposition of electron transmission will be used to highlight the importance of spin-polarized parts of the molecule for transport [3-7], and compared with the effect of introducing spin polarization in bridging ligands on spin coupling [8].



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Exciton Dynamics in Organic Optoelectronic Materials

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There has been a growing interest in electronic and optical properties in organic semiconductors due to their potential applications for optoelectronic devices. However, it is difficult to theoretically study the excited states and photophysical processes. First, computation of large number of excited states in large molecular systems is still a challenging issue in quantum chemistry. Second, to investigate the photophysical processes such as electronic energy transfer or charge separation, one has to simulate real-time dynamics with exciton-phonon coupling being incorporated. We have been developing the simulation method based on the fragment-based electronic structure method and quantum dynamics theory. The model exciton Hamiltonian is constructed by the ab initio electronic structure calculations utilizing the fragment molecular orbital method. Exciton dynamics coupled to the nuclear vibrations is modeled by the stochastic Schrödinger equation, which allows to describe ultrafast coherent dynamics and subsequent thermal relaxation.

In the first part, we present optical properties and exciton dynamics in the dinaphtho[2,3-b:2',3']-thieno[3,2-b]-thiophene (DNNT), a p-type organic semiconductor. The calculated absorption spectrum based on the first principle is in qualitative agreement in the experiment; it is composed of main excitations of Frenkel-dominant states with partial admixture of CT states and CT-dominant states with slight admixture of Frenkel states. Next we show real time dynamics in a DNNT thin film. The localized Frenkel and CT excitons is relaxed to the lowest exciton state in about 1.5 and 2.5 ps, respectively. We observe the mixing of CT excitons with Frenkel state in 50 fs after the excitation. Accordingly, electron-hole separation increases and shows an oscillation pattern as a result of delocalization of electron and hole and electron-hole Coulomb interactions. We discuss the roles of charge delocalization and localization in the Frenkel-CT mixings.

In the second part, we discuss the excited states of pentacene/C₆₀ interface. It is known that the interfacial charge transfer states across the interface play essential roles in the charge separation and recombination. The ab initio FMO calculations for an extended pentacene/C₆₀ interface allows us to discuss the effects of structural disorder, electronic polarization, and charge delocalization. The implication to the charge separation and recombination will be discussed.

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Photophysical properties of macrocycles: a computational and experimental study.

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Macrocyclic compounds are widely applied as industrial dyes, since they present a large π -conjugated system. Particularly, phthalocyanines can be employed also in different devices, such as solar cells and electrochromic devices, as well photodynamic therapy (PDT). On the other hand, new molecules can be developed aiming to increase the efficiency as photosensitizers. For instance, naphthalocyanines (Nc) are phthalocyanines derivatives with a more extended π -conjugated system, that is responsible for bathochromic shift in absorption bands in comparison to phthalocyanine. However, due to this conjugated system, these compounds tend to aggregate, what affect their photophysical and photochemical properties. In order to avoid such effect, a common strategy is to propose derivatives with large groups as substituents. In this work, we have conducted experimental and computational studies in order to verify the influence of different substituents on the photophysical properties of phthalocyanine and naphthalocyanine, as well on the aggregation energetics. Computational methodology was based on density functional theory (DFT), the inclusion of dispersion was made by means of Grimme's correction (D3-BJ) and solvent effects by IEFPCM continuum model. [1] TD-DFT calculations pointed out the molecular orbitals involved in Q-band transition, corresponding to HOMO to LUMO transition with a concentration of charge along x-axis, while the transition to LUMO+1 is in y-axis direction. Substitutions with tert-butyl groups was found not disturb this behavior, but it is important for molecular orbitals energies. DFT studies indicated that stacked-dimers are preferred to rotated-stacked conformation due the interaction between Zn(II) and nitrogen atom from different monomers.

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Modeling the Photochromism of Sulphur-Doped Sodalites using DFT, TD-DFT and SAC-CI methods.

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Photochromic materials are deeply investigated experimentally and theoretically because of their numerous possible high-tech applications going from adaptive glasses to optical memories. Geologists have known for almost one century the existence of natural photochromic minerals, calling this phenomenon tenebrescence, of the sodalite family. Although the community is mainly trying to develop new type of photochromic materials, almost no efforts were devoted to understand and developed these tenebrescent minerals known by the geologists for a long time.

In this presentation, we will focus on natural sulphur-doped sodalite minerals of $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{Cl},\text{S})_2$ formula, also known as hackmanites, that are computationally investigated for the first time, in order to understand their photochromic properties. By combining periodic boundary conditions and embedded cluster-type approaches, we bring a theoretical overview of the photochromism mechanism. Our TD-DFT calculations of sodalite systems containing electrons trapped into chlorine vacancies (called F-center) showed absorption spectrum and a simulated color in agreement with experiment. This modelling highlights the huge effects of F-center's environment such as the direct contribution of the β -cage on the trapped electron and a strong vibronic coupling of the absorption spectrum. TD-DFT and post-Hartree-Fock (SAC-CI) calculations were also operated on S_2^{2-} -containing systems in order to determine the exact mechanism of coloration and discoloration, supporting that the key step is a direct through space charge-transfer between S_2^{2-} ion and a chlorine vacancy. The geometry modification induced by this charge-transfer leads to a large electronic reorganization stabilizing the F-center thus explaining the high stability of the colored state of the mineral. The results and methodology presented during this talk are published in ref [1].

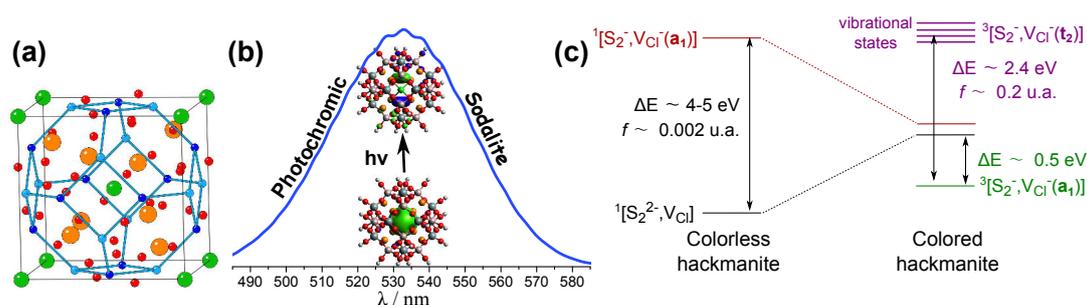


Figure 1: (a) Sodalite unit cell, the blue lines depict the β -cage cage. (b) Simulated absorption spectrum of the F-center including vibronic coupling. (c) Jablonski diagram of the photochromic phenomenon obtained by the combined TD-DFT/SAC-CI approaches.

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Shedding Light on the Approximations Underlying Ab Initio Multiple Spawning

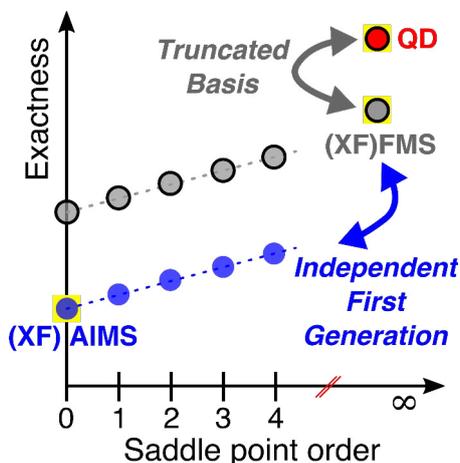
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Ab initio multiple spawning (AIMS) aims at an accurate yet efficient *in silico* description of photochemical and photophysical processes in molecules. AIMS describes the nonadiabatic dynamics of nuclear wavepackets by means of linear combinations of coupled frozen Gaussians, which follow classical trajectories and whose number can be adapted when required.

An important feature of the AIMS formalism is the flexibility of its coupling elements between Gaussians, which permits the incorporation of critical effects for a realistic simulation of photochemical processes. We recently extended AIMS to the description of intersystem crossing processes by including spin-orbit couplings (Generalized AIMS – GAIMS) and to simulate photoexcitation processes (eXternal Field AIMS – XFAIMS).[1, 2]

XFAIMS further offers the possibility to generate complex superpositions of nuclear wavepackets in different electronic states by using pump-probe schemes. Such intricate nuclear dynamics constitute a *unique* opportunity to test the influence on computed observables, like state populations or the time-dependent dipole moment, of (i) approximating the couplings between traveling Gaussians and (ii) the definition of initial conditions. Hence, I will show in this Contribution that XFAIMS allows us to shed light on the two central approximations of the AIMS method, and that – even within these two approximations – AIMS offers a qualitatively correct description of nonadiabatic phenomena involving complex interference effects between nuclear wavepackets.[3]



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Polarizable QM/MM for excited-state dynamics

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Many electronically excited processes involve non-adiabatic transitions between neutral and charge transfer (CT) states, e.g. in photosynthesis and organic photovoltaic cell operation. An understanding of the dynamics in these systems requires an accurate description of both neutral excited-states, CT states, and their intersections. Quantum Mechanics/Molecular Mechanics (QM/MM) holds a lot of promise since it limits the electronic structure calculations to a small chemically-active region, allowing a high-level treatment. It is important, however, to use a polarizable model that captures the electronic polarization of the MM system in response to a CT state. Here a problem arises: the MM system must polarize differently to neutral states compared to CT states, implying a state-specific approach. Unfortunately, this would mean each electronic state is of a different Hamiltonian, and therefore intersections between the states will not be described correctly.

Borrowing from our recently developed DWS-CASSCF method,[1] we have developed a new polarizable QM/MM approach that solves the above issue. The basic idea is to self-consistently optimize MM dipoles in a polarizable QM/MM calculation in response to a weighted average of the fields from each electronic state. When the electronic states are energetically separated, the weight becomes unity for the state of interest, and zero for all others, giving the state-specific approach in this limit. When electronic states cross, the field weights for the intersecting states becomes equal, meaning these states share the same Hamiltonian, and therefore the topology of the intersection is correctly described.

We have tested our new QM/MM-DWpol method on the electronic states of LiF, a simple and widely-studied system exhibiting a neutral and CT crossing. When a polarizable atom is placed near LiF, the energy of the CT state is lowered relative to the neutral states, thereby shifting the position of the state crossing. We show that our QM/MM-DWpol method reproduces the entire potential energy surface with near quantitative accuracy compared to high-level multireference configuration interaction calculations on the full system. Furthermore, our method has a computational cost that is comparable to traditional QM/MM approaches. We expect this development will open the way to studying excited-state charge-transfer reactions in complex systems with a high-level of accuracy.

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Hydrogen conversion in [NiFe]-enzymes and bio-inspired complexes

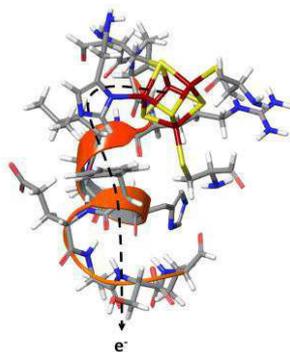
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Molecular hydrogen (H₂) is one of the future energy carriers in particular for individual transportation. Hydrogen converting enzymes can either oxidize hydrogen or reduce protons to release H₂. They utilize highly evolved active sites consisting of non-noble metals such as iron and nickel. The oxygen-sensitivity of standard [NiFe]-hydrogenase enzymes is overcome in a subfamily of membrane-bound enzymes which possess a novel type of [4Fe4S](Cys)₆-cluster to prevent oxidative damage to the active site [1,2,3].

The active site of the enzymes has led to the design of a large number of bio-inspired mono- and di-nuclear complexes (for a review see e.g. [4]). Quantum chemical calculations are indispensable to elucidate structural and electronic properties of those complexes and to identify critical parameters for catalytic activity in solution.

The enzyme can also be used in an enzymatic fuel cell. Brownian Dynamics (BD) simulations were used to investigate the diffusion of the enzyme to the graphite electrode surface, identify preferred orientations and amino acid residues establishing contacts between enzyme and surface. The QM calculated rates of electron transfer from the Marcus equation are in excellent agreement with experiments and identify different electron transfer routes via the histidine of the distal FeS-cluster to the electrode [5,6].



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Unraveling the magnetic transition temperature from changes in spin correlation

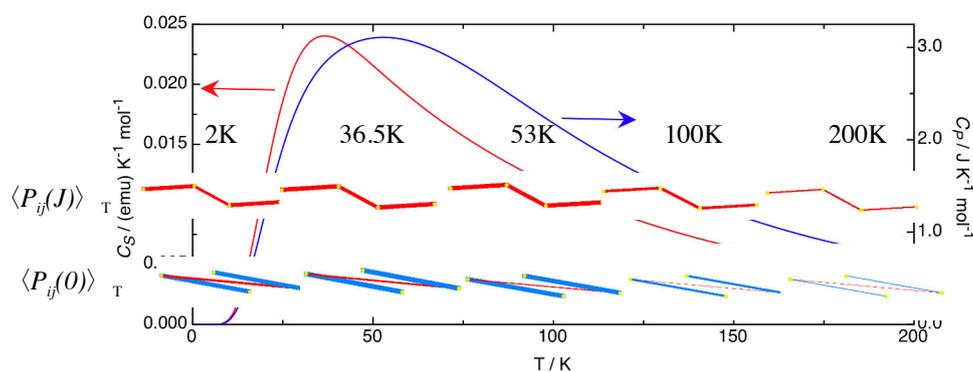
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The current definition of the critical temperature T_c for magnetic systems is ambiguous. Indeed, a maximum in $\partial[\chi T(T)]/\partial T$, the magnetic spin capacity (C_S) associated with a change in spin order/disorder, is the 'physically correct' definition of the magnetic transition temperature. The definition of the magnetic capacity is shown to be useful because it can be interpreted in terms of the molecular structure of the crystal using the magnetic wavefunction for each magnetic microstate. Analysis of the magnetic wavefunction using the concept of a Boltzmann magnetic bond order and the exchange density matrix P_{ij} (+0.5, -0.5 and -0.25 for antiparallel, parallel and non-ordered spin alignment, respectively) provides information about the spin correlation between magnetic units. Thus in the analysis of magnetic effects there are two second-order transitions, involving energy (the usual T_c from C_p), and spin ordering (C_S), respectively. We observe a systematic shift between the two phase-transition temperatures that we believe can be attributed to the loss of long-range spin correlation. The application of this new concept [1] on real magnets suggests it is a very promising tool in order to analyze and rationalize the main factors that govern the magnetism of molecular crystals, and to predict whether the magnet has potential. In addition, this type of analysis will enable further research to better understand what happens in the region close to the magnetic transition regime depending on the magnetic topology.



[1] J. Jornet-Somoza, M. Deumal, J. Borge, J.J. Novoa, M.A. Robb, *submitted*

The magnetic couplings sensitivity to Fock exchange in DFT is not due to spin over-delocalization

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Abstract: Following a recently proposed method[1,2] of decomposition of the magnetic exchange contributions (direct exchange, kinetic exchange and spin polarization) and using a new method[3] of spin decontamination, the interactions of both Hubbard and Heisenberg Hamiltonians have been extracted from Broken Symmetry DFT calculations[4]. Analytical expression of these interactions have been derived as functions of both the energy of various broken symmetry solutions and their expectation value of S^2 . These interactions strongly depend on the functionals and more particularly on the percentage of Hartree Fock exchange (HFX). The overestimation of the magnetic couplings calculated in DFT has always been attributed to the overestimation of the spin delocalization resulting from the use non-hybrid functionals or hybrid functionals with small amounts of HFX. Using non self-consistent calculations, it has been possible to separate the impact of the HFX amount from that of the spin delocalization. It will be shown that, contrarily to what it usually believed, spin delocalization has a little impact on the values of the interactions and that the HFX amount plays a crucial role. A deeper analysis rationalizes the obtaining of strong dependences of both the kinetic hopping integral and the on-site repulsion on the HFX amount while keeping the same density, which is physically aberrant as both interactions should be fixed for a given density.

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Quantum dot inter-Coulombic decay governed by the quantum size effect

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Quantum dots (QDs), i.e. three-dimensional semiconductor nanomaterials have a discrete electronic structure which sensibly depends on the size of the QDs. This quantum size effect makes QDs attractive device materials for instance for a potential next-generation infrared photodetector based on the elementary inter-Coulombic decay (ICD [1]) energy transfer process.

In the given example of QD ICD an acceptor QD (AQD) absorbs infrared light by which one electron is promoted from the ground to the excited state. On an isolated QD a radiative decay and a phonon-mediated decay channel exist of which the latter is faster by about one order of magnitude. With a second QD in the vicinity energy transfer becomes an additional decay channel, which leads to the emission of one electron from the second emitter QD (EQD) [2].

We recently showed by MCTDHF electron dynamics calculations how the size of each individual QD, including its time-dependent phononic fluctuations, governs the ICD rate[3, 4]. Moreover, we found a complex interdependence of the parameters depending on the competing effects of polarization and Coulomb repulsion.

We acknowledge financial support from Volkswagen foundation (Freigeist Fellowship), the Deutsche Forschungsgemeinschaft, and the Thai government.

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Ternary Gold Hydrides: A New Class of Stable and Potentially Superconducting Compounds

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Our focus in this work is theoretical predictions of stability, properties, and realistic routes to the synthesis of an as of yet unknown class of compounds, those based on hydrogen and gold. Binary alloys of gold and hydrogen cannot be made by the application of high pressure,[1] but we calculate that the introduction of certain alkali and alkaline earth metal counterions should enable the synthesis of stable AuH_2^- -based ionic solids. Related $[\text{A}]_2\text{PdH}_2$ (A=Alkali metal) compounds are stable,[2] some Au-H bonds can be stabilized in large organic scaffolds,[3] and fleeting AuH_x species are known from matrix isolation experiments.[4] The materials studied here would, once made, represent the first ternary gold hydrides likely stable under ambient conditions. Our work broaches use of chemical arguments to guide the design of chemically accessible metallic gold hydride ternaries predicted to be superconducting.

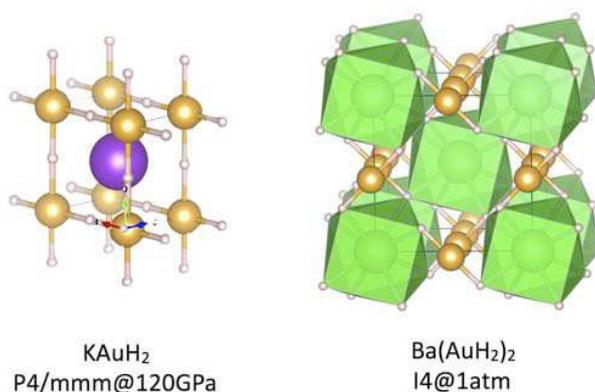


Figure 1. KAuH_2 and $\text{Ba}(\text{AuH}_2)_2$, two examples of gold hydride ternaries predicted to be stable and superconducting under different conditions.

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Density Functional Theory as a Predictive Tool for Superconductivity

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Density Functional Theory (DFT) of electronic structure is widely used to simulate many structures and systems in chemistry and physics [1]. In many cases, these simulations have been highly successful at explaining IR spectra, binding sites and activation energies [1, 2] while there are also some critical failures due to delocalization and correlation errors of commonly used functionals [2]. In some cases, such as the prediction of superconducting properties using band structures, experimental data more commonly inform *post-facto* estimates of physical properties [3]. In this work, we demonstrate the efficacy of DFT in modern computational programs for prediction of the superconducting transition temperature (T_c) for diboride structures. The key difference in approach compared with past estimates is the use of phonon dispersion (PD) plots to recognize the presence (or absence) of an anomaly and then to measure the extent and energy of the anomaly. PD plots are directly related to band structure models and, in the case of diborides, are a critical indicator of the electron-phonon interaction in a superconducting structure. DFT calculations are undertaken using the CASTEP module of Materials Studio 8.0 to calculate vibrational properties [4]. Both LDA and GGA methods with norm-conserving pseudo-potentials, a plane-wave basis set and a dense k -grid (at $k < 0.03 \text{ \AA}^{-1}$) provide the most consistent model outcomes for a wide range of AlB_2 -type compositions [5]. We find that for a range of chemical and physical variations to MgB_2 – such as pressure dependence [6], metal substitution [5, 7] and isotopic variations [8] – evaluation of the E_{2g} phonon anomaly provides a direct, *ab initio*, estimate of T_c for this class of materials. In addition, this approach leads to prediction of T_c values for new, as yet unknown, compounds of the same structure type [5, 7].

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Design of New Disulfide-Based Organic Compounds for the Improvement of Self-Healing Materials.

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Self-healing materials are a very promising kind of materials due to their capacity to repair themselves. Among others, diphenyl disulfide-based compounds (Ph_2S_2) appear to be among the best candidates to develop materials with optimum self-healing properties. However, few is known regarding both the reaction mechanism and the electronic structure that makes possible such properties. In this vein, theoretical approaches are of great interest. In this work, we have carried out theoretical calculations on a wide set of different disulfide compounds, both aromatic and aliphatic, in order to elucidate the prevalent reactions mechanism and the necessary electronic conditions needed for improved self-healing properties [1]. Two reaction mechanisms were compared, namely, the [2+2] metathesis and the [2+1] radical-mediated mechanism. No computational evidence for the existence of any transition state for the metathesis mechanism was found, which indicates that the radical-mediated mechanism is the one responsible in the self-healing process. Besides, this has been recently confirmed experimentally [2]. The formation of sulfenyl radicals strongly depends on the S-S bond strength, which can be modulated chemically by the use of proper derivatives. At this point, amino derivatives appear to be the most promising ones. In addition to the S-S bond strength, hydrogen bonding between disulfide chains seems to be relevant to favour the contact among disulfide units. This is crucial for the reaction to take place. The calculated hydrogen bonding energies are of the same order of magnitude as the S-S bond energies. Finally, reaction barriers have been analyzed for some promising candidates. Interestingly, these barriers are around 10 kcal/mol regardless the substituent employed. All these results suggest that the radical formation and the structural role of the hydrogen bonding prevale over kinetics. Having this in mind, some new compounds are proposed for the design of future self-healing materials with improved features.

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Computational Modeling of Thermal Energy Storage Materials

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Effective handling of reusable waste heat is one of the important future technologies for reducing energy consumption as well as promoting energy conservation. Among possible ways of handling waste heat, thermal energy storage is the key technology in thermal energy management. Basically, there are two major classes of materials for achieving thermal energy storage, phase change materials (PCMs) and thermo chemical materials (TCMs). Although some of them are familiar in our daily life and widely used in various social systems, the detailed molecular mechanism of thermal energy storage remains elusive at present. Especially, how to improve chemical properties of these materials, and also control chemical reactivity are important issues for developing new PCMs/TCMs. In the TherMAT project [1], we are now investigating the basic mechanism of thermal energy storage for both material systems based on a computational approach. In the WATOC 2017 meeting, I would like to present recent progress in our computational work.

As for PCM, sugar alcohols are known as one of the promising candidates for achieving large amounts of thermal energy storage. Based on the molecular and crystal structures of known sugar alcohols, we have computationally designed and predicted a new organic molecular material which can achieve larger amounts of thermal energy storage than ever before. In the first step, we carefully analyzed molecular properties of known C4, C5 and C6 sugar alcohols based on classical MD simulations [2]. Then we clarified the molecular factors that control physical properties, such as melting point and latent heat. On the basis of these detailed analyses, we proposed molecular design guidelines to achieve effective thermal energy storage; linear elongation of carbon backbone, separated distribution of OH groups, and even numbers of carbon atoms inside the carbon skeleton. Our computational results clearly demonstrated that if we carefully design molecular structures, non-natural sugar alcohols have potential ability to achieve thermal storage density up to 450-500 kJ/kg, which is larger than the best value of the present known organic PCMs (~350 kJ/kg) [3].

We also conducted first principle calculations for typical TCMs, and clarified the correlation between the electronic character and thermo-physical / chemical properties of alkali earth metal oxides.

[1] Thermal Management Materials and Technology Research Association:
<http://www.thermat.jp>

[2] Taichi Inagaki, Toyokazu Ishida, *J. Phys. Chem. C* **120**, 7903 (2016). [Cover Art](#)

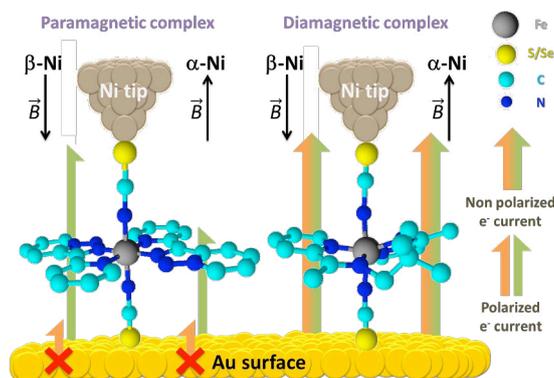
[3] Taichi Inagaki, Toyokazu Ishida, *J. Am. Chem. Soc.* **138**, 11810 (2016).

Spin Crossover Complexes: A Challenge from Theory to Single-Molecule Devices

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Spin crossover complexes (SCO), most of them Fe^{II} complexes, have remarkable magnetic properties based on ground-state spin switching (for Fe^{II} systems, between the diamagnetic $S = 0$ low-spin $t_{2g}^6 e_g^0$ and paramagnetic $S = 2$ high-spin $t_{2g}^4 e_g^2$ electron configurations) controlled by means of an external stimulus, *i.e.* temperature, light, pressure, solvent interactions or electric field.[1] From the theoretical point of view, such systems are big challenge because many exchange-correlation functionals completely fail in the prediction of the energy difference between the high- and low-spin states. Also, the calculation of the entropic vibrational contributions is fundamental to estimate the transition temperature between the two states. In this communication, our goal is to provide an extensive test of DFT methods to analyze SCO complexes with many different metals not only with the Fe^{II} cations. Furthermore, in our group we have employed such systems to perform experimental and theoretical studies of single-molecule junctions being particularly interesting because they present magnetoresistance effect at room temperature (see Figure).[2] DFT+NEGF methods have been employed to rationalize such property, to clarify which are the main requirements of the magnetic molecules to show such behavior. Theoretical results have been confronted with scanning tunneling microscopy data.[3]



[1] E. Ruiz *Phys. Chem. Chem. Phys.* (Perspective) **16**, 14, (2014).

[2] A. C. Aragonès, D. Aravena, J. I. Cerdá, Z. Acís-Castillo, H. Li, J. A. Real, F. Sanz, J. Hihath, E. Ruiz, I. Díez-Pérez *Nano Letters* **16**, 218, (2016).

[3] A. C. Aragonès, D. Aravena, F. J. Valverde-Muñoz, J. A. Real, F. Sanz, F., I. Díez-Pérez, E. Ruiz *J. Am. Chem. Soc.* **139**, 5768, (2017).

Accelerating metal-directed protein folding and molecular recognition with enhanced sampling techniques

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Metal ions are found in the core of several phenomena such as biomolecular recognition and protein (un) folding. Some of these important processes usually take place on the μ s to ms time scales. Low-energy states relevant for these processes may be separated by high-energy barriers, which are rarely crossed over the course of molecular dynamics simulations. Methods that enhance conformational sampling are needed to elucidate the role of metal ions in these biological phenomena at a reasonable computational cost. Accelerated molecular dynamics (aMD) enhances sampling in a relatively simple way (a priori knowledge of the underlying free energy landscape is not needed).[1,2] Recently, we explored the performance of aMD to predict the detailed mechanisms of protein folding. The folding and the free energy landscape of a set of fast-folding proteins was simulated with aMD. This allowed us to identify distinct conformational states (e.g. unfolded and intermediate) other than the native structure and the protein folding energy barriers.[3]

Here, we combine aMD simulations with electronic structure calculations for the metal parametrization[4] to study the the redox conformational protection of nitrogenase. A protein called Shethna Protein II (FeSII, homodimer), which contains two [Fe₂S₂] clusters, forms a stable ternary complex with nitrogenase that is able to protect this enzyme from oxygen. Interestingly, FeSII can alter from an open to a closed conformation depending on the levels of O₂. The hypothesis is that this conformational change, that connects the open and closed states, is linked to a change in the oxidation state of the [Fe₂S₂] cluster that involve unfolding and subsequent refolding of the N-loop of the protein. To this end, the [Fe₂S₂] cluster has been parametrized in different oxidation states and simulations from both open and closed conformations at different redox states are produced. Our aMD simulations show that the FeSII is able to alter from the open to the closed conformation involving folding and unfolding of the N-loop through a series of intermediate states.

[1] P.R. Markwick, J.A. McCammon, *Phys. Chem. Chem. Phys.*, **13**, 20053 (2011)

[2] F. Feixas, S. Lindert, W. Sinko, J. A. McCammon, *Biophys. Chem.*, **186**, 31 (2014)

[3] Y. Miao, F. Feixas, C. Eun, J. A. McCammon, *J. Comp. Chem.*, **36**, 1536 (2015)

**Role of aromatic, aliphatic and backbone interactions
in the stability of amyloids**

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The amyloid fibrils have been studied very intensively because of their importance in Alzheimer's disease and other neurodegenerative diseases. The role of aromatic amino acids in formation of the amyloid fibrils is somewhat controversial. Aromatic amino acids are very frequent in natural amyloids, leading to idea that aromatic residues are essential for amyloid aggregation [1,2]. However, studies have shown that amyloid fibrils can be formed from peptides without aromatic amino acids [3].

In order to elucidate role of aromatic amino acids in aggregation of amyloids, in our work we applied DFT method to calculated interaction energies between amyloid β -sheets [4]. We performed calculations on two types of on model systems (1) with and (2) without aromatic amino acids. The model systems used in our work we made from crystal structures of amyloids. The two types of amyloids have similar interaction energies indicating that both types of amyloids can be formed, what is in agreement with experimental data.

In spite of similar stabilities, the analyses of the factors contributing to the amyloid stability shows that two types of amyloids are stabilized by different factors. In (1) amyloids with aromatic amino acids the main contribution to the interaction energies are interactions between side chains; the most important are interactions between aromatic and aliphatic groups followed by aromatic/aromatic interactions. In (2) amyloids without aromatic amino acids the main contribution are interactions of side chains with backbone and hydrogen bonds.

[1] M. Tena-Solsona, J. F. Miravet, B. Escude, *Chem. Eur. J.* **20**, 1023–1031 (2014)

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[4] D. B. Ninković, D. P. Malenov P. V. Petrović, E. N. Brothers, S. Niu, M. B. Hall, M. R. Belić, S. D. Zarić, *Chem. Eur. J.* submitted.

**Design of AMPA receptor positive allosteric modulators: QSAR studies,
virtual screening, and molecular dynamics simulations**

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Glutamate is the major excitatory neurotransmitter in the CNS, and the malfunctioning of the glutamatergic system leads to serious neurological disorders and is associated with neurodegenerative diseases. The ionotropic glutamate receptors are ligand-gated ion channels that consist of four subunits forming the ion channel pore, the ligand-binding domains, and the amino-terminal domains. The positive allosteric modulators of an important type of glutamate receptors, AMPA receptors, are able to improve memory and cognition.

We have performed the molecular modeling of the ligand-receptor interactions and the QSAR studies for the AMPA receptor positive allosteric modulators (PAMs).

The molecular dynamics simulations for a series of AMPA receptor PAMs bound on the interface between two glutamate-binding domains have demonstrated a good correlation of the MM-GBSA and MM-PBSA binding energies with the experimental pEC₅₀ values.

The Molecular Field Topology Analysis (MFTA) QSAR method developed by us was quite helpful in the modeling of ligand selectivity and multi-target activity in terms of local properties such as the atomic charges, group van der Waals radii, and local lipophilicity. In addition, the 3D QSAR and pharmacophore models of the AMPA receptor PAMs have been constructed.

The combination of these techniques as well as the virtual screening of large compound libraries allowed us to identify and design new scaffolds for PAMs and create the focused libraries of promising PAM structures. These modelling studies have lead to the development of positive AMPA receptor modulators with experimentally confirmed high potency in electrophysiological studies, which improve memory and cognition in animal models.

The advanced predictive models developed by us earlier for the important ADMET properties such as blood-brain barrier permeability, human intestinal absorption, and hERG affinity and activity were used as additional filters in the design of neuroprotective compounds.

This work was supported by the Russian Science Foundation (grant No.17-15-01455).

AQUILES web server: open the eyes to blind docking

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The development of new drugs is an extremely expensive process that can be benefited from the use of a wide panel of theoretical tools including virtual screening, docking, molecular dynamics and *ab initio* computational chemistry approaches.

Our group has recently contributed to the design of novel molecules with real clinical applications by setting up an efficient blind docking workflow. Aiming to make this new technology accessible to any researcher, our protocol has been implemented in a blind docking server called AQUILES, which is already available via the Internet at

<http://bio-hpc.eu/software/blind-docking-server/>

In this contribution we discuss the potential use of AQUILES in the framework of anticoagulants, cancer, Parkinson, Fabry and Zika (see Figure 1).

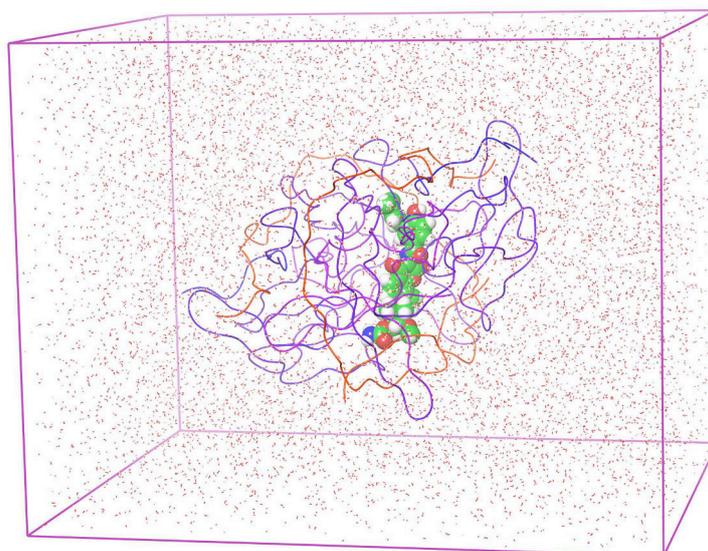


Figure 1: Chemical model of the new drug with a potent *in vivo* anti-Zika activity (invention currently under patent procedure) discovered with AQUILES.

Thermodynamics of Self-Assembly of Perylene Derivatives

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Functional organic materials composed of dye-based molecules that stack into various structures by non-covalent intermolecular forces have fascinating optical and mechanical properties. These novel materials are of increasing importance for many high-technology applications. Here is a need for a rational design of such materials based on the engineering of dye-dye interactions and the prediction of how these interactions impact the properties of nano- or bulk state materials. The required insight into the underlying physical processes can be derived from investigations on dye assemblies that constitute the intermediate state of matter between monomeric dyes and supramolecular materials. Perylene di-imide derivatives (PDIs) emerged as a prototype class of molecules for the elucidation of the transition from monomeric to bulk materials via the supramolecular state [1,2]. Their self-assembly into complex structures is determined by size and shape of the monomeric unit, system composition and thermodynamic boundary conditions. Given this diversity of factors, a molecular-level understanding of the various driving forces is essential for the rational material design.

In this project the free energy for the formation of dimers and higher aggregates are calculated for prototypical molecular building blocks carrying different functional groups in different solvent environments using molecular dynamics free-energy simulations based on force fields inherited from the area of biomolecular simulations. The temperature dependence of the free energy gives access to the entropic contribution while the change in potential energy during assembly provides the enthalpic contribution.

We discuss the influence of the molecular architecture and the solvent composition on the thermodynamic fingerprint of the aggregation and investigate the ability of classical molecular dynamics simulations to be used in rational materials design.

[1] F. Würthner, C. R. Saha-Möller, B. Fimmel, S. Ogi, P. Leowanawat, D. Schmidt, *Chem. Rev.* **116**, 962 (2016).

[2] E. Krieg, M. M. C. Bastings, P. Besenius, B. Rybtchinski, *Chem. Rev.* **116**, 2414 (2016).

Solvation in 2D: Microsolvated Ions on Inert Surfaces

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The present project aims to study the solvation process of alkali cations and halogen anions in the presence of weakly interacting surfaces. This investigation is a step forward toward understanding solvation in restricted environments. We have performed QM/MM simulations on solvatomers deposited on Xe layers on Cu(111) support. The system has been established in collaboration with our experimental partners in order to provide complementary results for STM studies of the same systems. The realistic description of surface polarization is achieved by including the neighboring Xe atoms into the QM subsystem and applying self-consistent image-charge interaction with the metal. In order to reduce finite size effects in our periodic model, the interaction between QM images are decoupled and the QM Xe atoms are embedded into the layers of their classical counterparts. Our computational approach has been thoughtfully tested in a related study of gas-phase ion solvation against high level *ab initio* benchmarks (with a special focus on treating dispersion interactions in this rather complex system) and converged path integral simulations. Our simulations provided remarkably different solvation structures in comparison with gas-phase solvatomers. The weak interaction with the surface can compensate for loss of water-water and water-ion interactions and therefore stabilize solvatomers that are unlikely or even unstable in gas phase. The sampled configurations of the performed NVT simulations will be used as initial conditions for future NVE trajectories. This ensemble of NVE simulations can be used for rigorous calculation of correlation functions and for obtaining (THz) spectra of the system being a direct probe of the hydrogen bond network dynamics.

Towards reliable computed thermodynamic data for aqueous metal ions: The case of cadmium.

Stefan Andersson², Francesca L. Bleken¹, Espen Sagvolden¹, and Ole Swang^{1*}

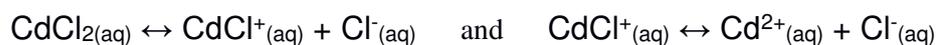
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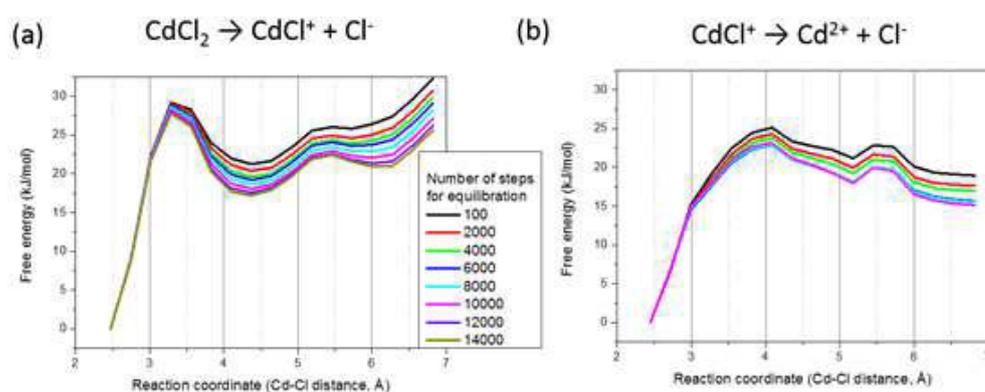
*: Presenting author

Cadmium, due to its toxicity, it is increasingly being replaced by other materials. It is mostly produced as a by-product of the refining of other metals, notably zinc. It is an unwanted pollutant in many industrial processes, and technology for cadmium separation will probably continue to be important in the future, even if production should diminish. Both production and abatement of cadmium rely on aqueous processes. Atom-scale modelling of energetics for reactions in aqueous solution is done routinely for reactions involving many classes of species. Metal ions are demanding cases, and the goal of the present study is to investigate opportunities for reliable computed reaction energies for metal ions in aqueous solution.

We present reaction and activation energies for the reactions



as calculated using two different atom-scale dynamics approaches based on DFT and forcefields, respectively, followed by discussion on structures, mechanistic aspects, and opportunities for computational support in the development of improved metal-separation technology.



Explicitly correlated *ab initio* benchmark study on water clusters (H₂O)_n, n=2–20: The right answer for the right reason?

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In a sequel to our recent revision[1] of the S66x8 noncovalent interactions benchmark, the BEGDB and WATER27 datasets of water cluster association energies have been re-examined at the MP2 and CCSD(T) basis set limit, with both conventional and explicitly correlated (F12) approaches. For the MP2 and CCSD–MP2 contributions, rapid basis set convergence is observed with explicitly correlated methods compared to conventional methods. However, conventional, orbital-based calculations are preferred for the calculation of the (T) term. For the CCSD-MP2 term, CCSD(F12*) converges somewhat faster with the basis set than CCSD-F12b. The performance of various DFT methods is also evaluated: Head-Gordon's ω B97X-V and ω B97M-V functionals[2] are found to outperform all other DFT functionals. Counterpoise-corrected DSD-PBEP86 [3] and raw DSD-PBEPBE-NL also perform well. In the WATER27 dataset, the anionic (deprotonated) water clusters exhibit unacceptably slow basis set convergence with the regular cc-pVnZ-F12 basis sets, which only have diffuse s and p functions. To overcome this, we have constructed modified basis sets, denoted aug-cc-pVnZ-F12 or aVnZ-F12, which have been augmented with diffuse functions on the higher angular momenta.

Our best calculated dissociation energies can be reproduced through n-body expansion, provided one pushes to the basis set and electron correlation limit for the 2-body term: for the 3-body term, post-MP2 contributions (particularly CCSD-MP2) are important for capturing the 3-body dispersion effects. Terms beyond 4-body can be adequately captured at the MP2-F12 level.

[1] B. Brauer, M.K. Kesharwani, S. Kozuch, J.M.L. Martin, *PCCP* **18**, 20905 (2016).

[2] N. Mardirossian, M. Head-Gordon, *J. Chem. Phys.* **114**, 214110 (2016).

[3] S. Kozuch, J.M.L. Martin, *J. Comput. Chem.* **34**, 2327 (2013).

GöBench: a joint initiative for experimental benchmarking of quantum chemical methods

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In any computational study, one struggles in finding the best compromise between method accuracy and cost. Defining and committing to an approach requires some *a priori* knowledge of how the latter may fair in the envisioned application. Computational benchmarks can help with the task. Through the use of standardized tests, one can more effectively assess the ‘goodness’ of the method, and compare to the choices made by other research groups. They also often serve as a first quality check to newly developed quantum chemical methods, from DFT functionals to wave function based approaches.

For several reasons which have been pointed out elsewhere[1], we have grown accustomed to benchmarking theory results with other purely theory-based reference values. Although this is for the most part well justified, it can lead to some dangerous side effects. One example would be the neglect of molecular dynamics when only vertical electronic excitations are benchmarked. Furthermore, we tend to play it safe. We only benchmark systems and properties for which we can compute a ‘reliable’ (or so we think) value. My argument is that by leaving out experiment from our benchmarking practices, we are losing opportunities to advance quicker and more effectively our computational tools.

In this talk, I present this argument in light of experiments and calculations from small (triatomics) to large systems (a few hundred atoms), highlighting the benefit of experimental reference values and cross-semination of theoretical works. I will also present our local initiative GöBench at the University of Göttingen, which intends to bring together a suite of experimental groups to provide new and challenging experimental data for the benefit of the Theoretical Chemistry community.

[1] R. A Mata, M. Suhm, *Angew. Chem. Int. Ed.* DOI: 10.1002/anie.201611308

Approaching CCSD(T)/CBS energies for large molecules with the linear-scaling local natural orbital CCSD(T) method

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Efficient, linear-scaling, local second-order Møller–Plesset (LMP2) and local natural orbital (LNO) coupled-cluster (CC) singles and doubles with perturbative triples [LNO-CCSD(T)] approaches are presented [1, 2, 3]. Using our highly optimized implementation correlation energies of the local scheme can be systematically improved towards the corresponding canonical CCSD(T) value within chemical accuracy for systems up to a few hundreds of atoms.

The error originating from the local approximations can be decreased in a simple, black-box manner using increasingly tighter, pre-defined threshold sets. The complete basis set (CBS) limit can be estimated, e.g., via extrapolation relying on triple- ζ and quadruple- ζ quality bases. In recent developments the redundancy in our local ansatz caused by the overlap of the fragments has been drastically decreased leading to an order of magnitude speedup in the integral transformation, and the MP2 and (T) amplitude evaluation steps [1, 2]. Extensions for the efficient evaluation of general order local CC and spin-scaled MP2 energies, and the perturbative terms of double-hybrid density functionals are also presented.

Benchmark calculations [1, 2] demonstrate that our implementation enables correlated calculations for realistic, three-dimensional molecules with more than 1000 atoms using at least triple- ζ basis sets (20000+ AOs) in a matter of days on a single processor (see Figure). Even better efficiency is achieved by utilizing our multi-layer scheme, where, e.g., LNO-CCSD(T) is employed for the most important, active part, while the environment is described at the LMP2 level [3].

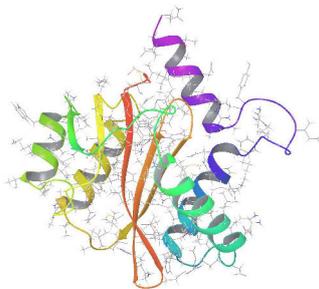


Figure 1: HIV-1 integrase catalytic domain (2380 atoms, 22621 AOs)

- [1] P. R. Nagy, M. Kállay. *J. Chem. Phys.*, **146**, 214106 (2017)
- [2] P. R. Nagy, G. Samu, M. Kállay. *J. Chem. Theory Comput.*, **12**, 4897 (2016)
- [3] B. Hégyely, P. R. Nagy, G. G. Ferenczy, M. Kállay *J. Chem. Phys.*, **145**, 064107 (2016)

Large-scale Valence Bond Applications: Excitons and Transition Metal Complexes

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Valence bond methods offer the advantage that the picture of electronic structure obtained is free from artifacts due to orthogonality, allowing the wave function to reflect the impact of physical effects unimpeded. This would be a great advantage in the study of excitons enabling us to ‘see’ the structure of the exciton. In addition, the localized nature of overlapping orbitals gives a clearer view of bonding and other important chemical ideas such as the octet rule and ligand field theory. Overlapping orbitals also have many advantages for computational scalability. A relatively new formulation of valence bond capturing all these advantages – Variational Subspace Valence Bond [1] – is described and its high scalability is demonstrated by application to excitons in lithium fluoride and complexes of copper oxide with carbon monoxide. All-electron calculations on systems with more than one hundred atoms using more than one million processes are presented.

[1] G. D. Fletcher, *J. Chem. Phys.*, 142, 134112 (2015).

Scalable polarizable molecular dynamics using Tinker-HP: millions of atoms on thousands of cores

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Tinker-HP is a CPU based, double precision, massively parallel package dedicated to long polarizable molecular dynamics simulations and to polarizable QM/MM. Tinker-HP is an evolution of the popular Tinker package (<http://dasher.wustl.edu/tinker>) that conserves its simplicity of use but brings new capabilities allowing performing very long molecular dynamics simulations on modern supercomputers that use thousands of cores. Indeed, this project gathers scientists from various fields including Chemistry, Applied Mathematics and Biomolecular Engineering and redefined completely the algorithmic of usual polarizable simulations package. The Tinker-HP approach offers various strategies using domain decomposition techniques for periodic boundary conditions in the framework of the $(N)\log(N)$ Smooth Particle Mesh Ewald or using polarizable continuum simulations through the new generation ddCosmo approach. Tinker-HP proposes a high performance scalable computing environment for polarizable force fields giving access to large systems up to millions of atoms. I will present the performances and scalability of the software in the context of the AMOEBA force field and show the incoming new features including the advanced SIBFA polarizable molecular mechanics approach and the density based GEM force field as well as newly available "fully polarizable" QM/MM capabilities. Various benchmarks and examples on biomolecular systems will be provided on several architectures showing that the approach is competitive with GPUs for small and medium size systems but allows addressing larger molecules on modern supercomputers. As the present implementation is clearly devoted to petascale applications, the applicability of such an approach to future exascale machines will be exposed and future directions of Tinker-HP discussed.

[1] F. Lipparini, L. Lagardère, B. Stamm, E. Cancès, M. Schnieders, P. Y. Ren, Y. Maday, J.-P. Piquemal, *J. Chem. Theory. Comput.* 10, 1638-1651 (2014).

[2] L. Lagardère, F. Lipparini, E. Polack, B. Stamm, E. Cancès, M. Schnieders, P. Y. Ren, Y. Maday, J.-P. Piquemal, *J. Chem. Theory. Comput.* 11, 2589 (2015).

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[4] F. Aviat, A. Levitt, Y. Maday, B. Stamm, P. Y. Ren, J. W. Ponder, L. Lagardère, J.-P. Piquemal, *J. Chem. Theory. Comput.* 13, 180-190 (2017).

[5] L. Lagardère, L.-H. Jolly, F. Lipparini, B. Stamm, G. A. Cisneros, N. Gresh, Y. Maday, J. W. Ponder, P. Y. Ren, J.-P. Piquemal, submitting (2017).

Vibronic Boson Sampling

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The intrinsic nature of parallelism of quantum states is anticipated to give extraordinary computational power to quantum processors for certain problems. A linear optical network is one of the simplest quantum processors that it could reveal the (computational) quantum supremacy against classical machines. A photon-sampling problem in a linear optical network, so-called Boson Sampling, is a specially designed mathematical problem, which is expected to be intractable for any classical machine. Molecular vibronic spectroscopy, where the transitions involve non-trivial Bosonic correlation due to the Duschinsky Rotation, is strongly believed to be in a similar complexity class as Boson Sampling [1]. At finite temperature, the problem is represented as a Boson Sampling experiment with correlated Gaussian input states. Here we show that every instance of Gaussian Boson Sampling with an initial correlation can be simulated by an instance of Gaussian Boson Sampling without initial correlation, with only a polynomial overhead. We refer such a generalized Gaussian Boson Sampling motivated by the molecular sampling problem as Vibronic Boson Sampling [2].

[1] J. Huh, G. G. Guerreschi, B. Peropadre, J. R. McClean, and A. Aspuru-Guzik, *Nature Photon.*, **9**, 615 (2015).

[2] J. Huh and M.-H. Yung, Preprint: arXiv:1608.03731 (2016).

PCMSolver: a modern, modular approach to include solvation in any Quantum Chemistry Code

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Many quantum chemistry packages are large collaborative efforts involving several communities with different expertise. The development and maintenance of the resulting codes is often a significant undertaking, and the inclusion of new features in a code becomes a challenging task, often requiring the knowledge of a large amount of code due to suboptimal design. In order to improve the efficiency of the code development work flow, and allow researchers to devote more efforts to the scientific discovery instead, a modular approach should be adopted.

A module can loosely be defined as a separate piece of code, providing a specific functionality through a library. In order to be widely deployable, a module needs several key-features such as: (1) a well defined Application Programming Interface; (2) unit- and regression-testing; (3) code development independent of the main Quantum Chemistry program.

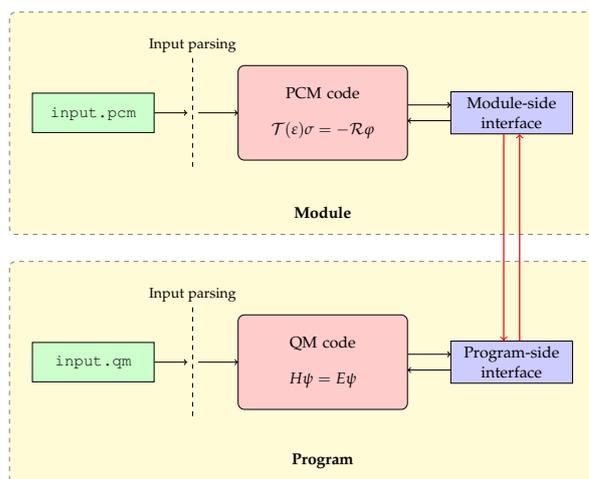


Figure 1: An illustration of the modular approach to solvation adopted by PCMSolver.

The inclusion of solvent effects in Quantum Chemistry is a clear example where such a modular approach can and should be adopted. The module provides the solvent reaction field, for a given potential of the molecular system. Most of the internals of the module (how the reaction field is obtained) are hidden inside the module, exposing to the main code only the functionality which is strictly required.

The advantage of such an approach is twofold: (1) once a new feature is available in the module, all codes which are interfaced to it could simply download the new version, largely reducing the coding efforts; (2) including solvation in a new code reduces to providing the interface to the module, thus leveraging on the already available features of both the module and the main code.

Using this guiding principles, we have developed PCMSolver, which now provides continuum solvation functionality to several codes, such as Dalton, LSDalton, Dirac, Psi4 and Koala.

In this contributions we will present PCMSolver, showing its features such as the different solvers and environments implemented, how it can be interfaced to any quantum chemistry code, and a few illustrative applications.

Combining frozen-density embedding with the conductor-like screening model using Lagrangian techniques

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We present the explicit derivation of an approach to the multiscale description of molecules in complex environments that combines frozen-density embedding (FDE) with the conductor-like screening model (COSMO). FDE provides an explicit atomistic description of molecule-environment interactions at reduced computational cost, while the outer continuum layer accounts for the effect of long-range isotropic electrostatic interactions. Our treatment is based on a variational Lagrangian framework, enabling a rigorous derivation of response properties. This method is used to compute Stokes shifts in the Tamm-Dancoff approximation (TDA). Using the second-order approximate coupled-cluster singles and doubles (RICC2) method for the subsystems, vertical excitation energies for some simplified protein models are computed, see Fig. 1. The interaction terms between the FDE subsystem densities and the continuum can influence excitation energies up to 0.3 eV and thus cannot be neglected for general applications.

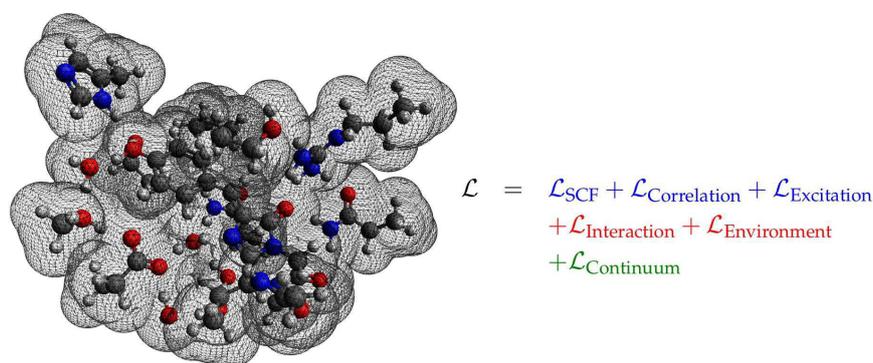


Figure 1: Symbolic COSMO surface of a simplified protein model (*left*) and the Lagrangian used for computing excited-state response properties from wavefunction FDE combined with COSMO (*right*).

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Multiexcitons and strong correlation via single-excitation wavefunctions: applications and future directions

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Due to the possibility of improving in photovoltaic efficiencies, significant effort has been directed towards understanding the singlet fission mechanism. Although accurate quantum chemical calculations would provide a detail-rich view of the singlet fission mechanism, this is complicated by the multiexcitonic nature of one of the key intermediates, the $^1(TT)$ state. Being described as two simultaneous and singlet-coupled triplet excitations on a pair of nearest neighbor monomers, the $^1(TT)$ state is inherently a multielectronic excitation. This fact renders most single-reference quantum chemistry methods incapable of providing accurate results.

In this talk I will discuss our recently developed strategy in which single-spin flip calculations are mapped onto a spin-only Hamiltonian, which is then solved by exact diagonalization to yield the target low-energy biexciton states. In addition, new tensor-based techniques for solving the resulting spin-Hamiltonian will be discussed including numerical examples.

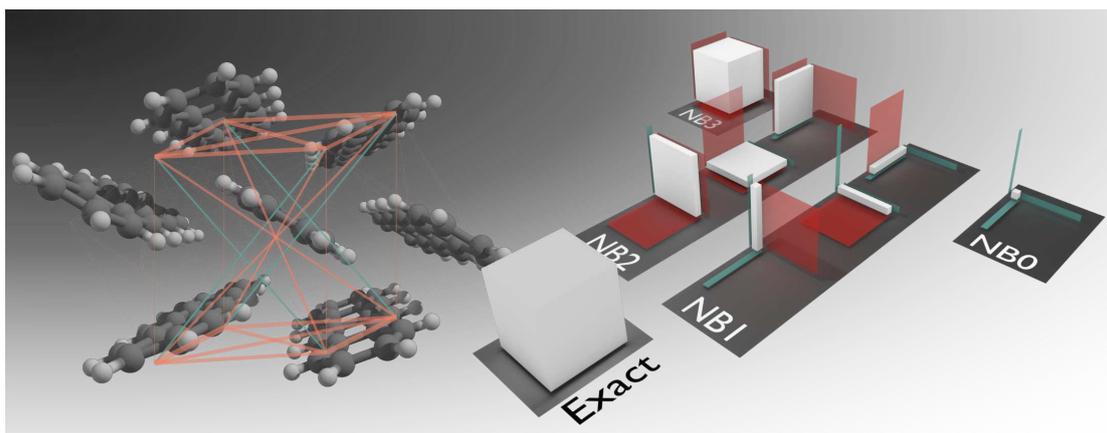


Figure 1: Schematic illustration of the n -body Tucker expansion for a 3-fragment system.

The computation of dielectric constants

Selim Sami¹, Riccardo Alessandri^{2,3}, Ria Broer², Remco W.A. Havenith^{1,2,4}

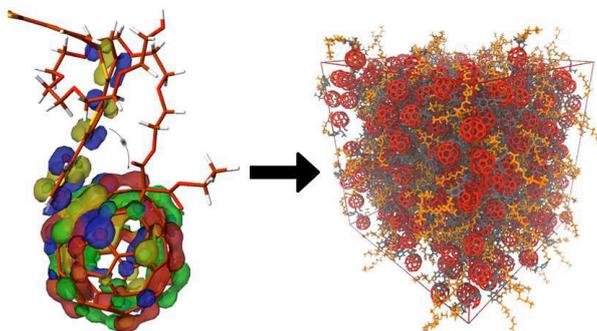
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The current generation of organic photovoltaic devices still lacks the required efficiency to be economically competitive. One proposed way to improve the efficiency is the use of materials with a high dielectric constant [1], thereby decreasing the exciton binding energy and facilitating electron-hole separation. In this presentation, a computational scheme, based on quantum chemical calculations and molecular dynamics simulations, to determine the dielectric constants for different frequency regimes is presented. The different contributions to the dielectric constant will be considered, together with the applicability of the method. For various fullerene derivatives, the dielectric constant is calculated and the applicability of these materials in organic solar cells is discussed. The results also point towards directions for the design of new organic materials with a high dielectric constant.



A multiscale approach combining Quantum Mechanics and Molecular Dynamics

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Organic photovoltaics with *p-f-n* junctions: Computational study of ferroelectric columnar molecular clusters

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In the field of photovoltaics, in which manufacturing cost is essential, organics that can be solution-processed at low temperatures offer great advantages as compared to their inorganic counterparts [1]. Although a tremendous progress in the OPV technology has been achieved over the years, organic photovoltaic devices still suffer from several losses or bottlenecks – a major one of them being recombination of photogenerated electron-hole pairs. Generally, an external bias voltage is required to efficiently separate the electrons and holes in organic material and thus prevent their recombination.

In this contribution results of *ab initio* theoretical explorations of photophysical properties of ferroelectric molecular stacks will be presented. It will be shown that in such systems the photogenerated, due to absorbed light, electrons and holes are driven by the polarization-induced internal electric field in opposite directions toward the cathode and anode, respectively, and thus directly contribute to the photovoltaic output without a need for construction of the *p-n* junction [2]. This provides an intriguing possibility to replace of the ‘intrinsic’ (*i*) layer in a *p-i-n*-type heterojunction architecture for organic solar cells [3] by the ferroelectric layer (*f*). As the term *p-i-n* means the PV device where the photo-active layer is sandwiched between two doped wide-gap layers; a *p*-doped layer and *n*-doped layer, the term *p-f-n* is proposed for this new junction.

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Accurate Ionization Potentials, Electron Affinities, and Photoelectron Spectra of Molecules from First Principles

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The accurate and computationally efficient prediction of ionization potentials (IPs), electron affinities (EAs), and full photoelectron spectra of molecules from first principles has been a long-standing challenge for computational materials science. In particular in the fields of molecular electronics and photovoltaics, the energetics of charged excitations are key factors determining the functionality and efficiency of devices. Hence, the ability to gain meaningful physical insight and to derive design rules for novel materials from first-principles calculations hinges on their ability to predict IPs and EAs with sufficient accuracy at bearable computational costs.

To assess the performance of different DFT and *GW* methods in the prediction of IPs and EAs, we recently benchmarked their vertical IPs and EAs for a test set of 24 organic acceptor molecules against CCSD(T) calculations in the complete basis set limit.[1, 2, 3] To further allow for a direct comparison of the calculated vertical IPs and EAs with experimental data from gas-phase photoelectron spectroscopy, we also implemented a scheme to calculate the full temperature-dependent, vibrationally resolved spectra based on DFT frequencies and a Franck-Condon multimode analysis.[4]

Not surprisingly, our benchmark study finds that those DFT and *GW* methods that employ a non-empirical, system-specific tuning procedure for determining an optimal amount of Hartree-Fock exchange in the exchange-correlation functional yield the most accurate results for IPs, EAs, and fundamental gaps. The downside of these functionals, however, is that they are not size-consistent. The severe consequences of this lack of size-consistency are demonstrated for the example of polyene chains of different lengths, for which we studied how the bond-length alternation, the IP, and the band-gap evolve with oligomer size and how this is influenced by using various different system-specific, non-empirically tuned DFT and *GW* methods.[5, 6]

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Dissipation and dephasing for molecules close to plasmonic nanoparticles: an *ab initio* approach.

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Quantum decoherence is a fascinating property of matter occurring when a given system interacts with an external environment [1]. The theory of open systems is successful in describing decoherence in terms of loss of information of the system, for instance, as dissipation and dephasing. Here, we have exploited a computational protocol based on the real-time propagation of the time-dependent electronic wave function, expanded in configuration-interaction eigenstates of the molecular target [2]. Computational results in Ref. [2] have shown the enhancement in the optical properties of a chromophore induced by plasmonic effects, due to the presence of a metal nanoparticle. The molecule is treated at full quantum level, and the electron dynamics is influenced by the mutual polarization between molecule and nanoparticle.

Dissipation and dephasing effects are introduced in the framework of the stochastic Schrödinger equation (SSE) [3], which is fully equivalent to the master equation approach for the reduced density matrix [4]. We have implemented three different interaction channels with the environment (i. e., beside the metal nanoparticle): relaxation to the ground state by means of spontaneous emission, nonradiative relaxation through internal conversion and pure dephasing of the wave function. The propagation of the SSE has then been performed by using a quantum jump algorithm [5].

We have applied this *ab initio* approach to the study of the evolution of the electronic and optical properties of a model chromophore (LiCN) close to a metal nanoparticle, under the influence of an electromagnetic field, as a function of the distance between the molecule and the nanoparticle [6]. Moreover, the interplay among the different channels has been investigated.

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Microhydration induces qualitative changes in the photochemistry of biomolecular building blocks

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In the past few years we have been studying ultrafast photodeactivation processes of hypothetical abiotic precursors of ribonucleotides [1, 2, 3]. Our results indicate that the photochemistry of these heteroaromatic species is significantly altered in water solution. It is evident that due to direct interactions of water molecules with a chromophore, new deactivation channels become available, which are not present in the gas phase. All these processes seem to have a common signature. After excitation to a bright state and initial relaxation, the system may enter a dark charge-transfer state, in which the electron is either ejected from the chromophore towards the solvent (in $^1\pi\sigma^*$ state) or the reverse process occurs (in $^1n\pi^*$ state). The redistribution of electronic density is followed by proton transfer processes (often multiple) which may lead to formation of conical intersections or intersystem crossings that qualitatively change the photochemistry and photophysics of hydrated chromophores.

For instance, the electron-driven proton transfer (EDPT) along water wires induces the formation of $^1\pi\sigma^*/S_0$ state crossing and provides a very efficient deactivation process, whose quantum yield may reach up to 60%, according to our nonadiabatic *ab initio* molecular dynamics simulations of microhydrated imidazole (Fig. 1a). On the other hand our calculations indicate that the long-lived dark state observed experimentally in cytidine, may be a $^1n_N\pi^*$ state characterized by water-to-chromophore electron transfer (WCET) [4]. This may lead to formation of protonated cytidine and the hydroxyl anion among the photoproducts, and subsequent photohydration, C to U conversion, or oxazolidinone formation reactions (Fig. 1b). These are just a few examples of the EDPT and WCET processes that will be discussed during the presentation.

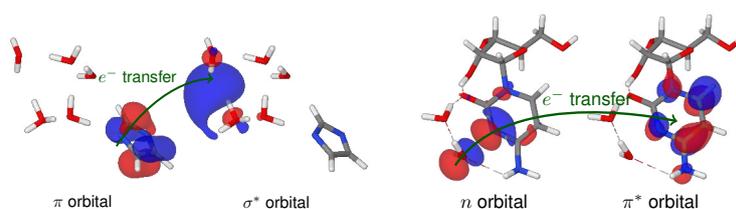


Figure 1: Electron-driven proton transfer in microhydrated imidazole (left) and water-to-chromophore electron transfer in the microhydrated 1-methylcytosine (right)

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Role of the environment in bioluminescence emission: QM/MM study

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The emitting light in beetle and fireflies arises from the electronic relaxation of oxyluciferin, an organic compound resulting from the oxidation of the D-luciferin substrate inside an enzyme called luciferase. The protein environment plays a role in the colour modulation of the light emitted.

In order to theoretically study such systems [1,2], the use of quantum mechanical/molecular mechanical (QM/MM) methods is required. Accurate QM level is needed for dealing with electronic transition and charge transfer phenomena. Taking into account the surrounding protein at the MM level is essential in order to understand the colour modulation and influence of the enzyme. The presentation will discuss some of the results obtained on the bioluminescent system using the coupling of the programs MOLCAS (CASPT2/CASSCF) or G09 (DFT) and TINKER (AMBER force field).

Present results based on new resolved crystallographic structures of blue-shifted coloured and red-shifted coloured species were compared to the more conventional yellow-green emitted firefly systems. The prediction and rationalisation of the influence of the mutation of some residues inside the cavity of the light emitter will be explored with theoretical studies. I will also give last results on the influence of taking into account the water environment while comparing calculated results to the experimental studies of absorption and emission of the in-solution light emitter.

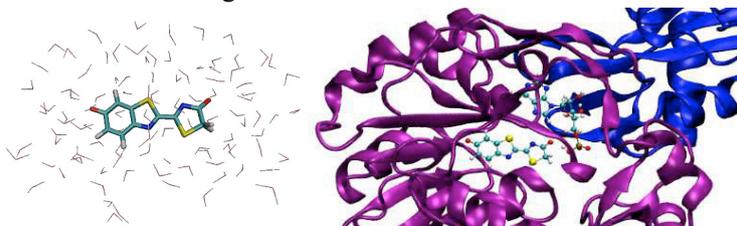


Fig: Oxyluciferin, the light emitter in different environment: water or luciferase protein

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Investigation of optical probes for membrane phase recognition

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Two sets of optically active probes for biological lipid bilayer tissues have been investigated as both Laurdan as well as azobenzene derivatives have been considered in a hybrid Quantum Mechanics-Molecular Mechanics approach. The differences in transition dipole moments between the probes in the various media are investigated and the influence of the media upon the probe's spectra in one photon absorption (OPA), two-photon absorption (TPA) and second harmonic generation (SHG) is discussed. It has also been shown that the applied theoretical approach enables novel simulations of fluorescence anisotropy decay experiments as well as fluorescence lifetime images.

For Laurdan and C-Laurdan, of which the latter is experimentally known to have a higher sensitivity to the membrane polarity at the lipid head-group region, a DOPC lipid bilayer at room temperature is considered. Throughout the simulations, a contrast in orientation for both probes has been found, which brings along differences in optical properties. The second harmonic generation (SHG) beta component is in this sense found to be twice as large for Laurdan with respect to C-Laurdan. The fluorescence anisotropy decay analysis confirms that Laurdan has more rotational freedom in the DOPC membrane, while C-Laurdan experiences a higher hindrance, making it a better probe for lipid membrane phase recognition [1].

Systems for which the change in properties of one component triggers the change in properties of the other are of utmost importance when 'on/off' states are needed. In an in silico study, a new derivative of the conformationally versatile azobenzene compound has therefore been considered [2]. Since the cis and trans conformers have different positions and orientations in the different lipid membranes (DOPC for the liquid disordered phase and DPPC for the gel phase), we found that the cis state is the 'on' state when the probe is inserted into the DOPC membrane, while it is in the 'off' state in the DPPC membrane. It has thus been seen that different environments will generate different responses on the same conformer of the probe.

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Accurate treatment for ground and excited states of atoms and molecules in strong magnetic fields

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For strong magnetic fields of around 1 atomic unit ($1B_0 \approx 235000$ T), the magnetic and the Coulomb forces in an atom or molecule are equally important. Such extreme conditions exist for instance on some magnetic white dwarf stars. One may easily imagine that chemistry in these fields changes drastically. In fact, observational spectra from magnetic white dwarfs show a strong magnetic-field dependence, leading to a lot more complexity, i.e., different transition strengths, line-shifts, and splittings. For laboratory experiments, such magnetic fields strengths are completely out of reach such that theoretical predictions become crucial. Previous investigations using full configuration-interaction theory have already shown how different chemistry can be in strong magnetic fields. For instance, molecules may become bound by a bonding mechanism that has not been seen on Earth, the *perpendicular paramagnetic bonding*[1], which can stabilize molecules with a formal bond order of zero.

In order to retain the predictive capabilities and the high-accuracy in the wave function, but extending the applicability to systems with more than three electrons, an implementation of coupled-cluster (CC) theory for the treatment of atoms and molecules in strong magnetic fields has been presented[2]. Recently, the investigation of excited states in strong fields has also become possible via equation-of-motion (EOM) CC theory[3]. In EOM, excited open-shell states can be accessed without having to resort to a multireference treatment by starting from a well-behaved single-reference wave function. As such states, particularly high-spin states with high angular momenta, are stabilized in magnetic fields, the EOM-CC approach appears to be an ideal choice in this context. In this presentation, results for ground and excited states of atoms and molecules in strong magnetic fields are discussed that have been obtained at the CCSD(T) or EOM-CCSD level of theory[2, 3, 4]. In particular, the focus will be on the effect of the magnetic field on binding energies including cases with perpendicular paramagnetic bonding, total energies, the influence of electron correlation as well as the magnetic-field dependence of transition moments.

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Recent advances in theoretical spectroscopy from *ab initio* molecular dynamics

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Spectroscopy is extremely helpful for the analysis of materials. Besides experimental data, calculations provide important insight and allow the targeted study of specific structures, their dynamics and interactions.

We present innovative methods for the calculation of spectroscopic signatures based on density functional theory-based molecular dynamics with a focus on vibrational spectroscopy. Besides the study of solvation effects [1,2,3], efficient approaches for Infrared and Raman spectroscopy for condensed phase systems [4,5], relying e.g. on periodic subsystem density functional theory, have been presented. Other developments have dealt with Sum Frequency Generation and Raman Optical Activity spectroscopy [6,7]. This paves the way for the computationally efficient and accurate study of molecules on (semiconductor) surfaces/interfaces and in gas/liquid phase at ambient conditions with consideration of anharmonicity and realistic band shapes in the spectra. Among various investigated systems, chiral ionic liquids have recently been explored in detail [8].

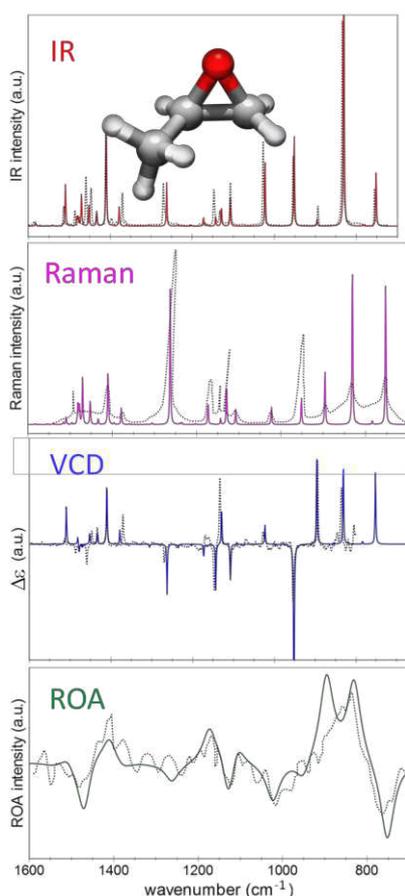
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Anharmonic Effects on Vibrational Spectra Intensities: Infrared, Raman, Vibrational Circular Dichroism, and Raman Optical Activity

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An accurate comparison between simulated and experimental vibrational spectra requires going beyond the double-harmonic approximation, including anharmonic effects on vibrational energies, as well as on intensities. While the former are independent of the spectroscopy, the latter can only be done through property- and transition-specific developments, ideally taking into account the anharmonicity of both wave function and properties. This results in a proper account of the intensity of non-fundamental transitions and more accurate band-shapes. Recent developments on a comprehensive and robust generalized version of the second-order vibrational perturbation theory (GVPT2) for vibrational averages and transition properties have made possible the simulation of fully anharmonic infrared (IR), Raman spectra, as well as their chiral counterparts, namely vibrational circular dichroism (VCD) and Raman optical activity (ROA), for medium-to-large molecular systems [1-4]. We will show that a very good agreement between computed and experimental spectra, considering both band positions and their relative intensities, which define the overall spectral pattern, can be achieved, using methyloxirane as benchmark. We will also discuss on the extension of the approach toward larger and more complex molecular systems.

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Infrared absorption spectroscopy beyond the dipole approximation based on the multipolar Hamiltonian: Theory and application.

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Recent advancements of vibrational spectroscopy combined with nano-optical techniques allow us to study molecular geometries, chemical reaction dynamics, or surface phonons at the scale down to the nanometer or even single molecule resolutions by adopting near field, i.e., a highly localized electromagnetic field around a metal tip or a small aperture. In these nano-spectroscopic measurements, molecules can interact with a nonuniform electric field because of the highly localized nature of near-field, requiring a theoretical method beyond the dipole approximation. One way to go beyond the dipole approximation is to consider a quadrupole interaction between molecule and near-field by considering the gradient of an electric field, especially in the study of surface enhanced Raman spectroscopy. It is not apparent, however, whether the interaction between a molecule and highly localized near-field can be described by first few terms of the multipole expansions. Also the spatial variation of electric fields depends on experimental setups, i.e., depends on the shape of a tip or aperture used. To study the near-field around nanostructures, researchers in computational nano-optics have developed a way to solve the Maxwell equation demonstrating that the field distribution is not unique at the nanometer scale.

Here we propose a theoretical method to account the full spatial variation of electric fields by using the multipolar Hamiltonian as our starting point [1]. The interaction between nonuniform electric fields and molecular vibrations is expressed as a vibrational normal-coordinate derivative of a spatial integral of the inner product of the total polarization of a molecule and an electric field so that the polarization is treated rigorously without invoking the conventional dipole approximation. The square of the derivative gives the infrared absorption intensity with an electric field with arbitrary shapes. The formulation is applied to small molecules. IR spectra with a model near field is clearly different from one obtained with uniform electric field (i.e., the dipole approximation). The peak intensities depend on the directions and intensity gradients of the applied electric field. As further applications, we compute an electric field around a metal nanoparticle by using computational electrodynamics techniques and use the computed near field to obtain IR spectra, giving excellent agreement with an experimental surface enhanced IR spectra. Our method thus allows us to combine computational electrodynamics and chemical calculations to study rapidly developing nano-spectroscopic measurements.

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Toward the accurate simulation of vibrationally-resolved spectra for spin-forbidden transitions

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Computational spectroscopy is nowadays routinely used as a predictive and interpretative tool to complement and support experimental results, provided the calculated results reach a sufficient level of accuracy. In this contribution, we present some of our recent developments for the simulation of vibrationally resolved electronic (vibronic) spectra for medium-to-large molecules, going beyond the simple Franck-Condon approximation.[1] In particular, we focus on transitions between states of different spin-multiplicity, which are forbidden under non-relativistic conditions.[2] The transition moments between such states cannot be obtained directly from most standard electronic structure calculations and a more accurate definition of the electronic Hamiltonian, including spin-orbit couplings, is needed.[3] Thanks to recent developments in non-collinear spin Density Functional Theory (DFT) [4, 6], scalar relativistic effects and spin-orbit couplings can be included within the electronic Hamiltonian variationally. Excited states and electronic transition energies and property moments can then be evaluated using two-component Time-Dependent DFT (2c-TDDFT).[5, 6] Furthermore, it is possible to go beyond the Franck-Condon approximation and obtain more accurate band-shapes by numerically differentiating the transition property moments, which are responsible for Herzberg-Teller effects. As an illustration of those aspects, the vibronic spectra of transition metal complexes can be simulated to study their photophysical properties as phosphorescent systems. The research leading to some of these results has been performed in the framework of the ERC Advanced Grant Project DREAMS “Development of a Research Environment for Advanced Modelling of Soft Matter”, GA No. 320951.

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Nuclear correlation effects in X-ray spectroscopy from a time-domain perspective

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To date X-ray spectroscopy has become a routine tool that can reveal highly local and element specific information on the electronic structure of atoms in complex environments. Despite working on energy scales that are much larger than those corresponding to nuclear motions, taking nuclear dynamics and the associated nuclear correlations into account is shown to be of importance for X-ray spectroscopy in certain physical situations [1]. Here, we develop a rigorous time-correlation method employing ground state molecular dynamics simulations [1, 2]. The importance of nuclear correlation phenomena is demonstrated by comparison against the results from the conventional sampling approach for gas phase and bulk water. In contrast to the first-order absorption, second-order resonant inelastic scattering spectra exhibit pronounced fingerprints of nuclear motions. The developed methodology is not biased to a particular electronic structure method and, owing to its generality, can be applied to, e.g., X-ray photo-electron and Auger spectroscopies. General strategies for possible improvements to the method will be discussed and current results will be presented.

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DFT calculations of NMR parameters of framework and extra-framework atoms in silicon-rich zeolites.

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Zeolites are crystalline microporous aluminosilicates that are important sorbents and catalysts. The determination of the positions of framework atoms and extra-framework cations is essential for the evaluation of the catalytic and sorption properties of silicon-rich zeolites. Multinuclear solid state NMR spectroscopy in tandem with periodic DFT calculations of the structure including extensive molecular dynamics conformational sampling of the siting of the cationic species and subsequent DFT cluster computations of the multinuclear NMR shielding values are shown to be a viable route to obtain the siting of framework atoms and extra-framework monovalent cations in silicon-rich zeolites. Periodic DFT calculations including extensive molecular dynamics conformational sampling of all possible Li⁺, Na⁺, and Cs⁺ sites were performed employing the cp2k (Li and Na) and VASP (Cs) programs. The ²⁷Al, ⁷Li, and ²³Na NMR shielding values were evaluated utilizing the Gaussian program and five or seven coordination shell clusters.[1-5] The ¹³³Cs NMR shielding for the Cs-zeolites was calculated using the relativistic Dirac-Kohn-Sham approach employing the ReSpect program.[6] Based on the comparison of our experimental MAS NMR results with the calculated ones, we reveal the siting of framework Al atoms and Li⁺,[7] Na⁺, and Cs⁺ cations in silicon-rich zeolites.

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Elastic behavior of White Micas solid solutions as a function of the pressure

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Phyllosilicates are found in igneous, metamorphic and sedimentary rocks in the Earth's crust and mantle. By subduction processes, these minerals help in bearing important amount of water in the Earth's interior. Muscovite (Ms) is the crossing point of two solid solutions (SS): one with Paragonite (Pg) and the other one with Phlogopite (Phl). In the first SS, Na⁺ and K⁺ are changing in the interlayer space; and in the second one, two Al³⁺ are changing with three Mg²⁺ in the octahedral sheet. These minerals are considered to be petrogenetic and Geobaro-thermo-meter indicators. So, the elastic behavior as a function of pressure (P) is an important issue to know.

Both SS can be described by the following ideal formula $K_{1-x}Na_xAl_{2-y}Mg_{y+y*0.5}(Si_{4-z}Al_z)O_{10}(OH)_2$, when $y = 0$, $0 \leq x \leq 1$ and $z \approx 1$ is the SS of Ms-Pg and when $x = 0$, $0 \leq y \leq 2$ and $z \approx 1$ is the SS of Ms-Phl. Our calculations have been performed in the $2M_1$ polytype. In this work, a DFT study of the crystal structure, polyhedral, atomic volume, elastic constants (C_{ij}) and gap of solubility of the two SS as a function of the P is accomplished with the Siesta program. The Ms-Pg SS has been performed to 6 GPa, and the Ms-Phl to 9 GPa.

The c axis is compressed five time more than a and b axes. EoS' have been calculated. For the Ms, atomic compressibilities have been also calculated, finding K⁺ and O show the largest compressibility in the interlayer space. From the excess free energy due to volume, the gap of solubility of the Ms-Pg SS increases as a function of the P, and decreases in the Ms-Phl SS. In Ms-Pg SS, C_{ij} increases as a function of the P, showing different functional behavior; two regions of compression have been found out: at low P (to 1 GPa) and from 1 to 6 GPa. Different formulae $C_{ij}=f(P)$ have been calculated in the different regions.

Mixed valency and local hybrid functionals**Martin Kaupp^{1,*}, Simon Gückel¹, Amir Karton², Paul J. Low²**¹*Technische Universität Berlin, Institut für Chemie, Theoretische Chemie, Sekr. C 7,
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The reliable prediction of mixed-valent (MV) systems close to the borderline between partially localized (class II of the Robin/Day description) and fully delocalized (class III) is a challenge for quantum-chemical methods, due to the need to accurately reproduce exchange and dynamical or non-dynamical correlation, and the often crucial role of environment (solvent, solid...) [1]. Using a pragmatic protocol [1] based on a custom-made global hybrid functional and suitable solvent models, we have been able to demonstrate the crucial role of conformation for electronic coupling and spectroscopy in organometallic MV systems [2,3], up to a break-down of the Robin-Day scheme due to a continuum of localized and delocalized conformations [3]. Application of the protocol to further systems, such as class II di-iron organometallics, has required an extension of our toolbox, as spin contamination and other limitations of the global-hybrid based scheme have been found. Here use of recent local hybrid functionals [4] with position-dependent exact-exchange admixture has been instrumental, in particular their recent TDDFT implementation in Turbomole [5]. Local hybrids allow to reproduce the inter-valence charge-transfer bands correctly, where global hybrids fail. Using a recent implementation of local hybrid gradients [6], similar functionals turn out to perform excellently for structure and energetics of gas-phase MV benchmark systems [7], where we may compare to virtually exact coupled-cluster data.

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Double-hybrid density functionals: is there anything new to tell?

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Over the past years, we have seen tremendous improvements in the development of quantum-chemical procedures and we now have access to methods that allow the accurate treatment of systems with even hundreds of atoms. However, the large number of available methods also makes it hard for the computational-chemistry user to understand their benefits or potential risks. As a consequence, one can therefore observe the trend to stick to a few familiar — albeit sometimes older — levels of theory, such as the B3LYP or M06-2X density functional theory (DFT) approximations. Meanwhile, the DFT-developer community has acknowledged so-called double-hybrid density functionals (DHDFs) as established methods for treating electronic ground-state properties. Combined with London-dispersion corrections, DHDFs can even be considered as the currently most accurate DFT approximations for (main-group) thermochemistry, kinetics, noncovalent interactions, geometries, and frequencies; for a review, see Ref. [1].

In this presentation, I will first give a brief overview of the current state of double-hybrid DFT for electronic ground states, before I will discuss recent studies that explored strategies to further modify the current approximations [2,3].

Most researchers in the DFT community are probably unfamiliar with earlier work that has shown DHDFs to be accurate candidates for the calculation of excitation energies [1]. In the second part of my presentation, I will therefore review these previous findings, before I will outline our recent, successful efforts to expand relatively recent ground-state DHDFs within the time-dependent DFT framework [4].

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Exchange-Correlation Potentials and Energy Densities in Spherically Confined Atoms

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One of the promising ways of developing density functionals lies in creating a simple physical system, in which accurate correlated electron densities are easily available and in which the amount of electron correlation can be tuned by varying a well-defined external parameter. To this end, we are using free atoms confined in a spherical cavity of a given radius R_c [1, 2]. The cavity radius R_c strongly influences the total atomic energy, the electron density, the exchange energy and density, and in some case the correlation energy and thus can be employed as the tuning parameter.

First, local exchange potentials corresponding to the Hartree–Fock electron density have been obtained using the Zhao–Morrison–Parr method [3] for a number of confined atoms. The exchange potentials obtained and the resulting density were compared to those given by the Becke–Johnson (BJ) model potential [4]. It is demonstrated that introducing a scaling factor to the BJ potential allows improving the quality of the resulting density. The optimum scaling factor increases with decreasing confinement radius [5].

We also studied correlation energies, correlated electron densities, and exchange-correlation potentials obtained from Configuration Interaction (CI) and DFT calculations in confined atoms. The variation of the correlation energy with R_c is relatively small for the He, Be²⁺, and Ne systems. However, in the neutral Be atom the CI correlation energy increases markedly with decreasing R_c . This makes beryllium a very convenient system for developing and tuning correlation functionals [6].

Finally, we calculated pure correlation energy densities $E_c^{\text{CI}}(r)$ from the CI wavefunction. To this end, we developed a method for obtaining $E_c^{\text{CI}}(r)$ directly from CI coefficients, making use of Nesbet's theorem. Subsequently, the parameters of a model density functional $E_c^{\text{M}}(\rho)$ were adjusted by the least-squares to reproduce $E_c^{\text{CI}}(r)$. The parameters depend on R_c , and this dependence was incorporated in $E_c^{\text{M}}(\rho)$. This strategy paves the way for a direct construction of local density functional from the correlated electron density.

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Linked-cluster formulation of screened electron-hole interaction from explicitly-correlated geminal functions without using unoccupied states

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The electron-hole or quasiparticle representation plays a central role in describing electronic excitations in many-electron systems. For charge-neutral excitation, the electron-hole interaction kernel is the quantity of interest for calculating important excitation properties such as optical gap, optical spectra, electron-hole recombination and electron-hole binding energies. Accurate determination of the electron-hole interaction kernel remains a significant challenge for precise calculations of optical properties in the GW+BSE formalism. The inclusion of unoccupied states has long been recognized as the leading computational bottleneck that limits the application of this approach for large finite systems. In this work, we present an alternative derivation in real-space representation that avoids using unoccupied states to construct the electron-hole interaction kernel. The central idea of our approach is to treat electron-electron correlation for both ground and excited state wave functions using a two-body correlator operator which is local in real-space representation. We demonstrate using diagrammatic techniques that the frequency-dependent electron-hole kernel can be expressed in terms of connected closed-loop diagrams. We show that the cancelation of disconnected diagrams is a consequence of the linked-cluster theorem in real-space representation and the resulting renormalized operators are equivalent to infinite-order summations of particle-hole diagrams. The derived electron-hole interaction kernel was used to calculate excitation energies in atoms, molecules, clusters and quantum dots and the results for these systems were compared with CIS, TDHF, TDDFT, EOM-CCSD, and GW+BSE calculations.

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Local Spins

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It is known that for singlet systems the spin density vanishes everywhere. Nonetheless, there are systems (*e.g.*, antiferromagnets, singlet diradicals) for which the physics indicates that the overall singlet state is resulting from singlet coupling of non-vanishing *local spins*. In order to study these local spins on the wave function level, one has to decompose the expectation value $\langle \hat{S}^2 \rangle$ of the total spin-square operator \hat{S}^2 . But $\langle \hat{S}^2 \rangle$ is a single number, for its meaningful decomposition additional conditions should be considered.

A long quest resulted in a set of requirements that permit to decompose $\langle \hat{S}^2 \rangle$ in a unique and physically relevant manner. In the lecture these requirements will be described and the derivation of the resulting formulas for single determinant and correlated wave functions will be discussed, along with some numerical examples and some further aspects of the formalism.

Spin-Orbit Coupling Effects of Open-Shell Systems with Coupled-Cluster Theory

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A coupled-cluster approach has been implemented at the CCSD and CCSD(T) levels to account for spin-orbit coupling (SOC) effects of closed-shell systems[1], where SOC is included in post self-consistent field (SCF) treatment. This SOC-CC approach is quite efficient due to the use of real spin-orbitals particularly for molecules with low symmetry. It has been shown to be able to describe SOC effects of even superheavy-element molecules with high accuracy using relativistic effective core potentials, since single excitation amplitudes can account for orbital relaxation effectively. To deal with open-shell systems, the equation-of-motion (EOM) approaches based on the SOC-CCSD method for ionized[2], electron-attached[3], and double ionized states[4] with a closed-shell reference have been developed.

EOM-CCSD for double electron attachment based on this SOC-CC approach with closed-shell reference will be reported. Rather accurate SOC splitting is achieved with this approach. Furthermore, this SOC-CC is extended to spatially non-degenerate open-shell systems in this work[5]. The unrestricted Hartree-Fock determinant corresponding to the scalar relativistic Hamiltonian is employed as the reference. Due to broken of time-reversal symmetry and spatial symmetry, this open-shell SOC-CC approach is rather expensive compared with the closed-shell SOC-CC approach. The open-shell SOC-CC approach is applied to some open-shell atoms and diatomic molecules with s^1 , p^3 , σ^1 , or π^2 configuration. Our results indicate that reliable results can be achieved with the open-shell SOC-CCSD(T) approach for these systems.

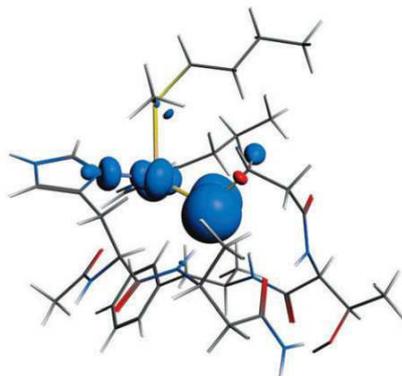
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Can Spin-State Energetics of Transition Metal Complexes be Accurate at Single Reference Level?

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The molecular spin state has a potentially crucial effect on the chemical properties of transition metal complexes. Thus, the difficulty in accurately predicting even the ground-state configuration, not to mention quantitative spin-state energy differences, is one of the great challenges faced by computational quantum chemistry [1, 2]. With the exception of a few density functional approaches [3], accurate quantum chemical methods for describing spin have long been restricted to relatively small systems [4], due to the many facets of electron correlation having to be properly described in order to obtain reliable results. Recently, the domain based local pair natural orbital coupled cluster theory with single-, double-, and perturbative triple excitations, DLPNO-CCSD(T), by Neese and co-workers [5] was augmented with the ability to treat open-shell systems. The set of open-shell complexes treatable at the CCSD(T) level of theory has thus grown immensely. However, is single-reference CCSD(T) accurate enough?



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Specific Ion Interactions with Biomolecules: Molecular Dynamics Simulations and Energy Decomposition Analysis

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Specific effects of ions depend not only on the charge of the ions but also on their other properties (such as size, polarisability and structure of hydrated complexes). The effects of salts on protein precipitation were studied by Hofmeister already at the 19th century, and led to the development of the famous Hofmeister series. Computer simulations have been very useful in the study of specific ion effects. The development of force-field parameters for simulations of ions was very instrumental in this respect. A realistic representation of interactions between ions and solutes in water, however, remains a challenge, because of the need to account for ion-solute, ion-water and solute-water interactions at the same time and with the same set of parameters. Here, we will discuss our recent applications of computer simulations to study the interactions between alkali cations and tetraether membranes or bovine serum albumin. Using computer simulations, we could develop a model to explain how certain microorganisms are able to withstand solutions with strikingly low concentrations of sodium and potassium [1]. We could also show that, unlike other proteins, bovine serum albumin does not have a clear preference to sodium over potassium [2]. Finally, using QM-based energy decomposition analysis we have found that the binding of Li^+ (and to a smaller extent also that of Na^+ and K^+) to protein ligands is not purely electrostatic, and involves an unnegligible contribution from polarisation. The consequences of this to computer simulations will be discussed. Finally, we will also discuss the potential to simulate proteins together with Zn^{2+} [3], which is a very common protein cofactor.

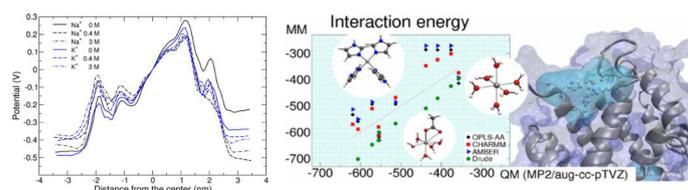


Figure 1: **Specific ion interactions - examples of effects and challenges.** Specific ion interactions can modify the potential of membranes (left) and proteins in a concentration-dependent manner. Forcefield accuracy remains an issue when it comes to a correct quantitative description of such interactions (right).

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Computational Insights into Sulphur Isotopic Fractionation in Carbonate-Associated Sulphate

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Sulphate incorporated into calcium carbonate minerals, or carbonate-associated sulphate (CAS), is a promising proxy for the sulphur isotope composition of seawater sulfate over Earth's history. However, the isotopic fractionation of sulphur between dissolved sulphate and CAS has not yet been systematically investigated, neither experimentally nor theoretically. In a set of carbonate precipitation experiments at variable sulphate concentration we find an intriguing dependence of sulphur isotope fractionation on the sulphate-carbonate ratios in solution (and the concentration of CAS). As sulphate is incorporated into the carbonate lattice at concentrations of hundreds to thousands of ppm, it is conceivable that it affects the energetics of the crystal lattice sufficiently to influence the equilibrium sulphur isotope fractionation.

Isotopic fractionation (α) can be calculated using the vibrational frequencies (ω_i) of each species:

$$\alpha = \beta_{CAS} / \beta_{solution}$$

$$\beta = \frac{Q_H}{Q_L} = \prod_{i=1}^{3N-6} \frac{u_{H_i}}{u_{L_i}} \cdot \frac{\exp\left(-\frac{u_{H_i}}{2}\right)}{\exp\left(-\frac{u_{L_i}}{2}\right)} \cdot \frac{1 - \exp(-u_{L_i})}{1 - \exp(-u_{H_i})}$$

where N is the number of atoms, Q is the partition function, H and L denote the heavy and light isotopes, respectively, and $u_i = \frac{h \cdot c \cdot \omega_i}{k_B \cdot T}$. [1]

We investigated this possibility by density functional theory and considered various factors affecting the calculations. We will present the dependence of sulphur isotopic fractionation between dissolved sulphate and CAS on the concentration of sulphate in the carbonate lattice. We will also evaluate CAS as a proxy for seawater sulphate isotopic composition.

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Tailoring Resonance Assisted Hydrogen Bonds

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Intramolecular Resonance Assisted Hydrogen Bond (RAHB) brings extra-stabilization to a molecule due to the creation of a *quasi*-ring, which can resemble a benzene ring. In a recent review¹ it was highlighted the involvement of RAHB as a driving force in the synthesis of organic, coordination and organometallic compounds. The extra-stabilization of the *quasi*-ring depends on different factors, being the availability of π electron within the new *quasi*-ring one of the more important ones. Thus, when RAHB is linked to one or more benzene rings (sharing a CC bond) the *ipso*-ring aromaticity influences the RAHB distance: the lower the aromaticity of benzene ring the shorter the HB distances, so stabilizing the system.²⁻³

In this work we will discuss two different ways of designing RAHB with different HB distances; (a) substituents effect⁴ and (b) topology and number of benzene rings in the structure. For the first case, we study all possible mono- and di-substitutions in the 3 and 4 position of o-hydroxybenzaldehyde considering three electron donating groups (EDG: NH₂, OH, and F) and three electron withdrawing groups (EWG: NO₂, NO, and CN). We show that it is possible to tune the HB bond distance in the RAHB by locating different substituents in given positions of the aromatic ring. A second way of tailoring the HB distance is adding benzene rings using different topologies, that is, linear and kinked chains. Following Clar's aromatic π rules, polycyclic aromatic hydrocarbons (PAH) have quite different aromaticity if they are in a linear or a kinked topology,⁵ so presenting more or less available π electron for sharing with a *quasi*-ring. In that case, not only the influence if the topology is taken into account, but also the number of benzene rings added.

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Effect of Biradical Character of Organic Molecules on Opto Electronic Properties

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Most organic molecules and polymers used in organic electronics have closed-shell singlet ground states. Certain donor-acceptor systems, however, are open-shell singlet biradicals.[1] Presence of biradicals leads to close packing in crystals as intramolecular and intermolecular electron coupling compete with each other. As a result conductivity along stacking directions is particularly strong for crystals of biradicals.[2] Another important characteristic of biradicals is that they are prone to intramolecular singlet fission.[3] Singlet fission is a process during which the absorption of one photon leads to formation of two triplet states.[4] Intermolecular singlet fission was first observed in tetracene crystals[5] but in donor-acceptor systems[3] intramolecular singlet fission[6] has been demonstrated. Although direct formation of triplet states from singlet ground states is spin forbidden, quantum yields can reach almost 200%. In this presentation the effect of open-shell character of building blocks for organic electronics will be explored based on time-dependent density functional theory calculations.

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Computationally Driven Design of Efficient Photosensitizer for Dye-sensitized Solar Cell Applications

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Abstract: In this talk, I will present some of our recent works on development of high-efficiency sensitizers for dye-sensitized solar cell application, which is a hot topic for solar energy conversion and utilization. The performance of dyes is very relevant to its atomistic details. Using density functional theory/time-dependent density functional theory calculations and semiempirical quantum dynamics simulations in conjugation with extended Huckel theory, our results showed that replacement of ancillary ligands of Ru(II) complexes dye with square-planar quadridentate ligands can efficiently extend the light-harvesting region to longer wavelength range, the interface electron transfer rate is improved due to the enhanced donor-acceptor coupling. Our results also demonstrated that the performance of dyes can be regulated via the controlled charged states. The addition of anionic ancillary ligands in cyclometalated Ru(II) complexes can efficiently improve the electron-donating ability, raise the occupied orbitals energy levels, enlarge the light-harvesting ability, increase the electron donor-acceptor coupling, and finally promote the interface charge separation. We also examined the role of anchoring group for DSSC applications. The hydroxamate anchoring group might be an alternative to the existing carboxylic acid anchors. This theoretical study explores the new configurations and design strategies of dyes for efficient light harvesting device.

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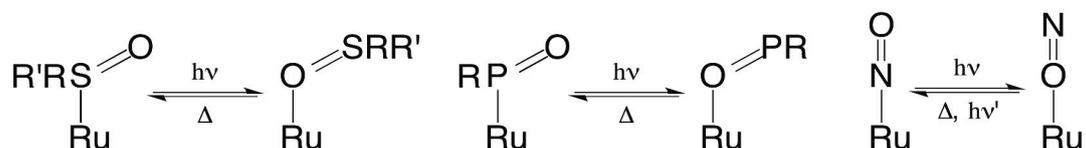
Computational Studies of the Photoswitching Mechanisms in Photochromic Ruthenium Complexes

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Photochromism represents an increasing area of research in photochemistry because of its actual and potential applications in nanosciences, biology, and photonic or optoelectronic devices. The vast majority of light-activated molecular switches displaying photochromic properties rely on organic compounds (e.g., diarylethenes, spiropyrans, fulgides...). However, transition metal complexes have also been designed to display photochromic properties. These systems are often based on linkage isomerizations between the metal center and various ambidentate ligands such as nitrosyl (NO), sulfoxide (RR'SO) and sulfur dioxide (SO₂). While all these photochromic systems have been scrutinized from an experimental point of view, sometimes completed by theoretical studies, the underlying photoswitching mechanisms are far from being fully understood. Computational photochemistry is an essential tool in order to rationalize the photochemical behavior of such compounds. Many computational studies have been reported for organic photochromic compounds but analogous studies of photochromic metal complexes are few. In this presentation, we report some of our recent theoretical results on the linkage photoisomerization mechanisms in photochromic ruthenium complexes Ru-RR'SO,^[1,2] Ru-RPO,^[3] and Ru-NO^[4] (see figure below) using density functional theory and multiconfigurational second-order perturbation theory. In particular, we will show that both adiabatic and nonadiabatic mechanisms are expected to compete, but also that triplet states of different natures can be involved along the photoisomerization pathways.



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Photosensitizing properties of functionalized thiolate-protected gold nanoclusters: insights from theory.

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In the course of developing electro- or photoactive devices, the integration of molecular systems with the unique opto-electronic properties of gold nanoparticles (NPs) has attracted a growing attention. The challenge consists in controlling and understanding the interactions between the NPs and the molecules to design new functional materials presenting emerging properties. Recent works have considered the opportunity of using thiolate-protected gold nanoclusters (GNC) $\text{Au}_x(\text{SR})_y$ where R is an organic ligand. In that vein, GNCs functionalized with glutathione groups have recently been incorporated as photosensitizers in photovoltaic cells, "Metal-Cluster-Sensitized Solar Cells" (MCSSCs), and in photoelectrochemical cells for water splitting [1]. Consequently, there is today a great challenge to understand the electronic properties of these hybrid organic- inorganic systems and the possible electron and/or energy transfer between a photoactive ligand and the GNC.

Within this framework, theoretical tools constitute a powerful complement to design more efficient hybrid architectures. An accurate computational strategy for studying the structural, redox and optical properties of thiolated GNCs using (Time-Dependent) Density Functional Theory [TD-DFT] will be presented. These three properties are of fundamental importance for both "photosensitizer" devices and optoelectronic applications. We will expose how it is possible to (i) to describe with a comparable precision both the GNC and the ligands' properties, (ii) rationalize the effects of the coating on the GNC properties and (iii) analyze the photoinduced energy/charge transfer between the GNC and the ligands [2-4]. Finally, for larger gold NP functionalized with photoactive ligands, we will analyse the interaction between the NP plasmon and the excitation of the molecule with the help of a Quantum Mechanics (QM) /Electrodynamics (ED) computational scheme. [5]

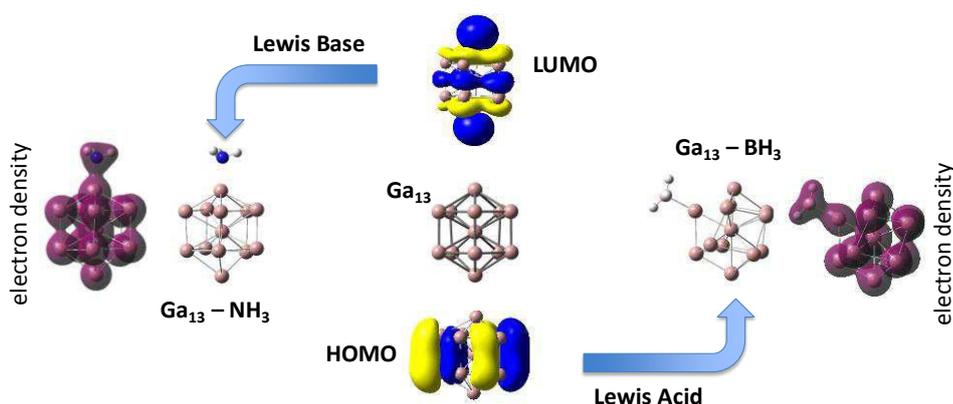
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Modifying the Reactivity of Gallium Nanoclusters with Ligands

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Doped gallium clusters (Ga_{12}X , $\text{X} = \text{B}, \text{C}, \text{N}, \text{Al}, \text{Si}, \text{P}, \text{Ga}, \text{Ge}, \text{and As}$) exhibit interesting electronic and structural variations as a function of the dopant [1-4]. To fully realise the potential of these nano-clusters for catalysis it is necessary to explore in detail the interaction of these species with a range of small molecules. This research uses *ab initio* and Density Functional Theory methods to determine the reactivity of novel gallium-based clusters with small molecules and identifies the structures and stabilities of cluster-molecule complexes. Adsorption of hydrogen, [5] Lewis acids and Lewis bases is found to be energetically favourable but there is significant isomerization with respect to the adsorption site. Consequently, adsorption energies vary not only with valence electronic configuration but also with the adsorption site. Regioselectivity of these interactions is analyzed in terms of cluster bonding and orbital interactions. The cluster-hydrogen interaction is strongly governed by the location and shapes of the frontier orbitals.



Ligand coordination modifies the electronic structure of the cluster, leading to an enhancement of reactivity. In particular, NH_3 coordination was found to lower the energy barrier for H_2 chemisorption by 10% and BH_3 coordination led to reduction of the barrier by 20%. These results demonstrate the potential for ligand coordination as a means of accelerating reactions on cluster surfaces.

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Hydrolysis of (germano)silicates: a new low-barrier mechanism from biased ab initio molecular dynamics.

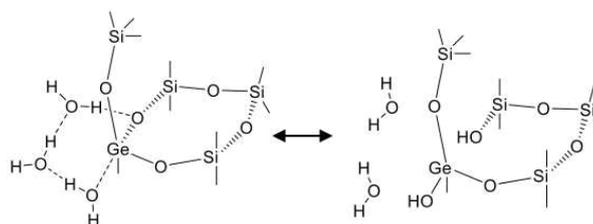
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The silicates, based on a tetrahedron-shaped anionic SiO_4^{4-} group, is one of the most abundant classes of compounds on Earth being heavily used in industry. However, the silicates, and in particular silicates doped with aluminum or germanium, are often being degraded and eventually destroyed upon prolonged exposure to humidity. On the contrary, a well-directed hydrolysis can be beneficial leading to synthesis of new materials such as hierarchical layered silicates with micro- and meso-porosity [1].

Therefore, with a goal to hinder or direct the silicate hydrolysis, numerous first principle studies have focused on understanding the hydrolysis mechanism. However, they were limited to static calculations not properly accounting for both the water dynamics in a fully solvated material and temperature effects [2]. In this study, we employed a (biased) ab initio molecular dynamics to accurately incorporate temperature effects and most importantly to allow for explicit treatment of water molecules in interaction with a (germano)silicate.

A new hydrolysis path has been found, which includes proton-transfer through a chain of surrounding water molecules (see Figure). This new mechanism has two- to three-times smaller reaction barrier ($\sim 50\text{-}90 \text{ kJ}\cdot\text{mol}^{-1}$) than the most stable mechanism proposed previously using limited solvation model [2] and should be thus a preferred mechanism if water is in abundance. In addition, the new mechanism can help explain the possibility of directed hydrolysis for some silicates; the lowest barriers ($\sim 50 \text{ kJ mol}^{-1}$) are found for well accessible exposed $\text{SiO}_4^{4-}/\text{GeO}_4^{4-}$ tetrahedra whereas markedly larger barriers ($\sim 90 \text{ kJ mol}^{-1}$) were calculated for less exposed silicate surfaces. Although, the current study considered a specific (germano)silicate, the UTL zeolite, we expect the new mechanism to be of importance for other (germano)silicates as well.



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Aromaticity from the point of view of the Vorticity of the Current Density Tensor.

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The induced current density vector field ($\mathbf{j}(\mathbf{r})$) has been extensively used for the study of aromaticity [1–4]. However, it has the disadvantage that the direction of the magnetic vector must be chosen a priori without the information about the direction of the most important currents. This does not represent a drawback for plane molecules because the main currents are parallel to the molecular plane and the magnetic vector must be perpendicular to it, but, for non-planar aromatic systems, such as polyhedral boranes and fullerenes, the main currents are not in a single plane. Therefore, the analysis of $\mathbf{j}(\mathbf{r})$ is cumbersome. The anisotropy of the current induced density (ACID) has overcome this problem by compressing the information of the induced current density tensor ($\mathbf{J}(\mathbf{r})$) in a scalar quantity [5,6]. However, it cannot differentiate between anti/aromatic compounds by itself. The vorticity of the induced current density ($\nabla \times \mathbf{j}(\mathbf{r})$) compresses the information of $\mathbf{j}(\mathbf{r})$ in mainly one direction [4]. Here, we analyze the topology of the trace of the vorticity of $\mathbf{J}(\mathbf{r})$ ($\text{tr}(\nabla \times \mathbf{J}(\mathbf{r}))$). This scalar field does not need an arbitrary magnetic vector to be defined and because of that it can be used to study 3D aromaticity. Its analysis shows that the topology of an aromatic and antiaromatic molecules are significantly different. It also can distinguish the most aromatic rings in polyaromatic compounds. Since $\text{tr}(\nabla \times \mathbf{J}(\mathbf{r}))$ is a scalar, its analysis is significantly easier than for $\mathbf{j}(\mathbf{r})$ and contrary to ACID scalar field, it can differentiate anti/aromatic systems by itself.

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Cesium cation- π interactions: DFT and QTAIM studies

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In a recent analysis of the Cambridge Structural Database (CSD) we have identified several crystal structures of cesium complexes which are stabilized by multiple Cs^+ - π interactions [1]. We have therefore decided to investigate a selected number of such complexes so as to unravel the nature of the Cs^+ - π interaction with the aid of both density functional theory (DFT) and Bader's quantum theory of atoms in molecules (QTAIM). These combined DFT and QTAIM studies are useful in the design of macrocyclic receptors and chemosensors [2,3] with high selectivity toward radiocesium (Cs-137). This radionuclide represents an environmental hazard ($t_{1/2}\sim 30$ years) which results from nuclear power plant accidents as well as from the use of radioactive materials.

Acknowledgments. The present research is supported by the Japan Society for the Promotion of Science (JSPS) "Grants-in-Aid for Scientific Research" and by the Graduate School of Engineering of Tohoku University.

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Hypervalency and reactivity from Wannier orbitals

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Compounds said to be hypervalent are very useful reactants in organic chemical syntheses where their remarkable reactivity is tacitly associated with their hypervalency. Hypervalent iodonium compounds are prototypes of these main-group compounds. In this presentation I focus on the hypervalency and reactivity of iodonium compounds.

QMMM simulations of selected iodonium compounds in solvent DCM have been done. Electron structure analysis of the trajectories has been performed to discern the valency of iodonium. Maximally localized Wannier orbitals have been generated and their spatial extensions and the distribution of their centers have been scrutinized. Wannier description provides a chemically meaningful picture that is particularly useful for describing bonding situations because it follows a strict definition of valence with 2 electrons, connecting in this way the traditional MO and Lewis pictures. The analysis reveals that the iodonium is not hypervalent in these compounds. The reactivity of these compounds can then be ascribed to the strong unquenched charge separation present in these molecules which represents a compromise between Coulomb interaction and the resistance of iodonium toward hypervalency.

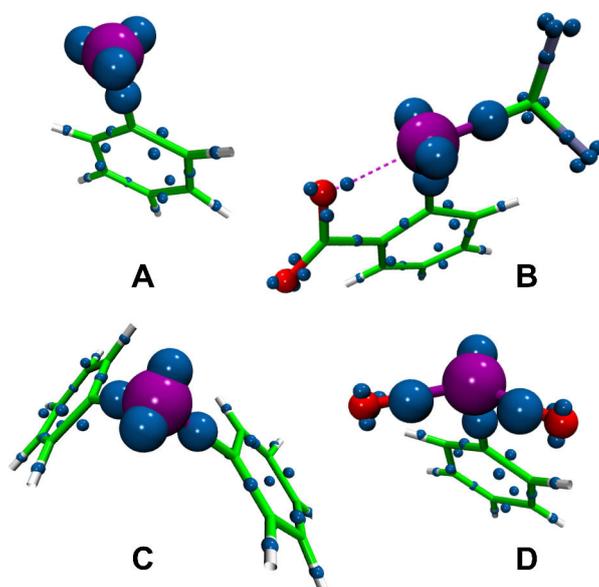


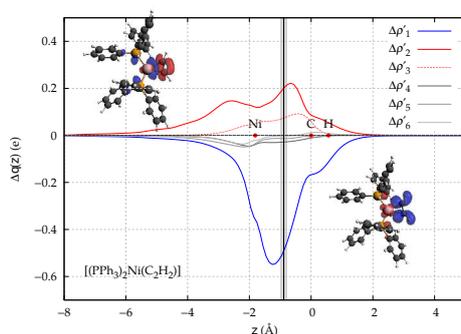
Figure 1: Typical structures taken from QMMM trajectories with the centers of the maximally localized Wannier functions. Centers in close vicinity of iodine are highlighted.

Charge-displacement analysis: a simple tool to reveal charge transfer effects throughout the whole periodic table (from Helium to Oganesson).

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Charge-displacement (CD) analysis was introduced almost ten years ago in order to characterize the chemical bond between noble-gas (Xe) and a noble metal (Au) in Xe-AuF [1]. It is a simple yet powerful tool to reveal and quantify the charge transfer component of the interaction in chemical regimes, from gas phase water's van der Waals complexes, electronic excited states to the super-heavy elements chemical characterization. The method is based on a partial progressive integration of the electron density changes that accompanies intermolecular interactions. Recently, charge-displacement analysis has been employed to analyze on quantitative grounds the Dewar-Chatt-Duncanson components of transition metal coordination complexes [2]. The CD method provides clear-cut measures of donation and back-donation charges that show a stringent correlation with selected experimental observables [3, 4]. The method has been extended to the relativistic four-component Dirac formulation and some preliminary results of this new implementation will be presented.



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The nature of the chemical bond in Be containing molecules:**Apostolos KALEMOS***Department of Chemistry,
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The present study focuses on the Be_2^+ , Be_2 , Be_2^- , Be_3 [1] and $\text{BeO}^{0,-}$, $\text{BeOBe}^{+,0,-}$ [2] species with the aim to unveil their bonding pattern. The ground states of the above molecules are examined mainly through single and multi reference correlation methods. Previous work is scrutinized with an eye to the instability problems inherent in various Hartree–Fock schemes. Under this point of view, we rationalize previous findings and put them in a unified context of what and why should be done in similar hard to crack cases. In all these species excited and/or ionized atomic states participate in a resonant way making chemically possible molecules that have been termed hypervalent and explains also the “incompatible” geometrical structure of some species.

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Theoretical Investigation of a strong cis-effect in an imidazole-imidazolium substituted alkene

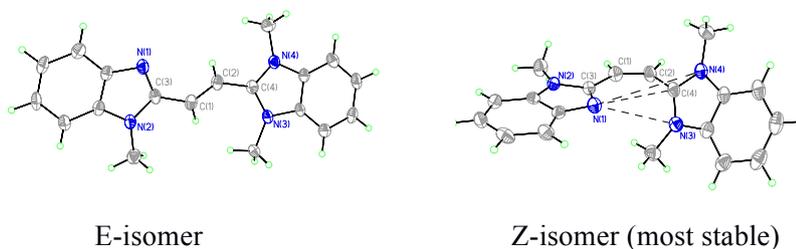
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²*School of Chemistry, University of Melbourne, Australia*

We report the first example of an alkene with two carbon-bound substituents (imidazole and imidazolium rings) where the Z-isomer has a greater thermodynamic stability than the E-isomer that persists in both the gas phase and in solution [1]. Theoretical calculations, solution fluorescence spectroscopy and gas-phase ion mobility mass spectrometry studies confirm the preference for the Z-isomer, the stability of which is traced to a non-covalent interaction between the imidazole lone pair and the imidazolium ring.

Theoretical calculations up to DLPNO-CCSD(T) are required, including solvent effects, to correctly identify the preference for the Z-isomer. A combination of MO, NBO, QTAIM and I-SAPT analyses provide an underlying rationale for the preference for the Z-isomer, which arises from non-covalent (electrostatic) interactions between the N lone pair of the benzimidazole cation and the central C of the benzimidazolium, and an increased localization of the central C=C double bond in the Z-isomer for the cation.



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Fragment Attributed Molecular System Energy Change (FAMSEC) in the study of interactions and molecular stability.

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FAMSEC [1] performs a dedicated energy partitioning of a molecular system without breaking existing bonds. By making use of IQA/IQF concepts, it allows monitoring energy of molecular fragments as well as their contribution to molecular energy on a structural change from an initial to a final state of a molecule (or molecular system). Consequently, most (i) (de)stabilized fragments and (ii) (de)stabilizing a molecule fragments in the final molecular state can be identified and their energetic contributions computed. Furthermore, the origin, on a fundamental level, of the energy contributions can be explored.

Usefulness of FAMSEC will be briefly demonstrated in identifying the origin of (i) increased energy of *cis*-2-butene [2] and *in-in* Xylene conformers (with the CH--HC contact) relative to respective equilibrium structures and (ii) relative stability of amino-acid β -alanine conformers: the lowest energy one with the red-shifted O–H \cdots N and the higher energy conformer with the blue-shifted N–H \cdots O intramolecular hydrogen bond [3]. Importance of using 4-atom fragments in exploring intramolecular interactions (bonds) and their contribution to molecular energy will be explained.

It is commonly accepted that reliability of the IQA data depends on how well molecular energy is recovered by use of IQA-defined energy terms. It will be shown that this is indeed the case in the direct evaluation of IQA data except HF and B3LYP for which $E(\text{IQA}) = E$ but large errors in the computed self-atomic and diatomic interaction energies are present. For post-HF levels (*e.g.*, MP2) and when a comparative approach is used, such as in FAMSEC, a new criterion is proposed to assess quality of IQA data for comparative analyses, $\Delta E(\text{IQA}) \approx \Delta E$, where $\Delta E(\text{IQA})$ and ΔE stand for IQA and electronic energy differences, respectively, between a final and initial-state of a molecular system. The closer $\Delta E(\text{IQA})$ approaches ΔE the closer FAMSEC data approaches values obtained at the CCSD/BBC1 level, regardless of the level of theory/approximation combination used [4].

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Efficiently modeling the electronic circular dichroism of amino and nucleic acids ensembles

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Modeling spectroscopic signals (absorption and circular dichroism) of biomacromolecular systems such as DNA and proteins, is far from being straightforward since it requires the computation of excited states for a relatively high number of atoms and coupled chromophores. So far, only few methodologies have been developed to model nucleic/amino acids ECD spectra and the systems that have been already efficiently tackled are B-DNA [1,2,3], G-quadruplexes [2,4] and peptides [5]. Moreover these methodologies are either computationally costly [2] or lack environmental effects [1]. In our case, we developed a protocol based on the coupling between the Frenkel exciton theory and a QM/MM description of the excited states. Moreover, the conformational space of the system and its dynamic behavior are explored using classical molecular dynamics simulations. The Frenkel excitons theory allows an approximation of the excited states of large molecular systems based on the excited states of relatively smaller QM partitions (coupled chromophores of the system), reducing considerably the computational cost. In the present contribution I will present our promising protocol combining the previously presented features and the results obtained so far on DNA [3], G-quadruplexes [4] and peptides [5].

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