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# Theoretical conformation analysis of a triazine-based, double decker rotor molecule with three anthracene blades

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In this theoretical study we investigate the relative stability of a rotor-shaped molecule based on two triazine cores connected by three anthracene-derived blades, which is useful for polymerization, by Density Functional Theory. The structure has been synthesized on a gram scale from readily available building blocks by exploiting the selectivity difference for the nucleophilic substitution of cyanuric chloride [1]. Since the rotor-shaped molecule can flip its anthracene shovels to a conformation with two pi-stacked anthracene rings in which the cog wheel-like structure is no longer existent and the desired polymerization gets unfeasible, a detailed understanding of the reaction barrier between the rotor-shaped and the pi-stacked structures and an insight into the solvation effects on the relative stability of the two structures is neccessary to predict their occurence. Our theoretical analysis reveals a delicate balance between solvent-solute and solute-solute dispersion interactions that determine the relative stability of the two stable conformers. We found that in the gas phase the structure with pi-stacked anthracene rings is by 3 kcal/mol more stable than the rotor-shaped molecule, if we take dispersion interactions into account. The reaction barrier between the two structures is larger than 20 kcal/mol. To study the influence of dimethly sulfoxide (DMSO) solvation on the relative energy of the conformations, Born-Oppenheimer molecular dynamics simulations have been carried out. We observed that on average the dispersion interaction energy between the rotor-shaped molecule and all solvating DMSO molecules in a given number of snapshots is by 5.4 kcal/mol more exothermic than the dispersion interaction energy between the pi-stacked structure and its DMSO solvent shell.

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# A Density-Dependent Dispersion Correction: Beyond the post-SCF and ground state density

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Since its seminal implementation in 2002 by Yang [1] and its popularization by Grimme in the mid-2000s,[2] the utilization of atom pairwise energy corrections to DFT is known to be of utmost importance and its development has represented a turn in the field of computational chemistry. In this context, the dDsC density-dependent atom pairwise dispersion correction [3, 4] was formulated with the aim of improving the performance of standard density functional approximations for both typical intermolecular vdW situations as well as the more subtle intramolecular interactions. In dDsC, both the damping function and the dispersion coefficients depend on the charge distribution within a molecule.

Most of the dispersion correction schemes are generally applied in a post-SCF manner under the assumption that the influence on the density is weak. We have recently established the suitability of using the a posteriori dDsC correction through comparisons with the more computationally demanding self-consistent implementation.[5] We evaluated the impact of self-consistency on final converged density as well as on various chemical properties, such as energies, geometries or frequencies and ab initio molecular dynamics of real-life systems relevant to the field of organic electronics.

The applicability of the -dDsC scheme is currently being extended to the description of excited-states, which are also affected by dispersion forces. The current state the work will be presented as well.

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# Computational study of the reaction between O($^3$P) and NO($^2$Π) at temperatures relevant to the Hypersonic Flight Regime

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Reactions involving N and O atoms dominate the energetics of the reactive air flow around the spacecraft when reentering the atmosphere in the hypersonic flight regime. This work aims to calculate the thermal rate constants of the reactive processes in the collision between O($^3$P) and NO($^2$Π) over a range of high temperatures. For this purpose, potential energy surfaces (PESs) for the ground and first three excited states of the $NO_2$ molecule are constructed based on high-level \textit{ab initio} calculations. These *ab initio* energy points are interpolated using the reproducible kernel Hilbert space (RKHS) method and Legendre polynomials. The global PES of $NO_2$ in the ground state is constructed by smoothly connecting the surfaces ofd the grids around the equilibrium $NO_2$ geometry by a distance-based switching function. The rate constants were calculated using Monte Carlo method. Results indicate that at high temperatures studied neither the lowest A-PES nor the zero point effects are relevant. In this respect, the ground state PES is a sufficiently good description of the system. One finding is that the rate of the "O1O2+N" channel becomes comparable (within a factor of around two) to the rate of the oxygen exchange channel from temperatures beyond 5000 K. A state resolved analysis shows that the smaller the vibrational quantum number, the higher the translational energy required to open it and conversely that the higher the vibrational quantum number, the less the translational energy is needed. This is in right agreement with what is predicted by Polanyi's rule. However, the oxygen exchange channel (NO2+O1) opens at any collision energy. Finally, this work stands as a validation of an efficient computational technology for the investigation of three-atom collisions.

## Understanding Supported Metallic Nanoparticles: An Ab Initio Approach

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Supported metallic nanoparticles are heterogeneous catalysis of common use in the petrochemical and fine chemical industries.[1] Nevertheless, these systems are far from being understood and they are normally modeled by using simple slab models and/or without the inclusion of the support, which is typically an oxide such as $SiO_2$, $Al_2O_3$ or alumino-silicates. In order to further understand their properties and catalytic activity more realistic models need to be used, which include both the metallic nanoparticles and the support. In this contribution, different models for metallic particles (Ni, Pt, Ru) supported on oxides ($SiO_2$, $Al_2O_3$)  will be presented and simulated by means of *ab initio* calculations. First, the construction of metallic particles containing Ru, Ni, and Pt of different particle shapes and sizes will be described, and the stability of the metallic nanoparticles will be compared for every evaluated metal. Also, chemisorption processes of the $CH_4$, $CO_2$, CO and $H_2$ molecules on such nanoparticles will be described. These species are important reactants and products of key processes for the production of synthetic fuels such as Fischer-Tropsch[2] or dry reforming[3]. The chemisorption studies will be compared with experimental results. Finally, the interaction between the metallic nanoparticles and the supports ($SiO_2$ and $Al_2O_3$) will be evaluated. All this information will provide a better understanding of these important type of heterogeneous catalysts, what could help in developing more active supported metallic catalysts in the future.
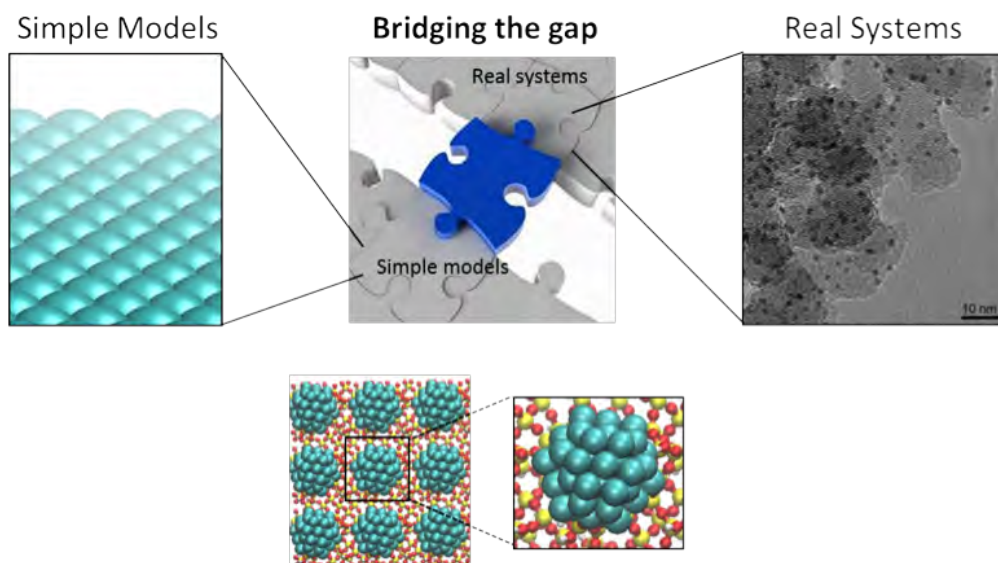
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# Theoretical modeling of mesoporosity development in zeolites in alkaline media: Hierarchical ZSM-5 and ZSM-22

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The hierarchical structuring of conventional zeolites by post-synthetic modification in alkaline media is one of the most efficient means to enhance their performance in diffusion-limited reactions. The extent and distribution of mesopores introduced has been observed experimentally to depend strongly on the intrinsic properties of the zeolite. In contrast, an atomistic-level knowledge of the demetallation process is almost nonexistent. One of the major obstacles to an improved understanding, is the difficulty in modeling the complex and non-periodic structure of mesopores in hierarchical zeolites. In this study, we develop strategies to gain further insight into the behavior of silica-rich zeolites upon treatment in alkaline media through density functional theory (DFT), representing the zeolites by cluster models of different fragments of their framework. The different modes of mesopore introduction are exemplified for the case of zeolites with 3D (ZSM-5) and 1D (ZSM-22) pore topologies. The calculations are complemented by experimental investigations to confirm the validity of the results.
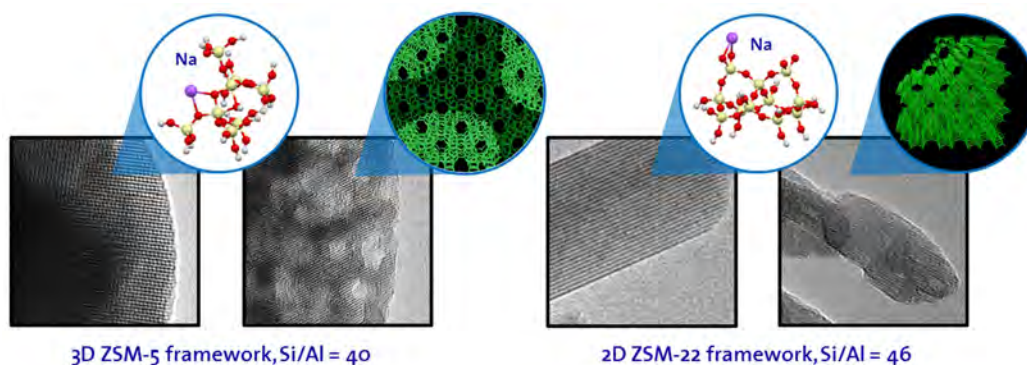


**Figure 1.**TEM images and structural representations of hierarchical ZSM-5 and ZSM-22 zeolites.

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## **Inter-system crossing with TDDFT: Jablonski diagrams from theory**

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We have recently rigorosuly derived a method for the computation of spin-orbit coupling (SOC), using the Breit-Pauli SOC hamiltonian, within linear-response time-dependent functional density theory (LR-TDDFT) [1] and implemented it in the software package CPMD [2]. Spin-orbit coupling is a quantum-relativistic effect which is particularly relevant to photochemistry, as it allows the phenomenon known as inter-system crossing (ISC) to occur. Examples of systems in which ISC is important include organic (ketones, for examples) and inorganic compounds (metallic photosensitizers). Our method for calculating SOC allows us to perform fully nonadiabatic *ab-initio* molecular dynamics, using a Landau-Zener surface hopping scheme for ISC and a fewest-switches surface hopping scheme for internal conversion [3]. We are currently testing our implementation on small organic molecules, but the efficiency of LR-TDDFT in obtaining excited state potential energy surfaces will eventually allow us to treat photochemical systems that are out of reach of wavefunction-based methods. Our final goal is to achieve a full dynamical description of photochemistry, from bio-molecules (such as nucleobases) to solar cell dyes, to OLED dopants (for which preliminary results are discussed).

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## Molecular scalar fields: From bonding descriptors to density functionals

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In this contribution we present a density dependent scalar field, which was introduced as a descriptor of bonding patterns in molecular system. It succeeds in revealing different types of intra- and intermolecular chemical interactions, ranging from covalent bonds to van der Waals interactions. We show how the introduced field can be applied to visualize and quantify the concepts of compactness in molecular crystal. We also examine how such descriptors can be used in the development of exchange-correlation density functionals. In particular, we present a local hybrid functional based on the field we have developed

**Monte Carlo Simulations of Bulk Liquid Water at Ambient Temperature and Pressure: Climbing the Jacob's Ladder of Density Functional Approximations**

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Despite the apparent simplicity of the $H_2O$ molecule, liquid water represents one of the most mysterious substances in our world. Water is a crucial component of basically all human activity and it plays an essential role in Life and Earth sciences. For this reason there have been several attempts to explain its behavior and anomalous properties. However, understanding the structural and electronic properties of liquid water is still a major challenge in condensed matter simulations. In fact, the $H_2O$ molecule has a large dipole moment and polarizability, is a multiple hydrogen donor and acceptor and can easily build network structures. As a consequence of these properties, theoretical models face the challenge to describe many different effects and their subtle interplay at a high precision. In this respect, Density Functional Theory (DFT) provides a formally exact way for solving the electronic Schrödinger equation. However, practical DFT calculations replace the unknown exact exchange and correlation energy by one of the various models of electron correlation, referred as density functional approximations (DFA). According to Perdew *et al*. [1], the various steps forward in the development of more accurate DFA can be assigned to various rung of "Jacob's ladder". In that picture, each rung of the ladder introduces more descriptors of the electronic system and yields models with improved accuracy. Currently, by climbing the ladder the information on 1) the electronic density, 2) its gradient, 3) the kinetic energy density, 4) the occupied orbitals and 5) the virtual orbitals, are progressively included. Here we present the performance of various DFA's, belonging to different rungs of the Jacob's ladder, in reproducing the structural properties of liquid water by means of Monte Carlo simulations in the NpT ensemble under ambient temperature and pressure [2]. A particular focus is given to the fifth and last rung, for which efficient and massively parallel algorithms have been developed and implemented in the CP2k simulation package [3].

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# Liquid-liquid equilibrium and thermodynamics modeling of systems containing jatropha oil + methanol + glycerol + biodiesel

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Biodiesel is among the promising renewable energy sources due to its numerous advantages. To obtain the optimal process design of biodiesel production, some initial information regarding the principle of the thermodynamics and phase equilibrium are required. Equilibrium relationship is very important in the process of converting vegetable oil into biodiesel. This paper reports experimental data for liquid-liquid systems containing jatropha oil + methanol + glycerol + methyl ester. Jatropha oil, methanol, glycerol, and ester were mixed in the different mass ratio. The mixture was allowed for 24 hours to attain phase equilibrium. The composition of the two phases was measured. The experimental data were used for adjusting parameters of the NRTL and UNIQUAC models. Binodal curves, tie lines and distribution for this quaternary system were also determined. The obtained data and thermodynamic model are necessary as the basic information for designing reactive distillation column applied for producing biodiesel from jatropha oil.

Keywords: biodiesel; jatropha oil; liquid-liquid equilibrium, UNIQUAC, UNIFAC

## Local density fitting within a Gaussian and plane waves approach

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A local density fitting technique is introduced for Kohn-Sham (KS) density functional theory calculations using a mixed Gaussian and plane waves (GPW) approach. The computationally most expensive step in construction of the KS matrix is the evaluation of the Coulomb matrix. The latter requires the calculation of two-electron integrals with the characteristic $O(N^4)$ problem. Baerends *et al*. [1] introduced a local resolution of identity approach (LRI), where the atomic pair densities are approximated by an expansion in one-center fit functions reducing the scaling order to $O(N^3)$. The LRI approach is used in the Amsterdam density functional code and proved to be accurate and efficient [2].

In this work, the LRI technique was adapted for usage in a GPW framework (LRIGPW) and implemented in the CP2K program [3] package. The fitted density is employed for evaluation of Coulomb as well as exchange-correlation potential. GPW scales already linearly with respect to system size since the plane wave expansion of the density is exploited to solve the Poisson equation in Fourier space. This leads to an $O(N)$ process for the evaluation of the Coulomb matrix. Thus, no improvements in terms of scalability can be expected for LRIGPW. However, the prefactor for building the KS matrix is reduced resulting in a system-dependent speed-up of the calculation. Furthermore, the scalability of the grid-based calculation and integration of the potential with respect to the number of CPUs can be simplified and improved.

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## Ab Initio Modeling of TiO$_2$-based Photo-catalysis for Water Reduction

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Hydrogen production gains importance due to the energy demand of the world. It can be accomplished by photo-catalysis that converts energy of sunlight into H$_2$ by reducing H$_2$O.[1] Among tested photo-catalysts for water reduction, TiO$_2$ appears to be a promising one because of its ease of preparation and stability.[2] However, TiO$_2$ has to be modified by adding photo-sensitizers (to harvest UV photons) and/or metal centers (for the reduction of water) to decrease its large band gap (~3.1 eV).[3]

In this study, we aim to theoretically design an efficient TiO$_2$-based photo-catalyst for hydrogen production by water reduction. To modify the band gap of TiO$_2$ and increase its photo-catalytic activity, pyridine-based molecules [4] are used as photo-sensitizers and cobalt as metal center. All calculations are carried out by employing density functional theory (DFT) as implemented in CP2K/QUICKSTEP package.[5] The factors playing an important role in designing water reduction photo-catalysts such as preferential adsorption sites of photo-sensitizer and metal centers on the TiO$_2$ surface, the mechanism of water reduction, possible intermediate products and energy barrier for hydrogen production are going to be discussed.
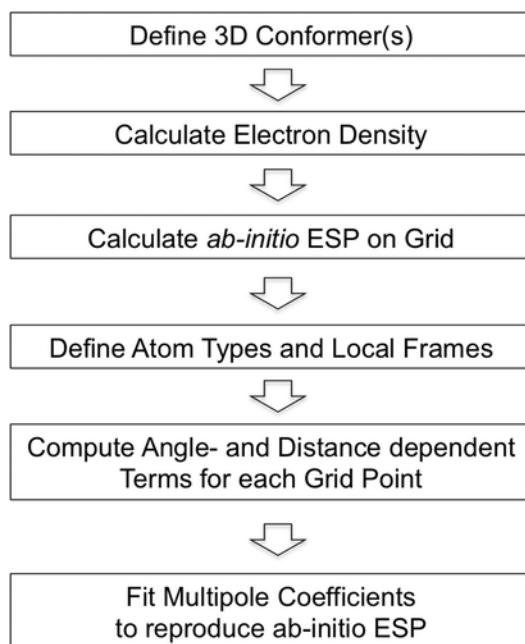
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# A new toolkit for fitting forcefield parameters used for Permanent Multipoles molecular simulations

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Permanent atomic multipoles (MTPs) are an extension to common point-charge (PC) representations in atomistic simulations[1][2][3]. MTPs are commonly fitted from an ab initio electrostatic potential, and the ability of simultaneously fitting several molecules and/or conformations usually increases parameters' transferability. In a second time when PCs or MTPs have been fitted, it is also possible if required to optimise Lennard-Jones (LJ) parameters by using a Molecular Dynamics (MD) package. Here we present a unified toolkit gathering in one package all the scripts and processing steps (see figure below and ref [3]), required for the MTPs fitting procedure. It provides: (1) ability to load coordinate files in several formats (XYZ, PDB, ...), (2) setting and execution of the ab initio simulation (Gaussian 09), (3) preparation of the fitting step (like custom atom typing), (4) execution of the fit and visualisation of results (JMOL, VMD). If LJ fit is also required then: (5) MTPs parameters are used for setting up and running a MD simulation. This software will be available under an open-source licence, facilitating a possible extension to other ab initio or MD packages.

Define 3D Conformer(s)

⇩

Calculate Electron Density

⇩

Calculate *ab-initio* ESP on Grid

⇩

Define Atom Types and Local Frames

⇩

Compute Angle- and Distance dependent Terms for each Grid Point

⇩

Fit Multipole Coefficients to reproduce ab-initio ESP

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# LFDFT Calculations of Praseodymium doped binary Fluorides compared with Experimental Results

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Research efforts for new materials as luminescent pigments for general lighting or as laser gain media for solid state lasers are currently growing world-wide. An activator ion which exhibits the potential for all these applications is trivalent Praseodymium. The emission spectrum of $Pr^{3+}$ is a very sensitive function of the host structure and can show $[Xe]4f^1 5d^1 \rightarrow [Xe]4f^2$ band emission solely in the UV range, or $[Xe]4f^2 \rightarrow [Xe]4f^2$ line emission ranging from the UV-C to the NIR [1].

Preparation and optical characterization of certain materials is a common process to classify these materials for any application. However, this process is very time consuming and cost-intensive. The calculation of energy diagrams of these certain materials can help to make a preselection.

In this study, we calculated the energy diagrams of Praseodymium doped divalent fluorides, viz. $M^{II}F_2$:$Pr^{3+}$ ($M^{II}$ = Ca, Sr, Ba) and $LnF_3$:$Pr^{3+}$ (Ln = La, Pr, Y) using an association of ligand field theory and DFT, named LFDFT. This model was developed at the University of Fribourg to make predictions of the photo-physical properties of given materials [2].

Sample preparation was performed at the University of Applied Science in Münster, Germany by a precipitation route followed by a calcination step. As starting materials high purity nitrates in case of the alkaline earth metals and chlorides in case of the lanthanides were used. Precipitation of the fluorides takes place after adding $NH_4HF_2$ to the solution. Calcination of the obtained materials leads to higher crystallinity [3]. Obtained luminescent materials were characterised by luminescence and reflection spectroscopy.

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**Computational Investigations of Potential Water Oxidation Catalysts.**

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Employing *ab initio* methods, we tried to calculate electronic and structural properties of a polyoxometalate (POM) used as a catalyst in oxidative water splitting [1]. We did this in vacuum, as well as in solution, using QM/MM for the latter. With the same methods we employed for the POM alone, we also looked at various aggregates of the photosensitizer Tris(bipyridine)ruthenium(II) with the POM in an attempt to not only explore the actual structure of such an aggregate, but also the possible influences of the sensitizer on the redox properties of the POM.
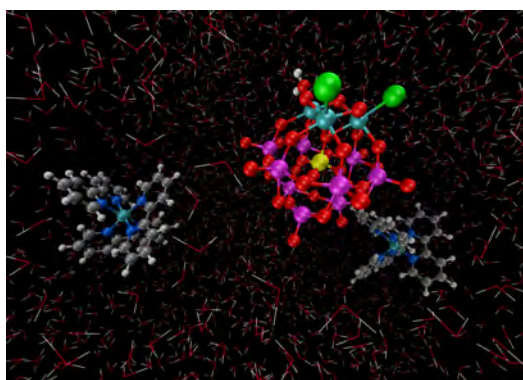


For a cobalt-cubane [2], another water oxidation catalyst, we are trying to determine the free energy change and the reaction barrier for a ligand exchange reaction where acetate would be replaced by water. We use the Nudged Elastic Band method to obtain a rough overview and Metadynamics to further investigate the free energy surface.

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# Computation of Molecular Parity Violation in View of Spectroscopic Experiments.

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Measuring the parity violating energy difference $\Delta_{pv}E$ between enantiomers of chiral molecules by spectroscopy is one of the frontiers of high resolution molecular spectroscopy and a considerable challenge, which so far has not been met with success[1-4]. Over the last decade, considerable progress has been made in the precise theoretical description of molecular-parity violation[4-8], its possible implications for the origin of molecular chirality and biomolecular homochirality, and its role in stereomutation dynamics of chiral molecules[1-4]. Accurate theoretical predictions of molecular parity violation importantly assist in a search for the most suitable molecular system. Following our previous work[5-8], we report molecular parity-violating torsional or inversion potentials $E_{pv}$ computed[8] with coupled cluster linear response method[9] for the series of fluoro-, and chloro-substituted allenes, carbodiimides, ketenimines, 1,2-diazetines, and lastly, 1,2-dithiin. These are both a challenging test molecules for theory, and a promising new candidates for experimental detection of the parity violating energy difference $\Delta_{pv}E$. We review our new implementation of computation of molecular parity violation within PSI3 and PSI4[10] open-source suite of *ab initio* quantum chemistry programs. Our work is supported by an ERC Advanced Grant.

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## Interactive Visualization of PDB and CSD in 3D-Shape Space

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Mining of chemical space for drug discovery, is often faciliated by the various chemoinformatics approaches; popular amongst them are similarity search, scaffold analysis and visualization of compound libraries. To aid in this process, recently we proposed two property spaces 1) Molecular Quantum Numbers (MQN)[1] and 2) SMIfp[2]. Both MQN and SMIfp provided reference feature spaces with capability for visualization of large databases via color coded principle component plane (PC-plane)[3]. However, MQN and SMIfp descriptors do not take into account shape or pharmacophore information from molecules. Furthermore, the use of MQN and SMIfp is limited to small molecules. Here we designed a 3D-shape fingerprint to enable the chemoinformatic analysis and visualization of molecules of any size. The fingerprint was then applied to the chemical space of proteins from the Protein Databank (PDB) and molecules up to 1000 atoms from the Cambridge Structural Database (CSD). Nearest neighbour searches by city-block distance (CBD) in this property space correctly identifies molecules with common shapes and functional groups, e.g. proteins and peptides with similar folds and functions. An interactive exploration is enabled by a web-browser and downloadable Java-applet application.
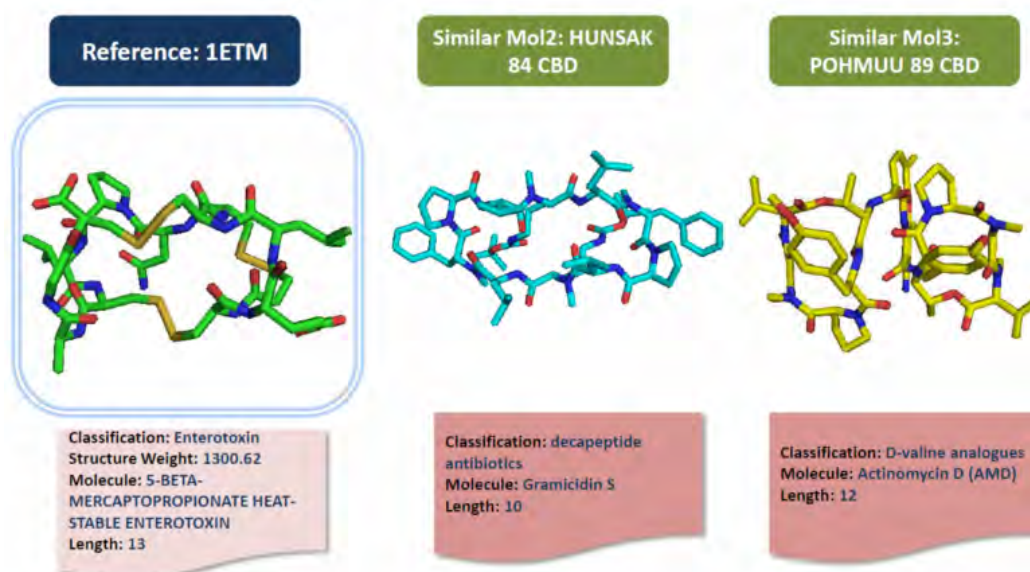
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## Excited state calculations with MPS-DMRG

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Since the initial formulation of the Density Matrix Renormalization Group algorithm (DMRG) [1], the method has been substantially improved. The development of Matrix-Product-State (MPS) DMRG [2,3] allows to solve the Schrödinger equation in the orthogonal complement of one or several given states, which we exploit to calculate several low lying electronically excited states. Furthermore, we provide some illustrations of how different DMRG parameters affect the performance and accuracy of a calculation [4].

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## Free-radical copolymerization of acrylamides, acrylates and α-olefins

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The transition state structures of models for free radical homo- and co-polymerization of acrylamide, methyl acrylamide, methacrylate, methyl methacrylate, and ethene have been determined using density functional theory. The reaction energies and barrier heights comport with the experimentally observed properties, including the prevalence of monomer alternation, type of stereospecificity, and overall reaction yield of the different co-polymers. For competing copolymerization additions, the thermodynamic and kinetic products are the same for most reactions, but may differ for the addition to methyl methacrylate radical. Experimentally, a Lewis acid catalyst has been found to increase the incorporation of nonpolar 1-alkenes with polar acrylamides and acrylates in a free radical polymerization process, as well as the overall yield. A computational study was undertaken to elucidate the mechanism of this catalysis. The presence of the Lewis acid was found to lower the transition state barrier for the addition of ethene to methyl methacrylate radical, while raising the transition state energy for the addition of methacrylate to the same, explaining the rise in monomer alternation in related co-polymerizations.
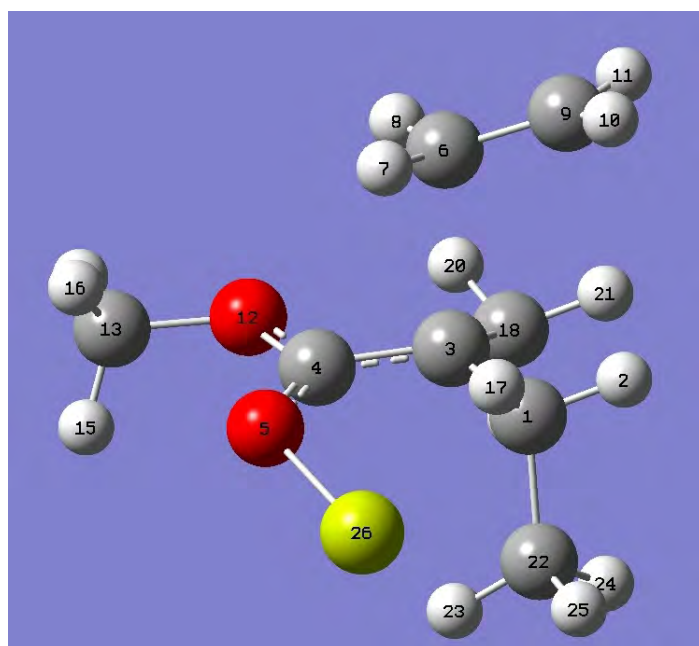
## Adaptive Tensor Network Parameterizations of the Electronic Wave Function for Application in Strong–Correlation Problems

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Theoretical studies of molecular systems give deep insight into the electronic structures of the systems' components and can predict properties before performing an experiment. Access to information about properties of molecular systems before their synthesis can be a great advantage. For instance, in order to understand catalytical processes at transition metal centers in terms of structure, energy, and other properties, it is mandatory to have an accurate representation of the electronic structure of (polynuclear) metal complexes.

Thus, a main task of Quantum Chemistry is to provide accurate data for geometrical and electronic properties of reactants in their electronic ground and excited states. The complicated electronic structure of (possibly polynuclear) open-shell metal complexes requires high-accuracy methods, which are usually unfeasible, but is accessible by broken-symmetry density-functional approaches, although these are usually not sufficiently accurate.

Here, we present the theoretical concept of a tensor network states ansatz that automatically adapts to a structure encoded in the one-electron states, the orbitals. In other words, the developed ansatz shall automatically find an optimal tensor network. This approach is based on so-called complete graph tensor network states[1,2].

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**Adjusting the Local Arrangement of π-Stacked Oligothiophenes to Promote Charge Transfer**

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We show[1] that substituting quaterthiophene cores with strong H-bond aggregators, such as urea groups, provides an efficient way to adjust the mutual in-plane displacements of the semiconducting units and promote charge transfer. Our two-dimensional structure-property mapping reveals that the insertion of substituents induces up to 2.0 Å longitudinal and transversal displacements between the π-conjugated moieties. These displacements lead to improved co-facial orbital overlaps that are otherwise inaccessible due to Pauli repulsion. Our results also emphasize that fine-tuning in-plane displacements is more relevant than achieving 'tighter' packing to promote charge transfer properties.

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## New Approaches for the Calculation of Local Properties

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Knowledge about local properties is extremely helpful for the analysis of molecular structures and interactions. Moreover, it is a valuable source of information in the characterization of dynamic processes and facilitates the interpretation of experimental data. In case of vibrational spectroscopy, for example, it is desirable to determine the impact of certain molecules/atoms on the bands in the experimental spectra. This may be straight-forward for small molecules but becomes more and more complex for larger systems.

Calculations provide additional insight allowing the targeted study of specific structures. In this way, it is possible to quantify the contributions of, e.g., solute and solvent molecules [1] or adsorbates on solids. We present novel methods for the calculation of local properties with a focus on Infrared and Raman spectroscopy. These approaches do not rely on computationally demanding localization procedures and are especially suited for the investigation of periodic systems such as liquids.

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## DMRG-SCF Gradients for State-specific and State-averaged Cases

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The present study suggests geometry gradient evaluations in state-specific Density-Matrix Renormalization Group Self-Consistent Field (DMRG-SCF) , as well as an approximation for the construction of an effective density for geometry gradient evaluations in state-averaged DMRG-SCF calculations. The algorithm used here is based on the general Multi-Configurational SCF (MCSCF) gradient equation [1-3],

$$\frac{\partial E^{\Theta}}{\partial x} = \frac{\partial L^{\Theta}}{\partial x} = \langle\Theta|\frac{\partial H}{\partial x}|\Theta\rangle + \sum_{pq,\Gamma}\omega_{\Gamma}\widetilde{\kappa}_{pq}\frac{\partial\langle\Gamma|\frac{\partial H}{\partial x}|\Gamma\rangle}{\partial\kappa_{pq}} + \sum_{\Gamma\gamma}\omega_{\Gamma}\overline{P}_{\Gamma\gamma}\frac{\partial\langle\Gamma|\frac{\partial H}{\partial x}|\Gamma\rangle}{\partial P_{\Gamma\gamma}}$$

in which Lagrange multipliers are indispensable in order to get a fully variational MCSCF specific state in the state-averaged treatment. Here, $x$ is a coordinate, $\Theta$ denotes the state, $L^{\Theta}$ is the Lagrangian of given state energy $E^{\Theta}$, $\kappa$ is the orbital Lagrange multiplier and $P$ is the CI Lagrange multiplier, $p, q, r, s$ denote orbitals, $\gamma$ denotes a determinant, and $\Gamma$ denotes any state-averaged state with weight $\omega_{\Gamma}$.

When solving for the Lagrange multipliers ($\kappa$ and $P$) used in the gradient equation, the linear response (LR) equation

$$\begin{pmatrix} E^{[2]}_{pq,rs} & E^{[2]}_{\Phi I,pq} \\ E^{[2]}_{pq,\Phi I} & E^{[2]}_{\Phi I,\Upsilon J} \end{pmatrix} \begin{pmatrix} \widetilde{\kappa} \\ \overline{P}_{\Gamma\gamma} \end{pmatrix} = \begin{pmatrix} \frac{\partial E^{\Theta}}{\partial\kappa} \\ \frac{\partial E^{\Theta}}{\partial P} \end{pmatrix}$$

where $E^{[2]}$ is the electronic Hessian) has to be constructed and solved. Since there are no CI coefficients and the Hamiltonian is large in the DMRG algorithm, we use our sampling-reconstruction technique to construct the most important CI coefficients from a DMRG wavefunction [4] and then use the reconstructed CI coefficients together with the LR equation to get the Lagrange multipliers. Then, the gradient equation can be solved, so that the geometry optimization aiming at a specific electronic state in state-averaged DMRG-SCF can be carried out.

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**Mechanism of ethylene polymerization by CrIII silicates via C-H activation: insights from DFT calculations**

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Mononuclear Cr(III) surface sites were synthetized and characterized by IR, UV-Vis, EPR and XAS. These sites are highly active in ethylene polymerization to yield polyethylene with a broad molecular weight distribution, similar to that obtained from the Phillips catalyst. CO binding, EPR spectroscopy, and poisoning studies indicate that two different types of Cr(III) sites are present on the surface, one of which is active in polymerization. In order to better understand the active sites and the polymerization mechanism, DFT calculations have been performed. Results show that active sites are tri-coordinated Cr(III) centers and that the presence of an additional siloxane bridge coordinated to Cr leads to inactive species. The proposed models reproduce very well the blue shift of the CO frequency observed by IR. Also, the polymerization mechanism initiates via C-H bond activation of ethylene in a Cr-O bond (formally as a s-bond metathesis step) while the propagation takes place by the known Cossee-Arlman mechanism. Several ways of chain termination were considered, and results indicate that the preferred way is through proton transfer (the reverse of initiation). In the light of these new results, we can conclude that these tri-coordinated Cr(III) sites initiate and regulate the polymer chain length via unique proton transfer steps in polymerization catalysis.

## Noncovalent interactions in isostrutural cocrystals and salts : A theoretical investigation

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Crystallographic studies of noncovalent interactions present in a series of isostructural cocrystals and salts of some aminopyrimidine derivatives which differ from each other by a chloro / methyl and few other substituent groups were of interest in the recent past [1][2] . It is logical that an exchange of chloro by a methyl group will yield isostructural compounds, but in some cases, few more substituents were also able to form isostructural forms with similar crystal packing. Experimentalists guess that a reliable and stable linear heterotetrameric synthon [3] is the driving force for the formation of such isostructual systems. To ascertain this fact and to see what other noncovalent interactions force the molecule to form such heterotetrameric synthons, we have computationally assessed the strengths and topologies of them. Atoms in a Molecules and Natural Bond Orbital methodology were also utilized to support these findings.

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# Theoretical account of the electronic structure and properties of systems with two-open-shell f and d electrons

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We deal with the computational determination of the electronic structure and properties of lanthanide ions in complexes and extended structures having open-shell f and d configurations. Particularly we present conceptual and methodological issues based on Density Functional Theory (DFT) enabling the reliable calculation and description of the f - d transitions in lanthanide doped phosphors.[1-2] We consider here the optical properties of the $Pr^{3+}$ ion embedded into various solid state fluoride host lattices, for the prospection and understanding of the so-called quantum cutting process, being important in the further quest of warm-white light source in light emitting diodes (LED). We use the conceptual formulation of the revisited ligand field (LF) theory fully compatibilized with the quantum chemistry tools: LFDFT. We present methodological advances for the calculations of the Slater-Condon parameters,[3] the ligand field interaction [4] and the spin-orbit coupling constants, important in the non-empirical parameterization of the effective Hamiltonian adjusted from the ligand field theory. The model shows simple procedure using less sophisticated computational tools, which is intended to contribute to the design of modern phosphors and to help to complement the understanding of the $4f^n$ - $4f^{n-1}5d^1$ transitions in any lanthanide system.

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# The Subtle Effect of the Solvent on Competing Reaction Mechanisms Involving λ³-iodanes: From the Reaction Profile to the Minimal Energy Pathway on the Free Energy Surface

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Hypervalent iodine compounds have become important reactants in synthetic chemistry [1]. However, relatively little is known about their reactivity. The electrophilic trifluoromethylation of *N*- and *S*-nucleophiles [2][3] by the λ³-iodane **1** might follow an $S_N2$ or a reductive elimination (RE) pathway. In addition, *S*-nucleophiles most probably react via single electron transfer (SET). Gas phase DFT calculations reveal that the $S_N2$ mechanism is clearly favoured over the RE with *N*-nucleophiles. The solvent effect on these two competing reaction mechanisms was investigated employing PCM-based methods which show that the difference between the two activation energies $\Delta\Delta G^{\ddagger}$ is decreased significantly in solution (MeCN), still, however, favouring $S_N2$. Trifluoromethylation of *S*-nucleophiles -- like thiophenolate -- occur via RE instead of $S_N2$ in gas phase and in solution. However, the reaction mechanism can be described also by an SET. An in-depth investigation by means of *ab-initio*-MD shows that the solvent effect is not defined adequately enough by PCM-based methods and that the RE is the most probable mechanism for the trifluoromethylation of *N*-heterocyclic substrates in which a *N*-trifluoromethyl nitrilium ion as intermediate is formed [1]. Our studies have also shown that the RE mechanism involving thiophenol(ate) is driven by an SET. Acetonitrile (MeCN) and dichloromethane (DCM) have been chosen as solvents since they are utilized in the corresponding experimental reactions.

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**Chemoinformatics Meets Quantum Chemistry: A Strategy for Computational Molecular/Reaction Analysis Based on The Global Reaction Route Maps**

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We have launched a project for molecular/reaction analysis based on big data of QM-based global reaction route networks. The global reaction data includes equilibrium structures, dissociation channels, and transition structures, which are automatically calculated by global search on a potential energy surface using the GRRM (global reaction route maps) method [1]. Applications for designing molecules and reaction routes are important part of the project. Data-mining and visualization technologies as well as chemoinformatics methods are essential to retrieve useful information from the reaction data. In the first stage of the project, we have developed a system, RMapViewer [2], to visualize and retrieve the GRRM outputs. Applications to global conformational search and reaction alanysis of model structures of iodine catalysts using the RMapViewer system have been in progress. We report here the overview of the project as well as the first attempts for the molecular/reaction analyses.
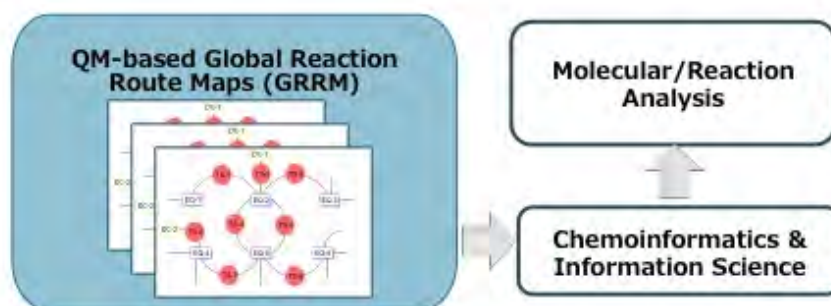
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# Non-uniform Continuum Model for Solvatochromism Based on Frozen-Density Embedding Theory

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Frozen-Density Embedding Theory (FDET) provides the formal framework for various types of multi-level numerical simulations such that a selected subsystem is described at quantum mechanical level whereas its environment is described by means of the electron density (frozen density, $\rho_B(r)$). $\rho_B(r)$ is usually obtained from some lower level quantum mechanical methods applied to the environment, but FDET is not limited to such choices for $\rho_B(r)$. The present work concerns such generalized applications of FDET, in which $\rho_B(r)$ is statistically averaged electron density of the solvent $(\rho_B(r))^{avg}$, The specific solute-solvent interactions are represented in a statistical manner in $(\rho_B(r))^{avg}$. The use of $(\rho_B(r))^{avg}$ was previously introduced for modelling solvatochromic shifts in absorption bands. The present focuses on emission, for which additional approximations are introduced for efficient and numerically robust the treatment of the coupling between the electron distribution in the solute and $(\rho_B(r))^{avg}$. A general computational protocol is proposed which leads to accurate (estimated error in the range of 0.05eV) description of solvatochromic shifts in both absorption and emission. It is tested on solvatochromism for coumarin 153, i.e., the case of local excitation for a relatively rigid chromophore and negligible spectral overlap between absorption of the chromophore and the solvent.

The embedding potential of water in ground state of Coumarin153
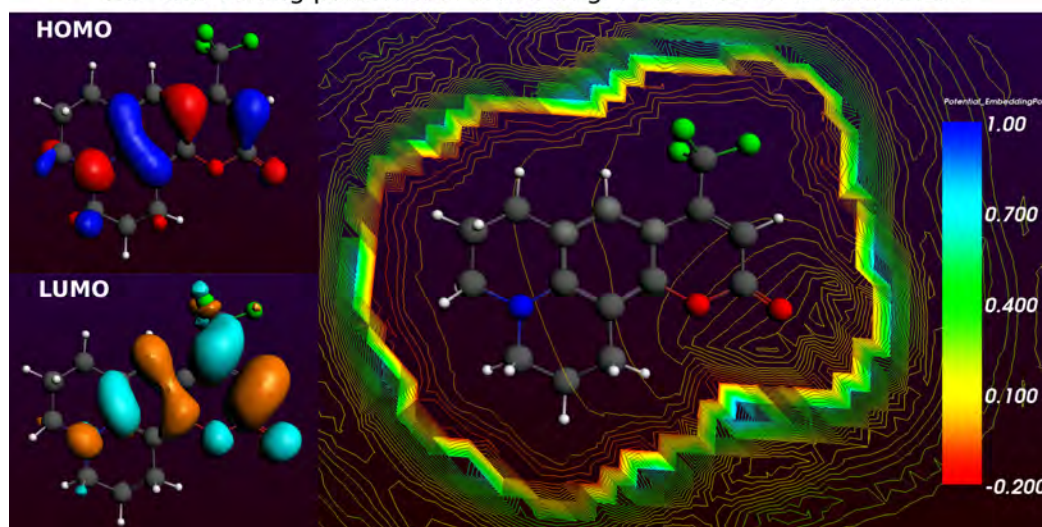
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## Excess electrons in anatase: a hybrid DFT and RPA study

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Anatase $TiO_2$ is employed in a variety of fields, such as (photo)catalysis, sensors and solar cells. Many of the proposed applications rely on charge transport phenomena, and a deep understanding of the anatase electronic properties is therefore crucial. In particular, the behavior of excess electrons in the system is still a matter of debate. While some studies describe highly localized states[1,2], small polarons, experiments report high charge mobility, more compatible with a less localized nature of the excess electrons, sometimes called large polarons[3]. In this work, the properties of excess electrons in anatase are obtained from hybrid DFT and RPA calculations, to shed light on the geometry and the stability difference between localized and delocalized electronic states with state-of-the-art electronic structure methods.

In anatase, we find that the polaronic state, which localizes on a Ti site, induces a long range lattice relaxation in the [100] and [010] directions. This distortion extends for almost 10 Å in the [100] and [010] directions. To fully accommodate this relaxation and to yield realistic results, calculations must therefore employ supercells of at least 4x4x1 unit cells. Hybrid density functionals predict energy differences between localized and delocalized electrons ($\Delta E_{loc-deloc}$) that strongly depend on the amount of Hartree-Fock exchange (%HFX) employed. When the %HFX is tuned such that the fundamental band is well described, the delocalized electronic state is more stable by 0.3 eV. This picture qualitatively changes if the hybrid DFT orbitals and eigenvalues are used as an input for RPA calculations. RPA results for Anatase show that the stability of the localized and delocalized states becomes very similar, slightly favoring the localized state, in agreement with experiment. Moreover, we show that $\Delta E_{loc-deloc}$ as obtained from the RPA calculations is distinctly less sensitive on %HFX used in the initial step of the RPA calculation.

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# Exciton coupling in π-stacked chromophores: a challenge for electronic structure approaches

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Organic semiconductors can be formed from conjugated organic molecules in a π-stacked arrangement. The optical properties of the resulting materials contain information of the arrangement of the π-conjugated building blocks at the molecular level, due to exciton coupling. To interpret experimental UV/Vis spectra, computational methods need to quantitatively account for the effects of aggregation on the optical properties. Here, we present a detailed evaluation of different quantum chemical methodologies applied to the simplest models system, a π-stack of two quarterthiophene molecules. We show that the performance of ab initio methods is mixed, and that only CC2 response theory yields the expected exciton coupling pattern. Density functional theory, on the other hand, suffers from overlocalization or overdelocalization of the electron density, depending on the functional used. These shortcomings were found to manifest themselves through distinct patterns in the computed optical absorption spectrum of π-stacked dimers.

# Dynamics of retinal chromophore in rhodopsin: from cis-trans isomerisation to activation

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Rhodopsin is a G-Protein Coupled Receptor (GPCR) that is present in rod cells of the human eye. This receptor is part of the class A GPCRs and forms a template for all the 662 receptors that are included in class A. Hence, if the process of rhodopsin activation can be understood, it could provide new insight into the activation mechanism of also other GPCRs. Rhodopsin is a membrane protein that consists of seven trans membrane domains, three intracellular loops, three extracellular loops, a C terminus, an N terminal domain and a retinal molecule that is covalently bound to the receptor in the active site. When rhodopsin is exposed to light, the covalently bound retinal is excited and isomerises from a cis to a trans configuration. The cis-trans isomerisation induces a cascade of conformational and configurational changes that lead to the active state of the receptor.

Over the last decades, the photo activation cycle of rhodopsin has been characterized. However, the relationship between the relaxation of the retinal to the trans configuration and its effect on the structure of the protein is not fully understood. Secondly, an atomic force microscopy study found that rhodopsin proteins were highly ordered in rows of two monomers in native membrane. Because of this high order the question arose whether rhodopsin transports the signal of its active state as a monomer or if a rhodopsin dimer is more efficient.

The presented work will cover the relaxation process of a rhodopsin dimer after light exposure. Only one out of the two retinal molecules present in the dimer was isomerised in order to monitor not only activation, but also the effect of activation on an inactive rhodopsin protein. Quantum mechanic/moleculer mechanics molecular dynamics, performed with CPMD, and classical molecular dynamics, using Gromacs, were employed to monitor the occurring events. Currently, also multiconfigurational time dependent hartree is performed on the rhodopsin protein in combination with the local control technique. This combination of techniques provides the opportunity to monitor the wave packet distribution after cis/trans isomerisation is induced by an optimal pulse.

## Visualizing and quantifying interactions in the excited states using molecular scalar fields

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Molecular scalar fields (e.g., ELF,[1] LOL,[2] SEDD[3]) have proven to be useful for visualizing and analyzing chemical bonding situations of ground state molecules. Our LOLIPOP[4] criterion, which is based upon the localized orbital locator (LOL), was shown to be a very efficient tool for identifying chemosensors with improved pi-stacking ability, but also for revealing fundamental relationships surrounding the underlying physics of pi-stacking interactions. Until now, however, emphasis was placed on ground state binding energies only. The analysis of bonding in excited states is relatively unexplored due to limitations rooted in the orbital dependency of the kinetic energy density. We here explore density-based indices that can capture similar structure-property relationships associated with the properties of excited states. In particular, our relationships rely on a modification of the Single-Exponential Decay Detector (SEDD).[3]

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## MD Simulations of Non-linear Hydrogen Transfer with Zero-point Energy Corrected MMPT Force Field

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The method of Molecular Mechanics with Proton Transfer (MMPT) in CHARMM was designed to achieve the bond breaking of hydrogen atom between the donor and acceptor atoms in proton/hydrogen transfer (PT/HT) simulations. The potential energy surfaces (PES) of PT/HT process are obtained from ab initio calculations and theorized into the potential functions of MMPT force field. In this work, the MMPT potential for hydrogen transfers in malonaldehyde (MAL) was refined with zero point energy (ZPE) correction and employed to investigate the hoping rates and the kinetic isotope effects (KIE) in this reaction. The ZPE correction significantly reduces the energy barrier of HT reaction in MAL, by which the KIEs are expected to be comparable with the previous works.

# Alchemical Coupling Approaches within Quantum Chemistry

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[1]University of Basel

We discuss alchemical changes in the context of quantum chemistry. Numerical results for HOMO eigenvalues of the He atom due to alchemical teleportation are discussed. The predictive power of alchemical Hellmann-Feynman-derivatives for the covalent bond potential of hydrogen fluoride and hydrogen chloride is investigated, as well as the hydrogen bonds in the water-water and water-hydrogen fluoride dimer, respectively. Based on converged electron densities for one configuration, the versatility of alchemical derivatives is exemplified by screening the entire binding potentials without any additional self-consistent field cycles and with reasonable accuracy.
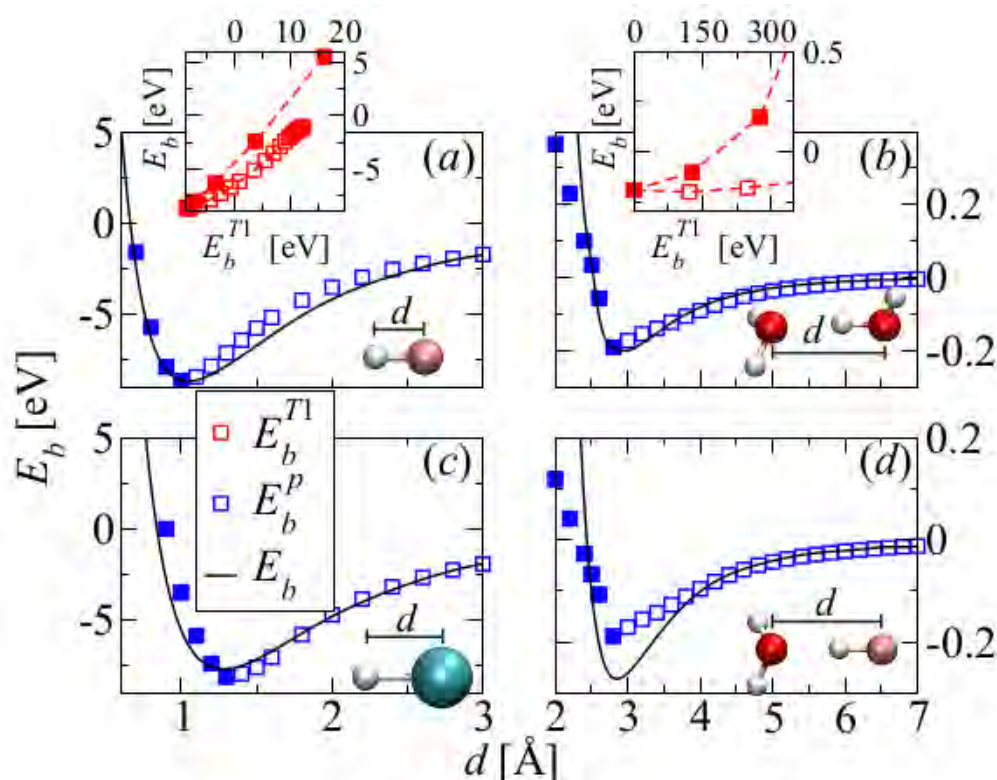
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**On-the-fly ab initio semiclassical dynamics: Identifying degrees of freedom essential for emission spectra of oligothiophenes [1]**

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Vibrationally resolved spectra provide a stringent test of the accuracy of theoretical calculations. We combine the thawed Gaussian approximation [2] (TGA) with an on-the-fly ab initio (OTF-AI) scheme to calculate the vibrationally resolved emission spectra of oligothiophenes with up to five rings. The efficiency of the OTF-AI-TGA permits treating all vibrational degrees of freedom on an equal footing even in pentathiophene with 105 vibrational degrees of freedom, thus obviating the need for the global harmonic approximation, popular for large systems. Besides reproducing almost perfectly the experimental emission spectra, in order to provide a deeper insight into the associated physical and chemical processes, we also develop a novel systematic approach to assess the importance and coupling between individual vibrational degrees of freedom during the dynamics. This allows us to explain how the vibrational line shapes of the oligothiophenes change with increasing number of rings. Furthermore, we observe the dynamical interplay between the quinoid and aromatic characters of individual rings in the oligothiophene chain during the dynamics and confirm that the quinoid character prevails in the center of the chain.

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**Accelerating Quantum Instanton Calculations of Kinetic Isotope Effects**

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While computing rate constants for reactions that exhibit strong quantum effects, running quantum dynamics can be avoided by a combination of Feynmann path integral formalism and Quantum Instanton approximation, that reduce the quantum problem to a classical one in a space of increased dimensionality [1]. Thermodynamic integration with respect to mass further simplifies computation of KIE's, allowing to use only efficient Monte Carlo integration procedures [2]. We accelerate these calculations using the following approaches. The first uses higher order Boltzmann operator splittings, allowing faster convergence to the exact quantum result [3]. The second uses advanced MC estimators, decreasing the statistical error and hence the MC simulation length needed for a given precision [4, 5]. The last one facilitates dividing surfaces' (DS) optimization and subsequent thermodynamic integration using new estimators for derivatives of related quantities with respect to DS's positions. We combine these approaches and test the improvements on the Eckart barrier, the $H+H_2$ rearrangement and the $H+CH_5$ reaction.

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