POSTER SESSION 1

Systematic Evaluation of Optimization Strategies Used to Investigate Organic Reaction Mechanisms in Solvent

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Two major strategies have traditionally been utilized to account for solvent effects on organic reaction mechanisms: structures have either been fully optimized in an intrinsic solvent using solvent models such as CPCM, SMD, etc., or structures have been first optimized in gas-phase prior to calculation of single-point solvation energies using intrinsic solvent models. Of the two, the second strategy is arguably the more popular method because optimizations are faster, and there is typically no loss in accuracy. However, the accuracy of computed trends and energies obtained by gas-phase optimizations/single-point energy solvent calculations may be affected by the type of solvent, as well as by the type of mechanism.

Investigations have been performed with various density functional methods to investigate how these two types of solvation procedure predicts mechanisms, energies and reactivity trends for a variety of reactions. We believe that these investigations will provide useful guidelines for when both strategies would be suitable for the investigation of reaction mechanisms.

Developing a DFT/TD-DFT Method for Designing BODIPY Based Anion Sensors and for their Mechanism Demonstration

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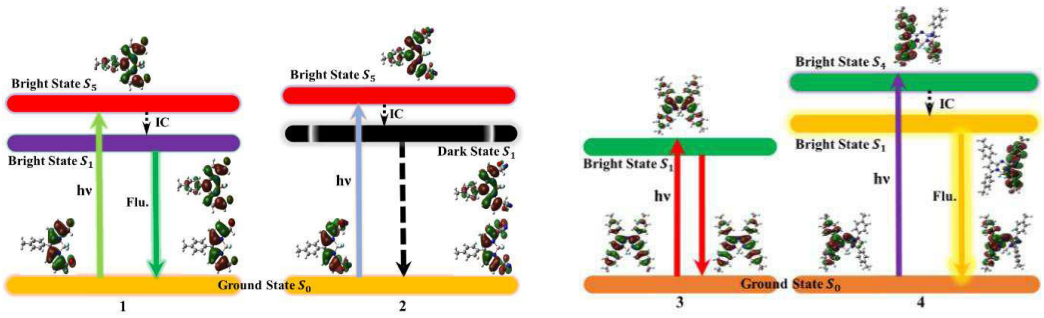
Abstract

We examined the cyanide anion (CN^-) sensing mechanism of 3,5-diformyl-borondipyrromethene (**1**) by calculating the photophysical properties of **1** and **2** (cyano addition product of **1**) with density functional theory (DFT) and time dependent-density functional theory (TD-DFT) methods using Gaussian 09 programs package. The negative values of energy changes (ΔE) and the free energy changes (ΔG) confirmed the feasibility of CN^- addition. The blue-shifted UV-vis spectra calculated for **1** and **2** show a good agreement with earlier reported results [1]. **1** and **2** show different excited state deactivation process as predicted by TD-DFT computations which designate the first excited state of **1** as a coplanar local excited state with π-σ^* transition. A slight charge separation character in the first excited state of **2** and loss of coplanarity at the formyl groups pave the pathway for non-radiative deactivation of the excited state and under their synergistic effect, the fluorescence of **1** after the CN^- addition is quenched notably. Thus, the different excited state features of **1** and **2** play a role in the CN^- sensing mechanism of **1**. Furthermore, it is experienced that out of the functionals employed here in this contribution (i.e., PBEPBE, CAM-B3LYP, M06-2X and LSDA) [2-5] DFT and TD-DFT computations performed at PBEPBE/*6-311+G(2d,p)*//PBEPBE/*6-311G(2d,p)* and CAM-B3LYP/*6-311+G(2d,p)*//CAM-B3LYP/*6-311G(2d,p* levels respectively are adequate for reproducing the excitation and fluorescence energies with a fine accuracy. Using this methodology, we designed an aza-BODIPY (**3**) which shows a fluorescence enhancement on cyanide binding (**4**) involving intramolecular charge transfer and partial configurational changes and it is for the synthetic chemists now to synthesize the designed molecule **3** for cyanide sensing in particular. This employed method can again be utilized for calculating the absorption and emission spectra of BODIPYs and its derivatives and it may pave a way for the designing of new potential BODIPY based anion sensing molecular candidates.



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Orbital Phase Theory in Diastereoselectivity of Electrophilic Addition to 4-Fluoro-1-methyleneadamantane

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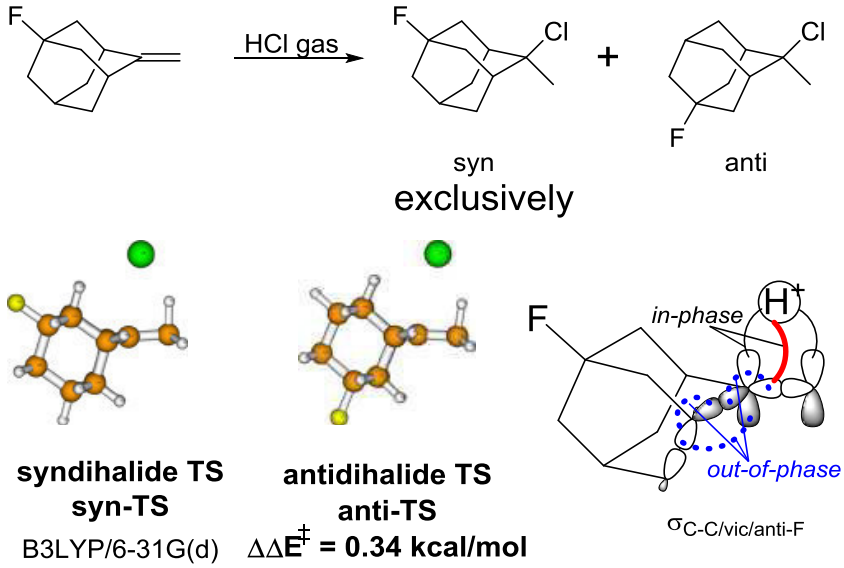
Recently we have shown that the cyclic orbital interaction including the geminal bond participation controls the diastereoselectivity in electrophilic addition [1]. We applied this idea to rationalize the diastereoselectivity in electrophilic addition to 4-fluoro-1-methyleneadamantane [2]. The vicinal C-C bonds anti to the fluoro group should be more electron-donating than those syn to the fluoro group due to the antiperiplanar effect with the fluoro group. Thus, the cyclic orbital interaction among $\psi^*_{H+} - \pi_{C=C} - \sigma_{C\text{-}C/vic/anti\text{-}F} - \sigma_{C\text{-}C/gem} - \sigma_{C=C} -$ should be more effective to stabilize the TS, i.e., the electrophile should approach in direction syn to the fluoro group. We performed the theoretical calculations of the model [3], which were subjected to the bond model analysis [4] to confirm the idea numerically and quantitatively.



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Radiative Association of ^{36}Ar and ^{38}Ar with Ionic Hydrogen

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Abstract
In a recent paper written by Barlow et al. [Science 342, 1343 (2013)], the ArH+ ionic system has been detected in the Crab Nebula. We accordingly propose in this work to examine the radiative association of the argon atoms 36Ar and 38Ar with ionic hydrogen H+ and to calculate the related temperature dependent rate coefficients. To do so, we have to construct the potentialenergy curves via which both Ar and H+ species approach each other and the permanent dipole moments. The corresponding data points are borrowed from the recent and reliable results of Stolyarov and Child [PCCP 7, 2259 (2005)]. Once the curves are constructed, the rate coefficients are computed quantum mechanically and analyzed in the temperature range 1 − 10000K.
Keywords : Radiative Association, Transition Dipole Moments, Potential Energy Curves, The Radiative Association Rate coefficients.

1. Introduction

Barlow et al. reported in Ref. [1] detection in the Crab Nebula of traces of the argonium cation 36ArH+. Their interpretations of spectra obtained with the Herschel Space Observatory enabled them to demonstrate the presence of the first noble gas in space and diffuse interstellar medium.

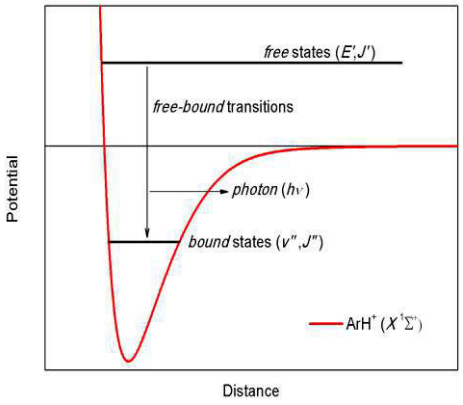
2 Radiative Association

The formation of the ground ionic species ArH+ starts by considering the following radiative association (RA) process :

$$Ar(^1S) + H^+ \rightarrow ArH^+(X^1\Sigma^+) + h\nu$$

The RA rate coefficient :

$$\alpha(T) = \left(\frac{8}{\pi\mu}\right)^{1/2}\left(\frac{1}{k_B T}\right)^{3/2}\int_0^\infty \varepsilon' Q(\varepsilon')\exp\left(-\frac{\varepsilon'}{k_B T}\right)d\varepsilon'$$



3. Conclusion

This theoretical work computes the radiative association rate coefficients of the ionic systems 36ArH+and 38ArH+ and examines their behavior with temperature. To do so, the X 1Σ+ potential-energy curve and permanent dipole moment have been constructed from recent and reliable data points. The accuracy of both constructed curves is checked by determining the rovibrational levels and comparing their values with those available in literature.

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Thermal Activation of Methane by a Concerted Double C–H Bond Insertion: Charge-Induced Catalysis

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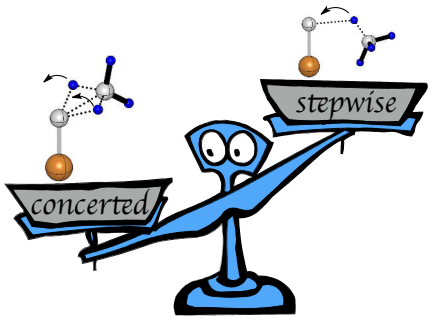
Abstract: In the context of methane C–H bond activation mediated by metal complexes under ambient conditions, classical hydrogen-atom transfer,[1,2] proton-coupled electron transfer,[3,4] as well as hydride transfer[5] scenarios have been proposed, and many of the key factors that control the reactivity have also been clarified. We report herein an unprecedented, mechanistically unique Cu^+-mediated insertion of a carbon atom into two C–H bonds of methane to form ethylene in a single, barrier-less step. In addition, arguments are provided showing that the copper atom in the ethylene forming reaction of $[Cu–C]^+$ with methane, can be replaced by an oriented external electric field of a positive point charge. Thus, the term "charge-induced catalysis" is suggested.[6]



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Optimizing Water Oxidation with Hematite by Simulations

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The design of highly efficient electrodes for photo-electrochemical water splitting is of both fundamental and practical importance [1-3]. We show in this presentation that the water splitting activity with hematite can be enhanced strongly by modification of the structure and the local chemistry [1, 2, 4, 5]. We will discuss the effects of surface orientation, active surface sites, presence of surface steps, lateral interaction, and oxygen vacancies in the subsurface layer on the oxygen evolution reaction (OER) activity [4, 5]. Particularly, the presence of oxygen vacancies is found to be efficient to control the OER activity. Figure 1 shows the free energies of intermediate species calculated for the (110) surface with/without oxygen vacancies (a), and the comparison of the calculated overpotentials with the literature (b) [7, 8]. An OER overpotential of as low as 0.47 V was obtained for an optimal oxygen vacancy concentration of 1.26/nm2. The obtained results are used to calculate the rate constants of the OER steps which will serve as input for state-space modeling [6] to simulate electrochemical impedance data that can be directly compared to experiments. We choose hematite as a model system. In general, this method helps in identifying reaction rate limiting parameters and optimizing OER materials.

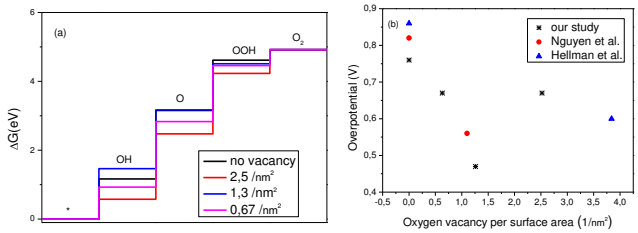

Figure 1 a) free energy diagram, b) Overpotential as a function of oxygen vacancy concentration.

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Study of surface reactivity of high index platinum surfaces

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The main challenges of the catalysis are to investigate and improve efficient, waste reducing and environmentally friendly processes. This can be realized by changing the composition of the chemical process or by tuning the shape of the catalyst itself. [1] The Pt nanoparticles as catalysts for instance show different catalytic reactivity by varying the surface shape and structure. [2] It has been established, that the higher density of atomic steps and kinks leads to more active sites on the surface. This might lead to an increasing reactivity for these stepped platinum surfaces.

In the present study we will analyze the dependence of the catalytic reactivity and selectivity of the industrially relevant reactions, such as condensation of light alcohols, on the kinked and stepped of Pt nanoparticles. These Pt surfaces provide thereby a lot of active sites for the mentioned reactions, thus detailed insight in the reaction mechanisms can be obtained. The theoretical calculations of the catalytic surface reactions will be performed using the exchange-correlation functional PBE [3] implemented in the Vienna ab initio simulation package (VASP) [4]. The analysis of the adsorption and coadsorption sites, adsorption energies, transition states and the favorable reaction paths of the investigated reactions will be the key objective of this research.

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Hybrid Algorithm based on *Tabu Search Method* for the Synthesis of Macromolecular Compounds with Imposed Properties

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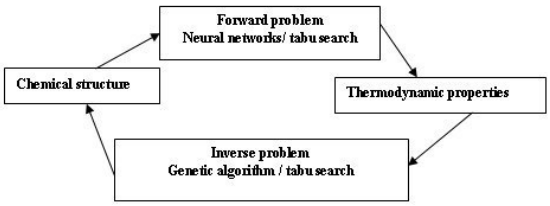
One of the most promising applications of Artificial Intelligence Methods (AI) is the computer-aided molecular design (CAMD). The CAMD can achieve the design of totally new molecules with desired properties according to our needs. In CAMD, two things must be known to some extent: the properties that are desired and how they relate to a molecule's structure. The structure–activity relationship is needed to both determine the necessary properties and build a molecule that has those properties. Artificial intelligence algorithms have paved the way for a multitude of applications, and the use of neural networks is increasing in the field of chemistry and biochemistry. The models of neural networks (NN) and their potential applications of classification, modeling, association, and mapping make them as a good partner in the CAMD. Usually the CAMD implies the use of combined artificial methods.

Our paper deals with a system build from Neural Network combined with a hybrid evolutionary algorithm Genetic Algorithm (GA). In order to improve the combinatory property of the GA path a Tabu Serach algorithm was attached.



Scheme 1. Hybrid algorithm

In the present study, we pursue two research themes in the genetic design framework. One is to investigate the efficacy of genetic design for problems with much larger and more complex design spaces. The second theme is to extend the original genetic algorithmic framework by incorporating higher-level chemical knowledge to better handle constraints such as chemical stability and molecular complexity by use of a *Multiobjective Tabu Search* . The fitness function of the system has been evaluated.

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Catalytic Roles of Metal-bound Hydroxide and Arginine in Pyruvate Class II Aldolase Investigated by QM/MM Metadynamics

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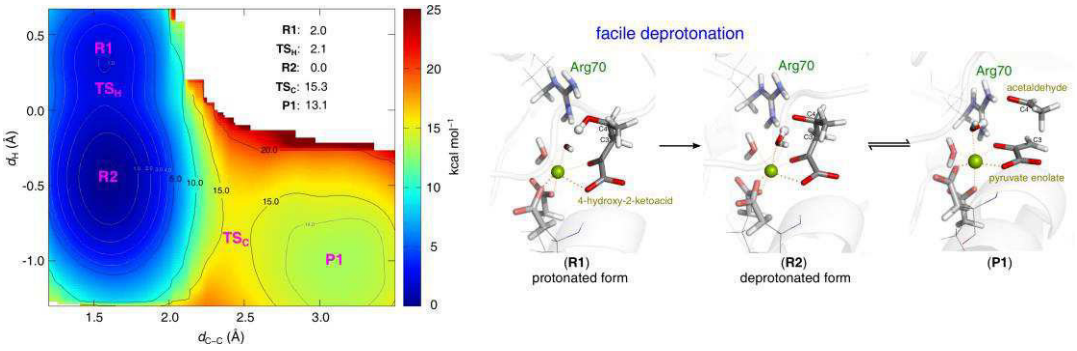
The retro-aldol reaction catalyzed by pyruvate class II aldolase is investigated with the QM/MM metadynamics. This enzyme consisting divalent metal ions as catalytic cofactors catalyzes the aldol cleavage of 4-hydroxy-2-ketoacid into pyruvate enolate and aldehydes, where the former binds to the metal ion. Aldol cleavage is mechanistically initialized by the deprotonation of the hydroxyl group of the substrate 4-hydroxy-2-ketoacid by the metal-bound hydroxide. The simulation demonstrates a small barrier of around 0.1 kcal mol^{-1} during the deprotonation, which suggests a practically barrierless process. The deprotonated form is then stabilized by the vicinal positively-charged arginine, facilitating the subsequent aldol cleavage. The C−C bond cleavage leads to the release of the aldehyde molecule, and the pyruvate enolate binds to the metal ion. The barrier for the C−C bond cleavage is estimated at approximately 15.3 kcal mol^{-1}, which reasonably agrees with the experimental rate constant (k_{cat}) of 205.4 s^{-1}. In addition to the metal cation coordinated by the pyruvate enolate in a chelating form, the arginine also contributes to stabilize the enolate oxyanion. In the overall catalytic process, the metal-bound hydroxide functions to deprotonate the reactant, which converts into the active form that continues on the C−C bond cleavage in the aldol cleavage reaction. The role of the arginine is to stabilize the deprotonated form of the reactant as well as the pyruvate enolate moiety by hydrogen bonding and electrostatic interactions.



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On the Origin of Reactivity Enhancement/Suppression Upon Sequential Ligation: the $[Re(CO)_x]^+/CH_4$ (x = 0 – 3) Couples

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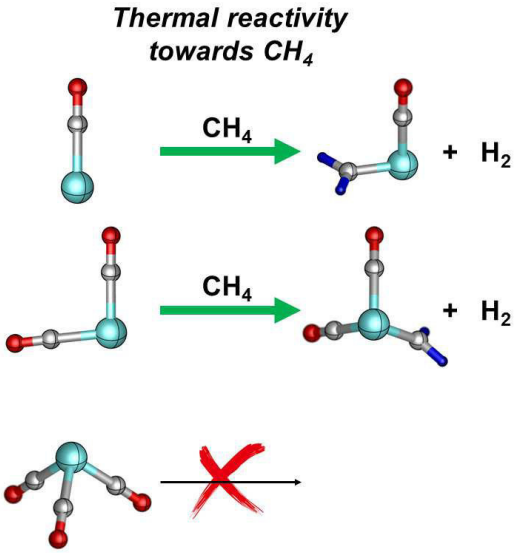
Abstract: The thermal gas-phase reactions of the rhenium carbonyl complexes $[Re(CO)_x]^+$ (x = 0 – 3) with methane have been explored by using FT-ICR mass spectrometry complemented by high-level quantum chemical calculation. While it had been concluded that addition of closed-shell ligands in general decreases the reactivities of metal ions[1], the current work provides an exception: the previously demonstrated inertness of atomic Re^+ towards methane is completely changed upon ligation with CO. Both, $[Re(CO)]^+$ and $[Re(CO)_2]^+$, bring about efficient dehydrogenation of the hydrocarbon at ambient condition. However, addition of a third ligand to form $[Re(CO)_3]^+$ quenches completely the reactivity. While the former reactivity enhancing effect can be traced back to a change of spin multiplicities of the metal center and the involvement of multi-state reactivity scenarios, the inertness of the latter is ascribed to the presence of a stable, closed-shell electronic configuration of $^1[Re(CO)_3]^+$.



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Theoretical study of Co(II/III)-complex catholytes used Li-ion redox flow batteries

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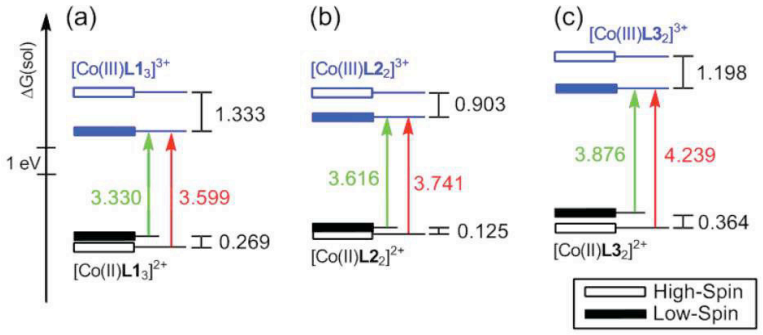
In the recent material chemistry field, redox battery with non-aqueous electrolyte is one of the hottest issue[1,2]. Different from electrolyte study, catholyte study have not be done much yet. Byon's group suggested transition metal include 6-coordinate compound as a catholyte of Li-ion redox flow battery system.

Herein we analyze the performance of suggested Co(II/III)-complex catholyte in Li-ion redox flow batteries. Spin-crossover[3] and entropy panelty are successfully describe experimental data. One step further, we suggest novel materials which show higher redox potential and capacity theoretically.



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Stochastic Basis Set Approach to Density Functional Theory

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Although density functional theory (DFT) is routinely used to study the properties of a wide range of molecular and crystal systems, its utility for studying large systems in materials science and biology is limited. This is due to the fact that the DFT computational effort, in terms of memory and CPU time, typically scales quadratically with system-size. While linear-scaling methods have been developed by several groups, these are often of limited applicability due to the non-locality of the density matrix in many types of large systems. An alternative approach has been developed [1, 2] which circumvents the calculation of the density matrix and the Kohn-Sham (KS) orbitals using stochastic orbitals. These stochastic orbital methods are useful for orthogonal basis-sets, such as plane-waves and grids. In this work we extend the methods to non-orthogonal basis sets which are common in quantum chemistry. The greatest hurdle is to bypass the need to invert the overlap matrix and this we accomplish by using the preconditioned conjugate gradient method. The projection of orbitals on the occupied space is carried out using Chebyshev propagators. Various observables are treated as random variables with mean equal to the deterministic KS values and variance which drops when the number of random orbitals is increased in accordance with the central limit theorem. Results for the calculation of silicon clusters are shown.

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Thermal properties of organic solids from the quasi-harmonic approximation

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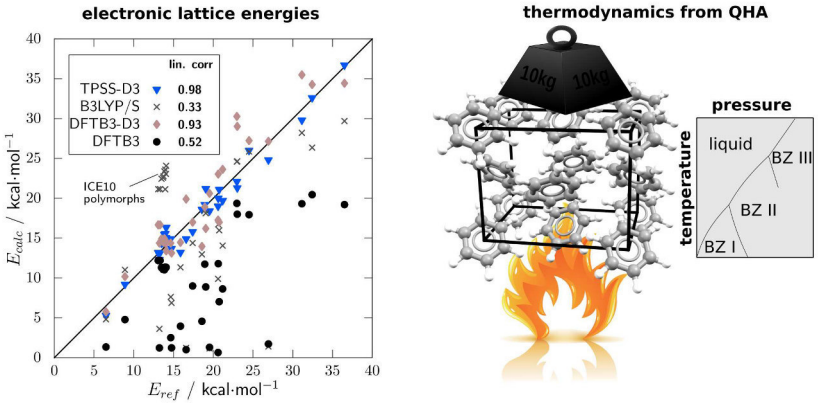
Kohn-Sham density functional theory and tight-binding approximations are the method of choice for efficient electronic structure calculations. Especially when reliable geometries and thermodynamic properties are needed, this will continue to be the case in the foreseeable future. In the past years the standard semi-local methods have been improved to incorporate non-local correlation effects leading to the omnipresent van der Waals interaction. Thus, their area of applicability has been extended to the important class of molecular crystals.[1]
I will present a combination of modern dispersion corrected tight-binding methods with a quasi-harmonic treatment of lattice dynamics to efficiently describe thermodynamic properties of organic crystals.[2, 3] The discussed systems range from the small and mostly rigid squaric acid to larger and more flexible pharmaceuticals like naproxen and carbamazepine. While the focus will be on structural features, the impact on relative free energies is discussed. This is of major importance for the control and prediction of polymorphism, which is highlighted by results from the 6^{th} blind test for organic crystal structure prediction.[4, 5, 6]



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Ethylene glycole decomposition on a Palladium subnanometric cluster: a graph theory based approach

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In the context of biomass feeds reforming [1, 2], ethylene-glycol (C_2) was selected as oxygenates model species and its decomposition on a subnanometric Pd cluster was investigated by means of DFT. Studies dealing with the reactivity of this molecule are of interest both to enhance practical goals of hydrogen production and to provide fundamental insights into the underlying competition among C−H, O−H, C−C, and C−O bond cleavages in polyols. The size of the catalytic system above, involving a small Pd cluster (Pd_{12}) and the simple C_2 species, allowed one to explore by computational techniques almost all the reactive routes associated to the ethylene-glycol decomposition. This determined the generation of a large grid of possible events, useful to deepen the energetic ordering of different reaction pathways that in principle would let to unravel the whole reaction mechanism, involving many and complexly tangled molecular events. So, to effectively analyze the decomposition path it is necessary to accurately characterize not only the elementary steps involved in the reaction network but also their sequences. The protocol followed for the reaction network analysis was organized into three

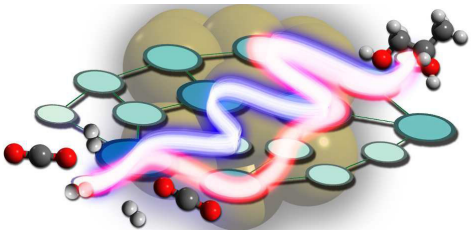

Figure 1: Paths found to be favoured, in ethylene-glycol decomposition on Pd_{12}.

steps: i) *ab-initio* calculation of the activation barriers and presieving of the possible molecular events, ii) organization of the graph representing the final reaction network, iii) analysis of the possible pathways and characterization of the final graph with centrality indexes. The analysis of the resulting network was performed considering that, as stated in the frame of the graph theory (GT) approach, a path is a walk in which no vertex occurs more than once. The differently long pathways found were ordered taking into account the total energy content (TEC), defined as the summation of all the activation barriers involved in the development of a given route.

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A comparative study of hydrogen bond and iminium mechanisms in organocatalytic and enzymatic reduction

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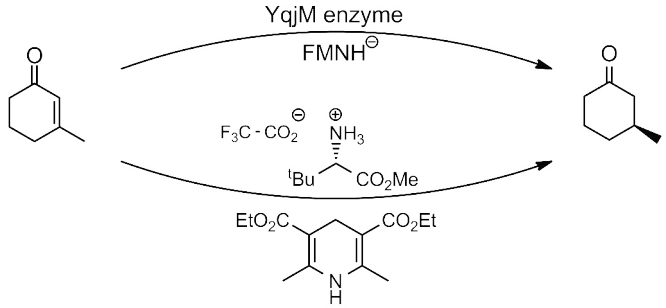
Reduction of α,β unsaturated ketones can be carried out via enzymatic or organocatalytic reactions. They have high importance in synthetic organic chemistry, since both yield chiral products.



In the organocatalytic scheme an iminium activated reaction mechanism is considered to be the most favored and was examined by Gutierrez *et al.*[1] On the other hand in the enzyme catalyzed case a hydrogen bond activated mechanism is advised and was studied by QM/MM methods.[2] However with a lysine amino acid present in the active center of the enzyme an iminium activated mechanism can be envisioned in the biocatalytic case as well.
In the present work the two possible mechanisms were examined for both the organocatalytic and enzymatic routes by DFT calculations, using the ωB97X-D functional. In the biocatalytic case the so called "Quantum chemical cluster" approach was applied, which means, that model systems, including the most important residues and ligands around the active center, have been built where the chain ends of the amino acids were frozen in their X-ray structure position. This approach also has the advantage that the biocatalytic pathways can be compared directly in free energies. QM/MM calculations were also performed to investigate the mechanisms in more details. Our results indicate that the iminium activation is more plausible than the hydrogen bond mechanism for both the enzyme and organocatalyst. These new insights can help to improve the efficiency of the organocatalytic reduction.

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Improved Accuracy of Hybrid Atomistic/Coarse-Grained Simulations Using Reparametrised Interactions.

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Reducing the number of degrees of freedom in molecular models, by so-called coarse-graining, is a popular approach to increase the accessible time scales and system sizes in molecular dynamics (MD) simulations. It involves, however, a loss of information. In order to retain a high accuracy in the region of interest, hybrid methods that combine two levels of resolution in a single system are an attractive trade-off. Hybrid atomistic (AT)/coarse-grained (CG) simulations have previously been shown to preserve the secondary structure elements of AT proteins in CG water but to cause an artificial increase in intramolecular hydrogen bonds due to the lack of hydrogen-bonding capacity of CG water, resulting in a reduced flexibility of the proteins.[1] Recently, it was found that the AT-CG interactions employed in these simulations were too favourable for apolar solutes and not favourable enough for polar solutes.[2] Here, the AT-CG interactions are reparametrised to reproduce the solvation free energy of a series of AT alkanes and side-chain analogues in CG water, while retaining the good mixing behaviour of AT water with CG water. The new AT-CG parameters are tested in hybrid simulations of four proteins in CG water. Structural and dynamic properties are compared to those obtained in fully AT simulations and, if applicable, to experimental data. The results show that the artificial increase of intramolecular hydrogen bonds is drastically reduced, leading to a better reproduction of the structural properties and flexibility of the proteins in atomistic water.

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Binding isotope effects as a tool to detecting HIV-1 RT binding sites.

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HIV-1 reverse transcriptase (RT) is one of three enzymes involved in the human immunodeficiency virus (HIV-1) replication cycle. Half of 26 antiretroviral approved drugs target RT at allosteric cavity or RNase H active site. Resistance of RT mutants to current therapies prompted us to explore computationally binding inhibitors not only to the allosteric cavity and RNase H active site but also to other, recently identified Knuckles, NNRTI Adjacent and Incoming Nucleotide Binding sites.

Our computational protocol was evaluated based on nine, FDA approved RT nucleoside (NRTI) and non-nucleoside (NNRTI), inhibitors.[1] According to our theoretical[2] and experimental[3] studies we have recently shown that N-(2-chloro-4-sulphamoylphenyl)-2-((4-(2,4-dimethyl-phenyl)-5-(thiophen-2-yl)-4H-1,2,4-triazol-3-yl)sul- phenyl)-acetamide, L-1, is an inhibitor of HIV-1 RT that binds in the hydrophobic allosteric pocket via van de Waals interactions and even more strongly to the RNase H active site using electrostatic attraction. Using promising L-1 scafold, aditional three triazole-based derivatives (L-2, L-3 and L-4) have been developed and docked to the allosteric cavity, the RNase H active site, the Knuckles, the NNRTI Adjacent, and the Incoming Nucleotide Binding sites. Complexes of the ligand with the protein have been obtained after long QM/MM MD simulations. Heavy-atom (^{13}C, ^{15}N and ^{18}O) binding isotope effects, BIEs, have been analyzed in the context of distinguishing between binding sites. Specific interactions between the ligands and RT binding sites have been characterized.

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Simulation of reversibly interlocked SWCNTs

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In chemical functionalization of single-walled carbon nanotubes (SWCNTs), usually one has to compromise between altering the structure of the nanotube via covalent attachment of the adsorbates or by forming rather fragile supramolecular complexes. An alternative, which combines having only non-covalently bound species but leads to very stable structures, is the concept of mechanically interlocking the CNT inside the adsorbate molecule. Specifically, we explore adsorbates which allow for a reversible ring closure in the rotaxane-forming step, therefore promising greater yields and a better control of the target structure. By performing molecular dynamics simulations with the generalized AMBER force field, we identified suitable structures and geometries and analyzed their behaviour under different reaction conditions.

Indirect-to-Direct Band Gap Crossover in Few-Layer Transition Metal Dichalcogenides

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Department of Chemistry, Tsinghua University, Beijing, China

Abstract: Layered transition metal dichalcogenides (TMDs) have been found to exhibit the indirect-to-direct band gap transition when they are thinned to a single monolayer. We disclose that the indirect-to-direct band gap crossover in TMDs is essentially a competition between the spin-orbit coupling and inter layer electronic coupling. For MoS2, MoSe2 and WS2, the indirect-to-direct band gap transition occurs in the monolayer where interlayer interactions completely vanish. The spin-orbit coupling effect of WSe2 is so large that the indirect-to-direct band gap crossover takes place in the trilayer, and for WTe2 such a crossover even happens in the tetralayer. The valley degeneracy of the band edges and the valley-dependent optical transitionsin few-layer TMDs have opened up the way to manipulate their valley degree of freedom for valleytronics and spintronics.

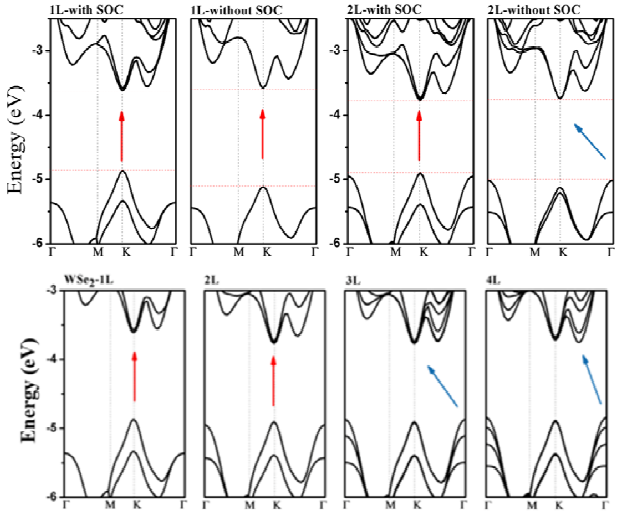

Fig.1 Top panel displays band structures for monolayer and bilayer of WSe2 for with and without spin orbital coupling (SOC). The bottom is the band structure of WSe2 as a function of the layer thickness. The indirect-to-direct band gap crossover in TMDs is essentially a competition between the spin-orbit coupling and inter layer coupling effects: SOC favors direct band gap while interlayer dispersion favors indirect gap.

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Interacting Quantum Atoms Approach Applied to the S66 Database of Noncovalent Complexes

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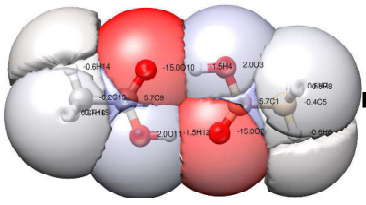
The interacting quantum atoms (IQA) method [1] decomposes the total energy of a molecular system in terms of physical components that are ultimately divided into one- and two-center (atomic) contributions within the context of the quantum theory of atoms in molecules. In principle IQA can assess, systematically and in great detail, the strength and physics of covalent and noncovalent interactions in biomolecular systems. Similarly, molecular mechanics (MM) potentials and QM-MM treatments could be assessed in terms of IQA descriptors. However, IQA is computationally expensive due to six-dimensional numerical integrations over the irregularly-shaped atomic basins that involve the first and second order density matrices. In addition, numerical errors may also affect the accuracy of the QM energy reconstructed by IQA. These factors still limit the size of molecular systems and the choice of QM methods that can be treated with IQA. Both methodological and technical advances are needed to extend the applicability of IQA to biomolecules comprising ~100 "QM atoms", but gaining further computational experience on smaller systems is also necessary. Hence, we examine the S66 database [2] of benchmark geometry and binding energies relevant to biomolecular models. For all the structures, we perform single-point and geometry optimizations using HF and selected DFT methods with triple-ζ basis sets followed by full IQA calculations. Pairwise dispersion energies are accounted for by the DFT-D3 method. We analyze the goodness of the HF & DFT binding energies, the magnitude of numerical errors, the relative weight of intra- and intermolecular interactions, the mode of binding, the similarities and differences depending on the level of theory, etc. Considering all the information, we make recommendations of model chemistries and IQA settings for larger systems.

S66 database

HF–D/VTZ
DFT–D/VTZ



$$\boldsymbol{\eta} \equiv \begin{bmatrix} E_{self}(\Omega_1) & E_{\text{int}}(\Omega_1,\Omega_2)/2 & \cdots & E_{\text{int}}(\Omega_1,\Omega_n)/2 \\ E_{\text{int}}(\Omega_2,\Omega_1)/2 & E_{self}(\Omega_2) & \cdots & E_{\text{int}}(\Omega_2,\Omega_2)/2 \\ \vdots & \multicolumn{3}{c}{\texttt{IQA descriptors}} \\ E_{\text{int}}(\Omega_n,\Omega_1) & E_{\text{int}}(\Omega_n,\Omega_2) & \cdots & E_{self}(\Omega_n) \end{bmatrix}$$

$$\Delta_{bind}\boldsymbol{\eta}, \quad \Delta_{bind}\boldsymbol{\eta}_{AB} \equiv \begin{bmatrix} A & A\cdots B \\ B\cdots A & B \end{bmatrix}$$

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Probing the Feasibility Limits of Coupled Cluster Theory: Highly Accurate Activation Barriers of Unexpected Reactions for Energetic Materials

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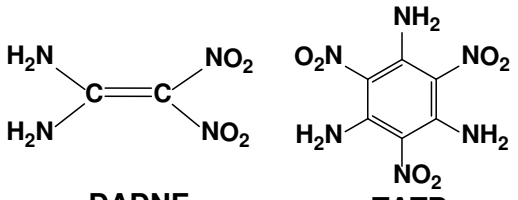
Kinetics and mechanism of thermal decomposition are crucial for enhancing safety and performance of energetic materials (EM). While direct kinetic experiments with EM are hindered due to numerous fast exothermic reactions occurring simultaneously, quantum chemical calculations are often a convenient alternative to experiment. However, the accuracy of routinely used DFT methods is often not sufficient to provide convincing evidence on the thermolysis mechanism of EM. To achieve reliable chemical accuracy on the activation barriers (~ 1 kcal/mol), the expensive high-level coupled cluster computations are always desirable. Unfortunately, the CCSD(T) calculations with the basis set of quadruple zeta quality are feasible for the systems with at most 7-8 atoms like C, N, O. However, the explicitly correlated CCSD(T)-F12 modifications allow for significant reduction of the basis set while retaining the proper accuracy. In our previous extensive benchmark studies for a series of energetic nitro species, we showed that even CCSD(T)-F12/VDZ-F12 thermochemistry is generally of the CCSD(T)/CBS(3,4) quality [1].
Here we present the two instructive examples of the highly accurate CCSD(T)-F12 computations for decomposition mechanisms of widely used high-performance insensitive EM: 1,1-diamino-2,2-dinitroethylene (DADNE, FOX-7) and triamino-trinitrobenzene (TATB). In particular, we managed to perform CCSD(T)-F12/VDZ-F12 calculations for TATB, which is comprised of **18 non-H atoms**.



For both species, CCSD(T)-F12 computations provided new important insights into the decomposition mechanism. In the case of DADNE, the calculations suggested the two competing primary reaction channels never discussed before: viz., the H-transfer (enamino-imino tautomerization) followed by radical decomposition (effective activation barrier ~48 kcal/mol) and intramolecular cyclization to oxazete-N-oxide, which is prone to fast subsequent molecular decomposition (overall activation barrier ~55 kcal/mol). In the case of TATB, the accurate CCSD(T)-F12 activation barriers of the three channels: viz., intramolecular cyclization followed by decomposition reactions, nitro-aci-nitro isomerization with subsequent cyclization and water elimination, and nitro-nitrite rearrangement, are very close to each other (~59 kcal/mol). All these findings were possible only with CCSD(T) convincing evidence, the DFT values were notably scattered.

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On the nature and reactivity of the Substrate/Dioxygen Bound Intermediate in Tyrosinase: QM/MM Study Correlated with Spectroscopic Data.

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Tyrosinase is an enzyme controlling the production of melanin by converting phenols to quinones. The active site responsible for the transformation is a "diamond" Cu_2O_2 core formed by the binding of dioxygen to the dinuclear copper center of the enzyme.

QM/MM calculations were employed to study the structure and reactivity of the ternary complex (**Figure 1**), based on the available crystal structure of -zinc substituted- tyrosinase with the molecule of substrate tyrosine bound in the active site of the inactive enzyme [1].

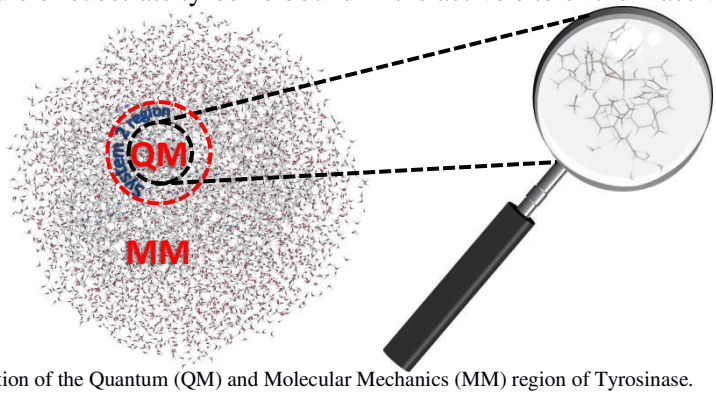

Figure 1 Representation of the Quantum (QM) and Molecular Mechanics (MM) region of Tyrosinase.

After reproducing the main features of the Zn_2/tyrosine crystal structure by the QM/MM calculations, thus verifying the reliability of the computational setup, the native form of the enzyme with the Cu_2O_2 core was studied. Reactant complexes were constructed and their spectroscopic features and reactivity were checked with respect to available experimental evidence on enzyme as well as model systems [2].

Despite the fact that accurate quantum chemical treatment of the Cu_2O_2 core is a highly challenging problem [3], the QM/MM(-DFT) calculations yielded a plausible description of the Tyrosinase reaction mechanism.

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Explicitly Correlated N-Electron Valence State Perturbation Theory (NEVPT2-F12)

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Explicitly correlated second order N-electron valence state perturbation theory (NEVPT2-F12) has been implemented in ORCA. Our NEVPT2-F12 algorithm is based on a fully internally contracted (FIC) wave function and includes the correction of semi-internal excitation subspaces. The basis set incompleteness correction for the CASSCF energy is considered as well. For all relative energies calculated in this work, the errors with respect to the complete basis set (CBS) limit for NEVPT2-F12 method are within 1 kcal/mol. If the number of active MOs is considered as a constant, the overall scaling of the computational effort is O(N^5). The algorithm exploits the resolution of identity (RI) approximation to improve the computational efficiency. The computational cost of a RI-NEVPT2-F12 correlation energy calculation for each root is comparable to a closed-shell RI-MP2-F12 calculation on the same system.

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Elucidation of the Singlet Fission Mechanism: A Theoretical Insight

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[2]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, v. Risorgimento 35, I-56126 Pisa, Italy

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Singlet fission (SF) is a fast (sub-ps) process in which the lowest excited singlet state of one molecule transfers parts of its energy to a neighbouring molecule resulting in two (local) triplets that are coupled into a singlet (^{1}TT). It can be beneficial for the improvement of organic photovoltaic cells since it exploits a high-energy photon with minimal thermal energy loss and it generates multiple excitons for charge separation. The elucidation of SF mechanism is crucial for the development of new and highly efficient SF chromophores. With the aid of theoretical chemistry and computational modelling, parameters that determine the SF efficiency as well as the states that are involved in the transition process from the lowest (diabatic) excited spin singlet state to the ^{1}TT state can be deduced. The SF efficiency can be determined by calculations of the SF rate and the rates of other competing processes. In the Fermi's golden rule approximation, the SF rate is proportional to the electronic coupling between the initial and final diabatic states [1]. We have developed a nonorthogonal configuration interaction approach to calculate this electronic coupling directly with a clear chemical interpretation of the photoexcited states involved [2,3], and in addition, we explore the potential energy surfaces (PESs) of the relevant excited states using nonadiabatic dynamics simulations [4]. Here, we present the details of our approach for calculating the electronic coupling and the preliminary results of the PESs of the relevant excited states of a biradicaloid molecule (see Figure 1), which has been previously investigated as a promising candidate for a SF chromophore [5].

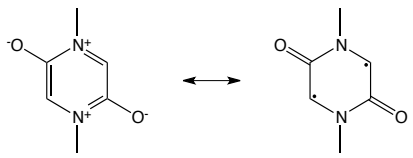

Figure 1. The resonance structures of the biradicaloid molecule

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Polynuclear $Li_{12}F_{13}^-$ superhalogen anion as a steric shielding agent with respect to selected metal ions

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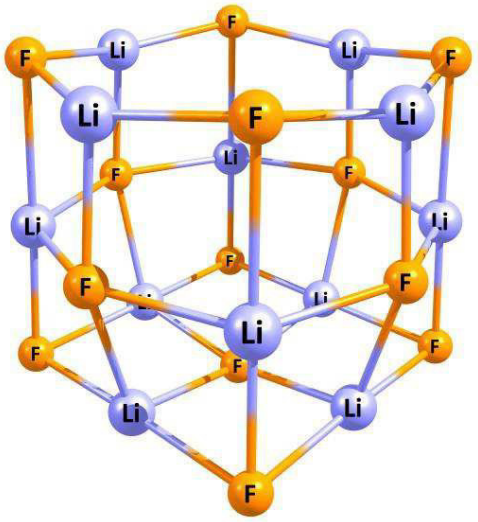
Polynuclear superhalogen anion $Li_{12}F_{13}^-$ and its ionic complexes formed by the interaction with selected metal cations (i.e., $Li_{12}F_{13}^-Na^+$, $Li_{12}F_{13}^-K^+$, $Li_{12}F_{13}^-Mg^{2+}$, and $Li_{12}F_{13}^-Zn^{2+}$) were proposed and investigated on the basis of ab initio calculations [1]. The thermodynamic stability, vertical excess electron detachment energy, and binding energies between ionic components were examined and discussed.



The $Li_{12}F_{13}^-$ anion has been proved stable against fragmentation and its vertical electronic stability was found to approach 10 eV. Due to its specific equilibrium structure that resembles a molecular basket, the $Li_{12}F_{13}^-$ anion was found capable of trapping positively charged metal ions inside to form strongly bound ionic complexes. The large values of binding energies predicted for the $Li_{12}F_{13}^-Na^+$, $Li_{12}F_{13}^-K^+$, $Li_{12}F_{13}^-Mg^{2+}$, and $Li_{12}F_{13}^-Zn^{2+}$ systems and their specific equilibrium structures indicate that the $Li_{12}F_{13}^-$ anion can be useful as a steric shielding agent which protect the metal ions from the interaction with the surroundings.

Acknowledgements: This work was supported by the Polish Ministry of Science and Higher Education (Grant Number: DS 530-8375-D499-16). The calculations have been carried out using resources provided by Wroclaw Centre for Networking and Supercomputing (http://wcss.pl) Grant No. 350.

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Analytic Hyperpolarizability and Polarizability Derivative with Fractional Occupation Numbers for Large Extended Systems

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A problem in the calculation for large extended systems is the steep increase of the computational cost, but another problem is the difficulty of SCF convergence because of a small HOMO–LUMO gap. This problem may be attributed to the fact that the orbital occupation number is integer and may be avoided by employing the fractional occupation number (FON) with reasonable computational cost.

In computing second- and higher-order derivatives, coupled-perturbed (CP) equations are usually solved. In the conventional CP equation, an explicit computation for dependent pairs can be avoided (non-canonical approach). However, with FON, one additionally has to consider the response term in partially occupied orbitals. The response term may be extremely large when degenerated orbitals are partially occupied, and the convergence of CP equations is then challenging. In an earlier study [1], we solved the problem in the first-order CP equation and made it possible to compute a second-order geometrical derivative. In the present study [2], we derived and implemented analytic third-order derivatives (hyperpolarizability and polarizability derivative) with FON. The expression obtained here employs limit values when the difference of orbital energies is small and is therefore applicable to the computation of third-order derivatives for the system with degenerated orbitals. The derived equations for the density-functional tight-binding (DFTB) method were implemented into GAMESS-US. We verified that calculated spectra with the implementation are accurate.

The developed method was applied to a series of zigzag-type graphene nanoribbon (ZGNR). By performing a parallel calculation for a ZGNR consisting of 1012 atoms using four E5-1650 v3 calculation node (24 CPU cores in total), a computation of energy, gradient, Hessian, dipole derivative, hyperpolarizability, and polarizability derivative of the ZGNR finished in 7.55 hours. The scaling of the computational cost was 3.98 with respect to the number of atoms. We expect that the developed method is useful in simulating infrared and non-resonance Raman spectra of large extended systems.

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Trends in catalytic activity of Ni-based electrodes for the hydrogen evolution reaction

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Metallic binary compounds have emerged in resent years as highly active and stable electrocatalysts toward the hydrogen evolution reaction. The origin of their high activity from a theoretical and experimental point of view is elucidated. Different metallic ceramics (Ni_3S_2, Ni_3N, and Ni_5P_4) are grown directly on Ni support in order to avoid any contaminations. DFT calculations were performed to obtain a deeper understanding of possible active adsorption sites and the observed catalytic stability. It is found that the heteroatoms P, S, and N actively take part in the reaction. Due to the anisotropic nature of the materials, a variety of adsorption sites with highly coverage-dependent properties exist, leading to a general shift in hydrogen adsorption free energies ΔG_H close to zero. Extending the knowledge gained about the here described materials, a new catalyst is prepared by modifying a high surface Ni foam, for which current densities up to 100 mA cm^{-2} at around 0.15 V are obtained.

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Improving the thermodynamics and transferability of coarse-grained models

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Coarse-grained (CG) simulations are becoming increasingly important for the modelling of soft matter systems, due to their ability to study large system sizes over long time scales. Common methods for parametrising CG models include iterative Boltzmann inversion (IBI) [1] and force matching [2]. While these usually give good structural accuracy, they often yield interaction potentials with poor transferability to different state points. This is mainly due to the fact that the pair potentials only include multi-body effects in an averaged out way, which is only correct at the state point at which the potential was parametrised. The thermodynamic accuracy of these CG models is often poor, particularly in reproducing free energies of mixing, which we have shown for a range of octane/benzene mixtures.

We show that parametrising CG models from multiple state points, using multistate IBI [3], can help with the problem of poor transferability in some circumstances. However, there are still issues with this approach. The resulting models do not necessarily improve upon the accuracy of calculated thermodynamic quantities relative to models derived from a single reference point. It has been proposed that including a correction to the pair potential, which depends on the local environment of the CG bead, could lead to improved accuracy and transferability. Here, we propose a method to parametrise such a potential, which aims to keep the structural accuracy of a CG model parametrised at a single state point, but provides more accurate thermodynamic quantities and is transferable over a range of concentrations and temperatures.

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Exploring Multistep Intersystem Crossing Pathways of Cinnamate-Based Sunscreens by Automated Reaction Path Search Methods

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Cinnamate derivatives are widely used molecules in the nature as the chromophore of photo-active yellow protein, sunscreens of many plants to protect their DNA *etc*. Understanding the nonradiative decay (NRD) mechanisms should realize new effective sunscreens and other photofunctional materials. In this study, we investigated the NRD pathways of jet-cooled *para*-methoxy methylcinnamate (*p*-MMC) and *para*-methoxy ethylcinnamate (*p*-MEC) by picosecond and nanosecond pump-probe spectroscopy. The possible NRD pathways were calculated by the single component artificial force induced method [1] combined with the (time-dependent) density functional theory.

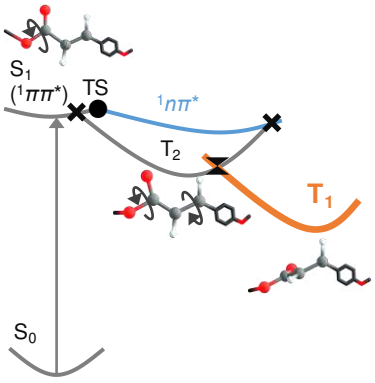

Figure 1. Schematic of the multi-step ISC pathway of *p*-MMC

We found that *p*-MMC and *p*-MEC at low excess energy undergo multistep intersystem crossing (ISC) from the bright S_1 ($^1\pi\pi^*$) state to the T_1 ($^3\pi\pi^*$) state mostly *via* stepwise ISC through T_2 state followed by the internal conversion from S_1 to the dark $^1n\pi^*$ state in ~100 ps as shown in Figure 1 [2]. This multistep ISC results in the torsion of C=C double bond by ~95° in the T_1 state [2]. This result suggests that the ISC processes play an indispensable role in the photo-protecting sunscreens in natural plants.

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Trajectory Surface Hopping Study of the Photodissociation Dynamics of Phenol

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Nonadiabatic transitions between adiabatic potential-energy surfaces, especially at conical intersections, are ubiquitously involved in the photophysics and photochemistry of polyatomic molecules. Because a full quantum treatment of the coupled dynamics of electrons and nuclei is computationally highly demanding for polyatomic molecules, the quasi-classical trajectory surface-hopping (TSH) model, in which the electrons are described quantum mechanically and the nuclear motion classically, is an attractive alternative to full quantum dynamics for the simulation of nonadiabatic photochemical processes. Two well-established approximations for the modeling of non-classical electronic transitions are the time-honored Landau-Zener (LZ) formula [1] and Tully's fewest switching (TFS) algorithm [2]. In the present study, the accuracy of these two TSH algorithms has been critically evaluated in comparison with exact nonadiabatic quantum dynamics calculations for a model of the photoinduced hydrogen-atom elimination reaction in phenol. The model comprises three electronic states (S_0, $^1\pi\pi^*$, $^1\pi\sigma^*$), two nuclear degrees of freedom (the OH stretching coordinate and the CCOH torsional angle) and exhibits two conical intersections ($^1\pi\pi^*/^1\pi\sigma^*$ and $^1\pi\sigma^*/S_0$) [3]. Considering photoexcitation from different vibrational levels of the S_0 state to the $^1\pi\pi^*$ state, we examined the time-dependent electronic population dynamics as well as the branching ratio of the two dissociation channels. The results of fully converged TSH calculations (up to 10^5 trajectories) are compared with the results of exact quantum wave-packet calculations. When an even number of quanta is initially populated in the torsional mode (which is the coupling mode at both conical intersections), both TSH methods qualitatively reproduce the time-dependent electronic population dynamics, but are inaccurate in the prediction of the electronic branching ratio. When an odd number of quanta is initially prepared in the torsional mode, the population dynamics of the $^1\pi\pi^*$ state is reproduced with reasonable accuracy, but both TSH algorithms fail to reproduce the time evolution of the populations of the $^1\pi\sigma^*$ and S_0 states and the electronic branching ratio. The failures of the TSH methods can be attributed to the importance of nonadiabatic tunneling effects in the photodissociation of phenol.

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Reactivity and Selectivity of Polycyclic Aromatic Hydrocarbons: Shape and Size Dependence

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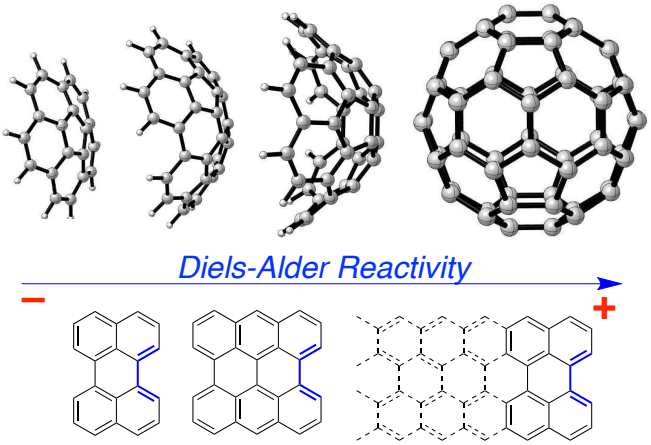
The Diels-Alder reactivity and selectivity of Polycyclic Aromatic Hydrocarbons (PAHs) have been explored computationally within the DFT framework. To this end, the [4+2]-cycloaddition reactions between maleic anhydride and both planar PAHs[1] and buckybowls[2] have been considered.

For bowl-shaped PAHs, it was found that there is a smooth convergence to the C_{60} barrier energy if the size of the buckybowl is increased.[3] Similarly, the process involving the bay regions of planar PHAs becomes more and more exothermic and the associated activation barriers become lower and lower when the size of the system increases.[4] This enhanced reactivity follows an exponential behavior that reaches its maximum for systems having 18–20 benzenoid rings in their structures, a value which can be extrapolated for the analogous process involving graphene. The origins of these reactivity trends have been quantitatively analyzed by means of the Activation Strain Model[5] (ASM) of reactivity in combination with the Energy Decomposition Analysis (EDA) method.



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Conformational Changes Induced by Fluorination: Extended Molecular Dynamics of Unguisin Peptides

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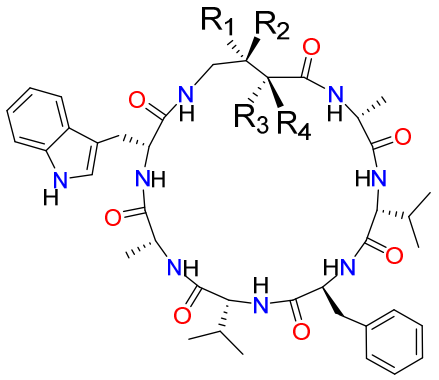
Stereoselective fluorination constitutes a valuable strategy to fine-tuning the conformation of functional molecules [1]. Potential applications in medicinal chemistry and biotechnology arise from the introduction of fluorine atoms in peptides because these are flexible systems where conformation determines function. Unguisin A is a natural macrocyclic heptapeptide that incorporates γ-aminobutyric acid (GABA) as one of the amino acid residues. Besides natural unguisin A, four stereoisomers of the GABA analog 2,3-difluoro-4-aminobutyric acid have been synthetized and their structures analyzed by nuclear magnetic resonance and molecular modeling [2]. To complement the previous results, we perform extensive molecular dynamics simulations in DMSO solution in order to explore the conformational space accessible to natural unguisin A and the four fluorinated variants. To parametrize the non-standard GABA residue in **3**-**7**, atomic charges are adjusted to reproduce the electrostatic potential computed for different conformers of the molecule and selected torsional angles along the GABA main chain are refined. For each trajectory, structural analysis of polar and hydrophobic contacts, conformational clustering, and quantum mechanical energy calculations are carried out to provide an accurate description of the fluorine-substitution effects.



R_1	R_2	R_3	R_4	
H	H	H	H	unguisin A (**3**)
H	F	H	F	*syn*-difluoro (**4**)
F	H	F	H	*syn*-difuoro (**5**)
H	F	F	H	*anti*-difluoro (**6**)
F	H	H	F	*anti*-difluoro (**7**)

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Development of the Quantitative Structure-Property Relationships (QSPR) for Predicting Char Yield of Polybenzoxazines

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Polybenzoxazines (pBox) are a relatively new addition to the family of thermoset polymers and offer great potential in fire resistant applications. Depending on the monomer structure employed, pBox can form char yields of up to 81 %. The char acts as a surface barrier which insulates and slows the escape of volatile decomposition gases into the fire front, thus protecting the remaining virgin materials from further degradation and resulting a slower fire spread across the area. Benzoxazines polymerise through a ring opening polymerisation reaction to form a highly crosslinked network and the presence of an additional polymerisable functional group in some of the benzoxazines, *e.g.* acetylenic, provides further crosslinks in the polymer system (Figure 1).

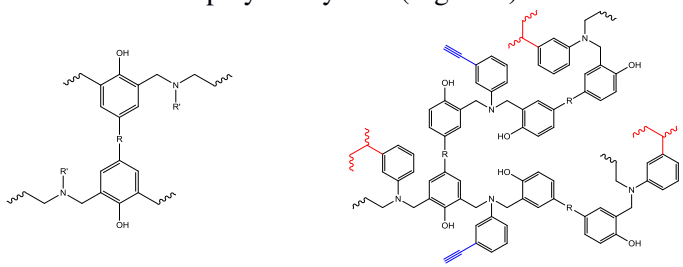

Figure 1. Possible crosslinked system in (left) polybenzoxazines and (right) polybenzoxazines with polymerisable functional group (R and R' = alkyl or phenyl).

In this work, a prediction model based on Quantitative Structure-Property Relationships (QSPR) was successfully generated to provide a tool for predicting the percentage char yield formed by pBox. This provides a picture of which structure will lead to a pBox with higher char yield and better flame resistance prior to synthesis. A data set containing thirty-three pBox structures with their experimental percentage char yields were collected from various sources. These were then compiled and used in the model development. This data set is considered small when compared to the analogous, Quantitative Structure-Activity Relationships (QSAR) method which normally works with thousands of data for the same purpose. The small data is due to the limited data available in the polymer literature. We have adapted the QSAR method, which has been widely used in medicinal and phamaceutical industries to polymers and the unique idea in this method is, to use monomer structures of the polymers of interest, rather than simulating the complex network structure of polymer system to develope the model. Despite the small data set used, the model has proven to be successful in providing prediction data with outstanding agreement to the experimental values, with an average error of less than 5% [1]. The generated model also shows impressive statistics for its predictive power over a series of internal and external validation tests as well as better predictions than the Van Krevalen group contribution prediction method. The model has performed well despite the limitations and we believe that this method has a great potential in years to come.

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Embedding metal atoms in icosahedral structures: biicosahedral metallaboranes as three-dimensional analogues of naphtalene

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Boron chemistry allows the concept of aromaticity to be extended from the two-dimensional planar hydrocarbon systems constructed with hexagonal benzene rings to three-dimensional borane deltahedra. The structures based on icosahedra (Fig. 1) such as the $B_{12}H_{12}^{2-}$ dianion and the isoelectronic carboranes exhibit special stability. Very stable metallaboranes and metallacarboranes are obtained by substituting BH vertices with transition metal units such as cyclopentadienylmetal vertices [1].

Consideration of the well-known very stable icosahedral $B_{12}H_{12}^{2-}$ as a three-dimensional analogue of benzene was extended by the recent synthesis of the biicosahedral $B_{21}H_{18}^{-}$ as a three-dimensional analogue of naphthalene. The preferred structures of metallaboranes derived from $B_{21}H_{18}^{-}$ have been examined by density functional theory [2]. The isoelectronic species $CpNiB_{20}H_{17}$ and $CpCoCB_{19}H_{17}$ have the 46 skeletal electrons expected by the Wade-Mingos and Jemmis rules for a structure consisting of two face-sharing fused icosahedra. The CpM units in these structures energetically prefer to be located at a meta vertex of the biicosahedron. The analogous ferraboranes $CpFeB_{20}H_{17}$ with only 44 skeletal electrons also have related biicosahedral structures. The presence of an agostic hydrogen atom bridging an Fe–B edge compensates for the two-electron deficiency in $CpFeB_{20}H_{17}$ relative to $CpNiB_{20}H_{17}$. The nucleus-independent chemical shift (NICS) values of these systems indicate them to be strongly aromatic.

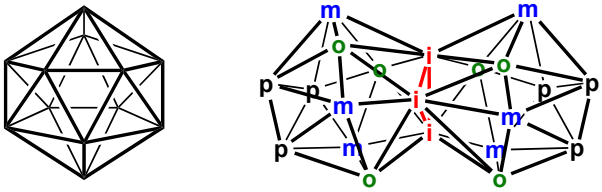

Figure 1. Comparison of the icosahedral structure of $B_{12}H_{12}^{2-}$ and the biicosahedral structure of $B_{21}H_{18}^{-}$. The ipso (i), ortho (o), meta (m) and para (p) vertices are labeled.

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Towards Rationalizing the Trends in the Electronic Structure of MX_2 3*d* Transition Metal Dihalide Monolayers

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Due to their wide possibilities of applications, monolayers formed by transition metal dichalcogenides, like MoS_2 have been in the focus of recent research. At variance, the interest in the isostructural transition metal dihalide monolayers is yet comparatively low. Only a few studies have been conducted to explore such species in a systematic way. [1,2]

In this study, we use periodic DFT methods at both LDA and GGA level to investigate, which combinations of 3*d*-transition metal and halide anion can form stable structures that may eventually be synthesized, and try to predict their electronic properties.

A somewhat surprising finding is that the valence isoelectronicity principle seems to only hold partially here: MX_2 monolayers formed by the same metal but different halide anions seem to have different ground state electronic structures with differing magnetic moments. In addition, we see that there are some differences between the electronic structures predicted by LDA and GGA calculations. Both findings are associated with differences in the relative stability between high spin and low spin states. We will try to illustrate that, despite the differences between the LDA and GGA data, the results obtained with the two types of functionals follow the same trend.

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Rapid, accurate, precise and reliable relative free energy prediction using ensemble based thermodynamic integration

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The accurate prediction of the binding affinities of ligands to proteins is a major goal in drug discovery and personalised medicine. The use of *in silico* methods to predict binding affinities has been largely confined to academic research until recently, primarily due to the lack of their reproducibility, as well as lack of accuracy and time to solution. In the last few years, an ensemble based molecular dynamics approach, called ESMACS, has been proposed that provides a route to reliable predictions of free energies meeting the requirements of speed, accuracy, precision and reliability.[1-3] Here, we describe our approach to thermodynamic integration, known as TIES, which substantially improves the speed, accuracy, precision and reliability of calculated relative binding free energies.[4] We report the performance of TIES when applied to a diverse set of protein targets and ligands. The results are in very good agreement with experimental data (90% of the predictions agree to within 1 kcal/mol) while the method is reproducible by construction. Statistical uncertainties of the order of 0.5 kcal/mol or less are achieved. Work is ongoing to extend the application of TIES to calculate the relative binding affinites of protein mutations (TIES_PM). This methodology, which is being pursued in the CompBioMed Centre of Excellence (http://www.compbiomed.eu/), has the potential to positively impact the drug design process in the pharmaceutical domain as well as in personalised medicine, with concomitant major industrial and societal impact. TIES is an automated workflow that can be completely run in 8 hours or less, depending on the architecture and hardware available. To exhibit this feature as well as the excellent scalability of TIES, in an unprecedented study we harnessed the combined power of Phases 1 and 2 of PRACE's Tier-0 SuperMUC at the Leibniz Rechnzentrum in Garching, resulting in accurate relative binding affinity predictions of more than 50 biomolecular systems[5] at a sustained performance in excess of 1 petasflop throughout.

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Molecular Modeling, Docking, NBO, and Vibrational Studies of New α-aminophosphonates as Antitumor Agents Targeting MCF7

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The quantum chemical calculations are performed using density functional theory (DFT) to study the effect of the molecular and electronic structures on the biological activity of the investigated compounds. A novel series of Diphenyl (aryl) (4-oxo-quinazolin-4(3H)-ylamino) methyl phosphonates 3a-3d is obtained from the reactions of 3-amino-4(3H)-quinazolinone with different aromatic aldehydes and triphenylphosphite in the presence of copper triflate as a Lewis acid catalyst. The calculations show that the electron-withdrawing substituent increases the biological activity of the α-aminophosphonates more than the electron donating group which was in a good agreement with the experimental results. Also, a good agreement between the experimental FT-IR and the calculated one was found. From NBO study, the sum of the total values of stabilization energies E (2) for compound 3b are much greater than those of compound 3c which leads to increase the conjugated interaction in compound 3b and reduced the gap energy which shifts the absorption wave length near IR region and thus enhances the efficiency of compound 3b as photocurrent compound. The molecular docking simulation is done to show the mode of interaction between the studied molecules and MCF7-cell line.

The Master Factors Influencing the Potency of BACE-1 Alzheimer Inhibitors: Computational & Molecular Docking Studies

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Density functional theory (B3LYP/6-31G (d)) is performed to study the effect of molecular and electronic structures of the investigated BACE-1 Alzheimer inhibitors on their biological activities and discuss the correlation between their inhibition efficiencies and quantum chemical descriptors. IC_{50} values of the investigated compounds are mostly affected by the substituted R_2 Phenyl (S_2) moiety. The calculations show that the presence of electron withdrawing group increases the biological activity. SAR studies show that the electronic descriptors, E_{HOMO}, ΔE, lipophilicity, hardness and ionization potential index, are the most significant descriptors for the correlation with the biological activity. Molecular docking simulation is performed to explain the mode of interaction between the most potent drug and the binding sites of BACE-1 target. A good correlation between the experimental and theoretical data confirms that the quantum chemical methods are successful tools for the discovery of novel BACE-1drugs.

Maximum Probability Domains: Theoretical Foundations and Computational Algorithms

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The Lewis model of the chemical bond treats electrons as discrete pairs, localized in a certain region of space. On the other hand, the molecular orbital approach to quantum chemistry considers electrons as delocalized over the entire space. Many new ways to extract Lewis-structural information from the wave function have been suggested, providing links between quantum and traditional chemistry.

One of these novel approaches is the use of maximum probability domains (MPDs) [1, 2]. This method statistically localizes electrons in domains, by determining those regions of spin-position space for which the probability of finding a given number of electrons is maximal. This method has successfully been applied to interpret covalent and ionic bonding [3, 4]. However, MPDs have not yet been characterized by other chemical descriptors, which leaves their links with other conceptual quantities ill described. Furthermore, MPDs obtained from current implementations suffer from numerical inaccuracy, which clouds their properties [5].

In this poster, I will introduce the theory of MPDs, extend it with novel concepts and novel algorithms [6]. I will show how this theory can be applied to a range of chemical phenomena, and how this interpretation can lead to increased chemical understanding.

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DFT studies on Catalytic CO_2 fixation by Monoethanolamine

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The theoretical investigation of catalytic carbon dioxide (CO_2) fixation by monoethanolamine (MEA) was performed at the M06-2X/6-31+g(d,p) level to explore its reaction mechanism. The calculation results demonstrated that the most favorable pathway initially started with the nucleophilic addition of MEA on CO_2, followed by proton transfer aided by the extra MEA to form carbamate ion and then carbamic acid. The carbamate ion could absorb another CO_2 and render MEA back for further CO_2 capture. However, this process could be harmed by the formation of 2-oxazolidone. Thus, the kinetic of 2-oxazolione formation was also studied. Noticeably, thermodynamic control plays a major role to precede the reaction, which proves that 2-oxazolidone cannot take place. The degradation of MEA must proceed through another mechanism.

Tunneling of hydrogen transfer reactions on and in interstellar ices

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The darkness readily observed between the stars on a clear nightsky is far from empty. The low temperatures (T = 10 − 20 K) in so-called dark molecular clouds in combination with the typical low particle densities (n = 10^4 cm^{-3}) make it seem unlikely for chemistry to take place efficiently. The chemistry that occurs can be partly explained by the presence of small ice-coated dust grains on which molecules freeze out. These grains thus act as a molecule reservoir, while also being an energy sink for exothermic reactions. Barriers at cryogenic temperatures can only be overcome, however, when tunneling is invoked as a crucial component of the reaction mechanism. Hydrogen is the most abundant element in the interstellar medium and many surface reactions involve hydrogen transfers, ultimately leading to the formation of saturated species such as H_2O, CH_3OH, C_2H_6 [1]. Therefore, tunneling can also affect the deuterium fractionation, *i.e.*, the D/H ratio, of the products [2].
Rate constants for tunneled reactions are calculated through instanton theory, while the ice surface is taken into account via, *e.g.*, small clusters or multiscale modeling approaches (QM/MM). We elaborate on the influence of an ice environment on reaction rate constants, how and when an ice can be approximated without taking into account all degrees of freedom, and how the rate constants are to be interpreted in the light of astrochemical mean-field models and observations.

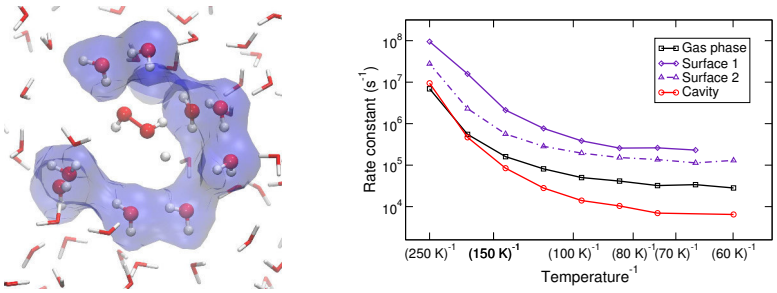

Figure 1: Left: QM/MM setup of the reaction between H and H_2O_2 inside a cavity in an amorphous ice; solid spheres indicate the QM atoms. Right: Unimolecular rate constants of the same reaction in the gas phase, on a surface, and in the cavity.

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Proton collisions on prebiotic candidates: HCN oligomers

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Among the complex organic molecules detected in space, in the interstellar medium, on meteorites or comets, special interest is devoted to the potentially exobiologic-relevant species. In the hypothesis, widely discussed, of a possible exogen origin of life, the transport of such compounds and their survival, particularly their resistance to the solar UV radiation or cosmic rays is indeed a fundamental question. Hydrogen cyanide has been detected for a long time in the interstellar medium, planetary atmospheres and even comets and appears as a feedstock molecule at the origin of life. Its easy oligomerization drives strong interest on its first polymers, cyanomethanimine and aminomalononitrile, furthermore that the E-cyanomethanimine has been detected recently in the star-forming region Sgr B2(N). We have thus undertaken a detailed theoretical study of the charge transfer collision dynamics induced by impact of HCN dimers and trimers with protons, which could be an important process in particular in proton-rich environments [1]. The present results are compared to previous studies on proton-induced damage on different prebiotic compounds, 2-aminooxazole and hydantoin, as well as DNA and RNA building blocks, nucleobases and sugar 2-deoxy-D-ribose moiety [2,3], in order to analyse the behaviour of these different possible precursors and extract some qualitative trends on damage of prebiotic species under spatial radiation.

The theoretical treatment has been developed through *ab-initio* quantum chemistry molecular calculations followed by a semiclassical collision dynamics. With regard to the various temperatures of astrophysical environments, the calculations have been carried out in a wide collision energy range. The conformational effect could be also evidenced. The charge transfer appears more efficient for these non-cyclic species than previously observed for species with a planar ring. This might induce a highest resistance in proton-induced collisions for HCN oligomers, or even for the 2-deoxy-D-ribose in its furanose form (non-planar 5-membered ring) compared to nucleobases or prebiotic compounds as 2-aminooxazole or hydantoin constructed on a planar ring. This might point out a possible sensitivity relied to the geometry of the ring. Such conclusions have however to be handled with care as they consider only reactions in the gas phase as shown by calculations considering solute-solvent interactions with a controlled analysis of water clusters [4]. Further developments are in progress.

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Active Site Protonation and the Reactivation of Acetylcholine Esterase

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Organophosphorus compounds such as Tabun, VX or sarin, are highly potent neurotoxins that target the enzyme acetylcholine esterase (AChE). This enzyme is a member of the serine protease family, with a major role in neurotransmission. When AChE is inhibited, cholinergic synapses are overactivated, leading to either death by respiratory system failure, or permanent and severe neurological conditions. Since AChE inhibitors are covalently linked to one of the key residues of the active site, reversibility is not spontaneous. Current strategies for reactivation are therefore based on strong nucleophiles [1] but show limited applicability despite decades of research in this area.

A few years ago, our group demonstrated that the inhibition mechanism could be more complex than previously envisaged [2], due to hydrophobic interactions and a network of hydrogen bonds. Thus, when the reactivation simulation project was started, careful attention was devoted to the protonation of key active site residues. By using highly correlated QM/MM calculations (Figure 1), it was shown that the key parameter for reactivation is not nucleophilicity of the reactivator but its acid/base properties in the active site [3]. On this basis, as well as new work using free energy reactive molecular dynamics, a novel mechanism of reactivation that maintains the protonation state of key active site residues that does not rely on the main entrance channel will be shown.

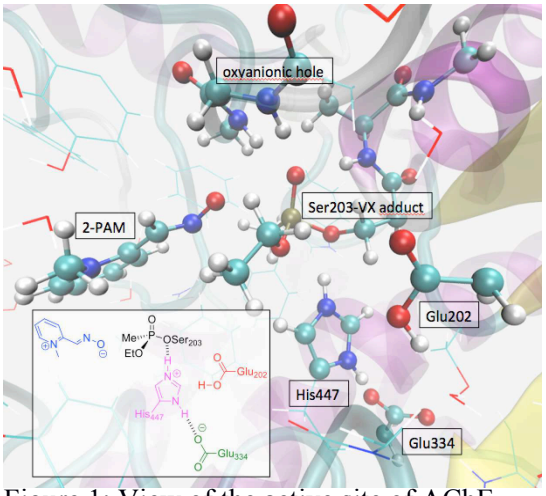

Figure 1: View of the active site of AChE, inhibited by an organophosphorous and in presence of a common reactivator (2-PAM).

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Splitting the Coulomb Hole into its Dynamic and Nondynamic parts

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The account of electron correlation in quantum calculations is a most important challenge in current computational chemistry. Whereas the dynamic part of electron correlation accounts for the interactions due to the movement of the electrons, the nondynamic correlation is important in systems where the ground state cannot be described by a single determinant.

The wavefunction includes information regarding electron-electron interactions. However, it becomes more intuitive to use the pair probability (or reduced two-electron density matrix). The intracule density [1], a contraction of the pair probability, is the probability function for the interelectronic vector that retains the information of electron correlation, but with the advantage of working with funtions of lower dimensionality.

The introduction of electron correlation decreases the probability of finding two electrons close to each other, and in turn the probability of finding them in longer interelectronic distances increases. This consequence of electron repulsion can be easily assessed by means of the Coulomb hole, defined as the difference between the exact or FCI (correlated reference) intracule and the HF (uncorrelated reference) intracule densities [2]. In our approach, we use the Hartree-Fock-like (HFL) density matrix functional as a qualitative separator between the dynamic and nondynamic correlation parts [3].

In this context, a systematic study over a group of diverse diatomic molecules has been performed with the aim to assess the magnitude of the electron correlation, and to reveal the nature of the type of correlation present in the molecule.

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Protein Oxidation mechanisms via OH radical

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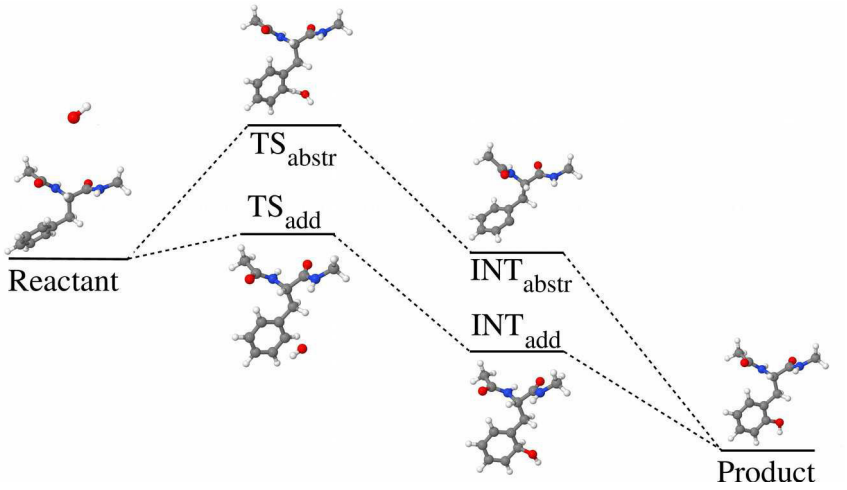
Proteins perform a wide variety of essential tasks in an organism. However, their oxidation is an unavoidable process which could render structural changes or even enzyme inactivation. In this sense, the main responsible for such oxidation event are reactive species, chemically unstable species which promote oxidation. Those species are accidentally formed from time to time and have been related to aging [1]. Carbonyl groups are common oxidized products, usually employed as markers to reveal the oxidation level. On the other hand, protein oxidation yield selective backbone cleavage which is applied in sequencing.

Overall, protein oxidation is of great interest, due to the consequences that brings to the macromolecule and its possible applications. In essence, this work is devoted to the understanding of the oxidation reaction involving the hydroxyl radical (·OH) and proteins. Different reaction mechanisms were systematically analyzed with the purpose of ranking the most vulnerable locations at the side chains. Moreover, possible oxidized products are considered and discussed as well as their relevance.



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QM/MM Investigation of Structure–Spectroscopy Correlations in the Intermediate Q of Soluble Methane Monooxygenase

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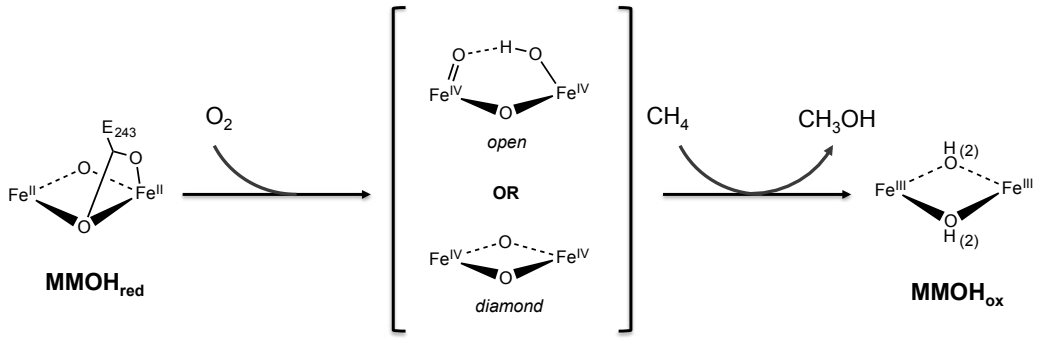
In nature methanol is produced by methane monooxygenase, a metalloenzyme expressed with a dicopper core as a membrane protein or, in case of copper deficiency, with a diiron core as soluble methane monooxygenase (sMMO). Although several catalytic intermediates have been identified spectroscopically, the electronic structure of the reactive intermediate Q formed in the final step before binding and activation of methane remains under debate. There is contradictory support for either a diamond (bis-μ-oxo) or an open (μ-oxo) core[1] from different spectroscopic techniques and computational studies, with the diamond core being favored so far. However, new spectroscopic studies[2] furnish evidence in favor of an open core structure, which would be more consistent with the fact that biomimetic model complexes with an open core motif show higher activity in methanol production.[3] Here we revisit the active site of sMMO with an updated set of models and spectroscopy-oriented quantum chemical calculations to provide an experimentally consistent interpretation of the electronic and geometric structure of intermediate Q.



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Reaction Mechanism of Hydrogermylation/Hydrostannylation of Unactivated Alkenes with Two-Coordinate E^{II} Hydrides (E = Ge, Sn)

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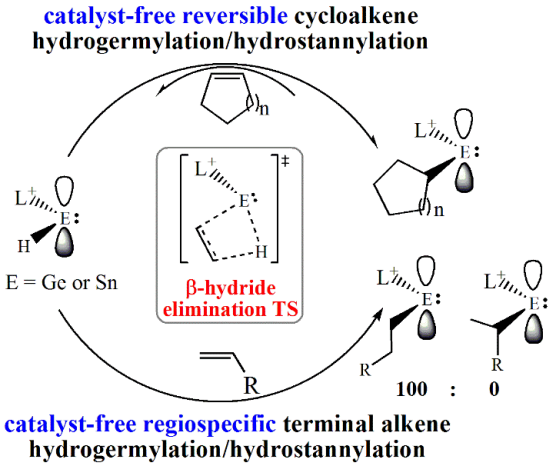
Abstract: Quantum chemical studies have been performed to elucidate the mechanism of the catalyst-free hydrometallation reactions between two-coordinate hydrido-tetrylenes :E(H)(L^+) (E = Ge, Sn) and a range of unactivated terminal and cyclic alkenes. The calculations suggest that the addition reactions of the germylene and stannylenes to the cyclic and acylic alkenes occur as one-step processes via formal [2+2] addition of the E-H fragment across the C-C π bond. The reactions have moderate barriers and are weakly exergonic. The steric bulk of the tetrylene amido groups has little influence on the activation barriers and on the reaction energies of the anti-Markovnikov pathway, but the Markovnikov addition is clearly disfavored by the size of the substituents. The addition of the tetrylenes to the cyclic alkenes is less exergonic than the addition to the terminal alkenes, which agrees with the experimentally observed reversibility of the former reactions. EDA-NOCV analysis of the transition state for the hydrogermylation of cyclohexene shows that the reaction takes place with simultaneous formation of the Ge-C and (Ge)H-C' bonds. The dominant orbitals of the germylene are the σ-type lone-pair MO of Ge which serves as donor orbital and the vacant p(π) MO of Ge which acts as acceptor orbital for the π* and π MOs of the olefin.



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Influence of Semiempirical Dispersion Correction on the DFT Description of Inorganic Layered Compounds: Alkaline-earth Fluorohalides (MFX)

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Alkaline-earth fluorohalides, MFX, have received a lot of attention in material and optical sciences owing to the remarkable photophysical and photochemical properties, which they can exhibit upon incorporation of photoactive rare-earth ions. The MFX host compounds crystallize in the tetragonal *P4/nmm* Matlockite structure: they exhibit a layered ionic structure which corresponds to a simple -F^- - M^{2+} - X^- - X^- - M^{2+} - F^- - stacking of the ion layers along the c axis (see Figure). Due to their layered structure and especially the presence of the anionic double layer, the description of the structures and properties of the MFX compounds within density functional theory (DFT) may suffer from the inaccurate description of the dispersion interactions, which can be observed with local, semilocal, and hybrid density functionals. This deficiency of standard approximate functionals could indeed explain the overestimation of the c parameter reported for PbFI. To investigate this question, periodic DFT calculations have been performed to study the crystal structures, mechanical and spectroscopic properties of the MFX compounds (M = Ca, Sr, Ba, Pb and X = Cl, Br, I). The PBE and B3LYP functionals and their DFT-D2 dispersion-corrected variants were employed. For these layered ionic compounds, it proved necessary to modify the semi-empirical D2 dispersion correction.

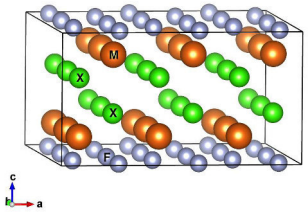

Figure 1: The tetragonal *P4/nmm* Matlockite structure of MFX alkaline-earth fluorohalides: 3 x 3 x 1 supercell showing the layer stacking.

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Investigation of Catalytic Dehydrocoupling of Dimethylamine-borane by Titanocene: A DFT and Topologic Study

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With the increasing demand of clean energy carriers, ammonia borane and its related amine borane (AB) compounds [1] have emerged as attractive candidates for potential hydrogen storage vectors. In this context, mechanistic studies for the catalyzed dehydrogenation/dehydrocoupling of amine-boranes and phosphine-boranes have seen a quick development over the last decade. [2] Inexpensive, environmentally friendly, easily synthesized and stable organometallic compounds that efficiently catalyze the reaction are worth studying.

The dehydrocoupling of $HMe_2N{\cdot}BH_3$ to form $[Me_2N{\cdot}BH_2]_2$ catalyzed by titanocene was investigated both experimentally [3, 4] and theoretically. [5] However, the exact mechanism of this reaction still remains uncertain. Theoretical studies based on DFT calculation and topological tools were used to characterize precisely the reaction pathway and 3-centre 2-electron (3C/2e) intermediates. The following aspects will be developed:

- The 3C/2e interactions between metallic centre and B-H σ bond are characterized in both intermolecular intermediates (σ complexes) and intramolecular ones (agostic complexes).
- The empirical dispersion correction (GD3BJ) is shown to yield structures and relative energies for the different reaction pathways, in better agreement with experimental observations.
- The solvation effect associated with different basis sets may be a remarkable parameter that influences the energetic properties of this kind of reaction. Further investigations should help in finding an inexpensive and highly-efficient catalyst.

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Optimal Faujasite structures for post combustion CO_2 capture in swing adsorption processes

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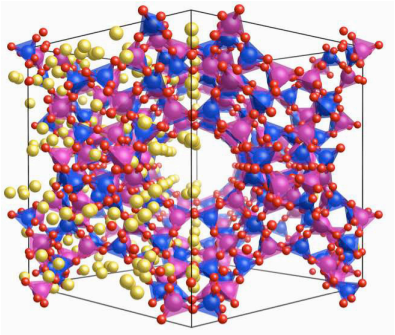
Carbon dioxide is the primary greenhouse gas generated by human activities, mainly from the combustion of fossil fuels for energy and transportation. Despite the development of alternative renewable energy sources, fossil fuels still dominate in almost all near future projections [1]. Therefore, many efforts have been addressed to the development of cost-efficient technologies for separation and capture of carbon dioxide. Solid adsorbents like zeolites or metal-organic frameworks are promising candidates [2].

In the present work, Grand Canonical Monte-Carlo (GCMC) simulations are used to assess optimum faujasite structures, the well-known family of zeolites, in CO_2 capture processes. Pressure Swing Adsorption (PSA), Vacuum Swing Adsorption (VSA) and Temperature Swing Adsorption (TSA) procedures have been considered to evaluate purity, selectivity, working capacity and isosteric heat in ten faujasite structures with different Al content. Results indicate that faujasites with high Al content are the most effective for TSA whereas intermediate Al content structures perform better at VSA conditions and ultimately, low Al content faujasites are more suitable for PSA process [3].



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Ni-Phosphine Bond Strengthening Trough Coordination of the Strong σ-Donors ECp* (E= Al, Ga)

J. Hornung[1], J. Weßing[1], P. Jerabek[2], G. Frenking [3], C. Gemel[1], R. A. Fischer[1]

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The coordination chemistry of low valent group 13 ligands ECp* (E=Al, Ga, In Cp* = Pentamethylcyclopentadienyl) has been investigated intensively in the past 20 years, both theoretically and experimentally.[1] A large variety of heteroleptic complexes and clusters $[TM_a(ECp^*)_b(L)_c]$ (TM = transition metal; L=2 electron donor ligand, e.g.: PR_3, CO, hydride…) have been investigated.[2] Most of these heterobimetallic compounds exhibit an 18VE count on the transition metal. However, in the chemistry of these molecules, low-coordinated $TM(ECp^*)_n$-fragments play a crucial role, especially in the activation of strong bonds (C-H, C-C, Si-H), but also in the formation of higher nuclear clusters.[2]

We present the first systematic investigation about the in-situ formation of unsaturated bimetallic transition metal/group 13 metal complexes through experimental and computational methods. For this investigation, the series $[Ni(ECp^*)_a(PR_3)_{4-a}]$ (a=0-3) has been chosen as a model system. Complexes of this type are synthetically easily accessible by simple substitution reactions from $Ni(cod)_2$ (cod = 1,5-cyclooctadiene) and are thermally very robust and stable. Phosphine dissociation has been investigated experimentally by variable temperature UV-Vis-spectroscopy as well as computationally by energy decomposition analysis (EDA) with the natural orbital for chemical valence extension (NOCV). In accordance with the experimental results, the Ni-phosphine interaction energy increases with increasing number of ECp* ligands. Closer investigations show that this can be related to an increase in electrostatic interactions introduced by Ni-P bond polarization by ECp* ligands.

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Effects of Interphase Region on Glass Transition Temperature of Grafted Carbon Nanotubes Reinforced Epoxy Composites

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Abstract: Carbon nanotubes (CNTs) have been widely used to modify glass transition temperatures (T_gs) of polymers, due to their outstanding mechanical properties, as well as long aspect ratios and high surface areas [1-3]. Researchers have found that T_gs of the composites were affected dramatically by the interphase, while there still appeared to be lack of an agreement on how the interphase works.

In this work, in order to verify roles of interphase played in T_gs of CNT/epoxy composites, three types of interphase were produced between the carbon nanotubes (CNTs) and the cured epoxy resin matrix. It was achieved by selection of pristine CNTs (p-CNTs), amino groups grafted CNTs (NH_2-CNTs) and hydroxyl groups grafted CNTs (OH-CNTs) as the reinforcement, respectively. Molecular dynamics (MD) simulations were conducted to study T_gs of the CNT/epoxy composites. For the simulation, p-CNTs and OH-CNTs reinforced epoxy composites were constructed separately, where the CNTs were not covalent bonded to the epoxy resin matrix. In the NH_2-CNT/epoxy composites, two kinds of interphases between the amino groups in CNTs and the epoxy resin matrix were constructed, namely, with or without covalent bonds. The MD simulation results showed that T_gs of NH_2-CNT/epoxy composites with covalent bonds increased, while T_gs of OH-CNT/epoxy composites and NH_2-CNT/epoxy composites without covalent bonds decreased, compared with p-CNT/epoxy composites. The simulation results were also consistent with the dynamic mechanical analysis (DMA) results, which were also conducted in this work. Effects of interphases on T_gs of the CNT/epoxy composites were further explained by the MD simulations through investigating the microstructures of the CNT/epoxy composites. T_gs of the NH_2-CNT/epoxy composites increased with the formation of covalent bonds, while the interfacial interactions between the NH_2-CNTs and the epoxy resin matrix were enhanced. It could be indicated from the highest total interaction energy between the CNTs and the cured epoxy matrix, the lowest mean square displacement values of atoms in the matrix. While T_gs of the OH-CNT/epoxy composites decreased due to the weak interfacial interactions, where no such covalent bonds were formed. It can be inferred that the covalent bonds between the CNTs and the polymer matrix are beneficial and critical to increase T_gs of the CNT/polymer composites.

DLPNO-CCSD(T) Scaled Methods for the Accurate Treatment of Large Supramolecular Complexes

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The theoretical description of supramolecular complexes requires the use of accurate and cost-effective quantum-chemical methods to account for noncovalent interactions (NCI) in a balanced way. Over the last years, the development of novel theoretical approaches has led to methodologies showing an unprecedented degree of accuracy in the context of NCIs. The efficient domain-based local pair-natural orbital (DLPNO) approach developed by Neese *et at.*[1] has recently been coupled to the CCSD(T) method, offering a quantum-chemical method, dubbed as DLPNO-CCSD(T), that exhibits the high accuracy of the semicanonical CCSD(T) but with a significantly reduced computational cost. However, stringent thresholds such as in the TightPNO setup are required for the accurate treatment of NCIs.

Herein, we present scaled variants of the DLPNO-CCSD(T) method, dubbed as (LS)DLPNO-CCSD(T) and (NS)DLPNO-CCSD(T), to obtain accurate interaction energies in supramolecular complexes governed by noncovalent interactions.[3] The scaled DLPNO-CCSD(T) variants provide nearly TightPNO accuracy, which is essential for the quantification of weak noncovalent interactions, with a noticeable saving in computational cost. The new protocols have been used to study the role of CH–π *versus* π–π interactions in the supramolecular complex formed by the electron-donor truxene-tetrathiafulvalene (truxTTF) and the electron-acceptor hemifullerene ($C_{30}H_{12}$). (NS)DLPNO-CCSD(T)/CBS calculations reveal the higher stability of staggered (dominated by CH–π interactions) *versus* bowl-in-bowl (dominated by π–π interactions) arrangements in the truxTTF•$C_{30}H_{12}$ heterodimer. Hemifullerene and similar carbon-based buckybowls are therefore expected to self-assemble with donor compounds in a richer way other than the typical concave–convex π–π arrangement found in fullerene-based aggregates.

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The molecular mechanism of ligand unbinding from the human telomeric G-quadruplex

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Abstract:

G-quadruplexes become attractive drug targets in cancer therapy recently. The proposition of new drugs for the G-quadruplexes is essential to understanding the specific interactions between the ligand and receptor and to the underlying mechanisms of the binding–unbinding processes involving biomolecules and molecular recognition. In this study, we have investigated the mechanical properties and kinetic pathways of the ligands (BMVC and BMVC0) unbinding from the G-quadruplex by using steered molecular dynamics and umbrella sampling simulations. Based on the structural analyses and the PMF calculations, we have shown detailed atomistic insights and relevant free energies involved in the unbinding processes, which have not been determined in ensemble assays. These results could help to identify accessible binding sites and transient interactions. The simulations for both these ligands clearly reflect their distinct rupture force and PMF profiles, which can be correlated with G-quadruplex–ligand binding affinities, suggesting that this protocol could be applied to other G-quadruplex ligands to assess their robustness and rank a series of derivatives with similar potencies. On the other hand, the dynamics of the hydration shell water molecules around the G-quadruplex exhibits an abnormal Brownian motion, and the thickness and free energy of the hydration shell were estimated. A two-step relaxation scheme was theoretically developed to describe the kinetic reaction of BMVC and G-quadruplex interactions. Our findings confirm the seminal experimental data, highlighting the importance of using computer-based simulations to predict and complement experiments. This demonstration of simulations combined with theoretical analyses is valuable for further investigations on various G-quadruplex systems and could be helpful in structure-based drug design.

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Mechanically Controlled Electron Transfer in a Single-Polypeptide Transistor

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Abstract:

Proteins are of interest in nano-bio electronic devices due to their versatile structures, exquisite functionality and specificity. However, quantum transport measurements produce conflicting results due to technical limitations whereby it is difficult to precisely determine molecular orientation, the nature of the moieties, the presence of the surroundings and the temperature; in such circumstances a better understanding of the protein electron transfer (ET) pathway and the mechanism remains a considerable challenge. Here, we report an approach to mechanically drive polypeptide flip-flop motion to achieve a logic gate with ON and OFF states during protein ET. We have calculated the transmission spectra of the peptide-based molecular junctions and observed the hallmarks of electrical current and conductance. The results indicate that peptide ET follows an NC asymmetric process and depends on the amino acid chirality and α-helical handedness. Electron transmission decreases as the number of water molecules increases, and the ET efficiency and its pathway depend on the type of water-bridged H-bonds. Our results provide a rational mechanism for peptide ET and new perspectives on polypeptides as potential candidates in logic nano devices.

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DFT Study of the Selectivity of DOPA-decarboxylase

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Abstract: L-DOPA is commonly used as a xenobiotic for patients with conditions such as Parkinson's disease. Clinically administered L-DOPA is transformed into dopamine by DOPA-decarboxylase. In order to be pharmacologically effective, L-DOPA must not be metabolized before it crosses the blood brain barrier. In order to prevent premature metabolism, DOPA-decarboxylase may be inhibited in the periphery. By selectively designing an inhibitor for the DOPA-decarboxylase enzyme, the effectiveness of the L-DOPA can be extended. A suite of dopaminergic derivatives have been developed as potential inhibitors of the DOPA-decarboxylase enzyme. The inhibitory effectiveness of these dopaminergic derivatives has been measured via in silico models in which the strength of interaction between each substrate and the enzymatic active site was analyzed. A crystal-structure of the DOPA-decarboxylase active site, docked with a known DOPA-decarboxylase inhibitor, Carbidopa, was isolated from the Protein Data Bank (PDB ID: 1JS3). The positions of novel dopaminergic derivatives were optimized in the active site using M062X/6-31G with implicit solvation and with flexible amino acid side-chains. Interaction energies between the ligands and the protein were calculated using M062X and MP2 with the 6- 311+G* basis set. At present, 6-nitrodopamine appears to be an effective competitive inhibitor of the DOPA-decarboxylase enzyme.

DFT Study of the Selectivity of Monoamine Oxidase B (MAOB)

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Abstract: MAOB is an enzyme located on the outer mitochondria that is responsible for degrading penylethylamine, benzylamine, and dopamine. MAOB inhibitors are generally used as a treatment for Parkinson's disease because they stop the breakdown of dopamine. By selectively designing an inhibitor for the MAOB enzyme, the breakdown of dopamine can be reduced leading to an increase of the neurotransmitter. A suite of dopaminergic derivatives have been developed as potential inhibitors of the MAOB enzyme. The inhibitory effectiveness of these dopaminergic derivatives has been measured via in silico models in which the strength of interaction between each substrate and the enzymatic active site was analyzed. A crystal-structure of the MAOB active site, docked with the widely employed diabetes drug pioglitazone, was isolated from the Protein Data Bank (PDB ID: 4A79). The positions of novel dopaminergic derivatives were optimized in the active site using M062X/6-31G with implicit solvation and with relaxed amino acid side-chains. Interaction energies between the ligands and the protein were calculated using M062X and MP2 with the 6- 311+G* basis set. At present, we have designed novel inhibitors that bind much stronger than dopamine.

Design of novel inhibitors for the aldehyde dehydrogenases I: Left Orientation

Caroline Magee, Emma Selner, Larryn Peterson, Mauricio Cafiero

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Abstract: L-DOPA is commonly used as a xenobiotic for patients with conditions such as Parkinson's disease. L-DOPA is transformed into dopamine by DOPA-decarboxylase. Dopamine derived from L-DOPA is deactivated via metabolism by a series of enzymes including Aldehyde dehydrogenases (ALDH). The targeted inhibition of the ALDH enzyme may help to prolong the effectiveness of L-DOPA, resulting in a net increase in pharmacological efficiency. By selectively designing an inhibitor for ALDH, the effectiveness of the L-DOPA can be extended by regulating the metabolism of dopamine derived from L-DOPA. The effectiveness of a series of potential inhibitors has been measured via *in silico* models in which the strength of interaction between each substrate and the enzymatic active site was analyzed. A crystal-structure of the ALDH enzyme with an inhibitor bound in its active site (PDB ID: 4WP7) was used to create a model of the active site. Novel dopaminergic derivatives were optimized in the active site using M062X/6-31G with implicit solvation and with relaxed amino acid side-chains. Ligands can fit into the active site in a number of ways; in this work we examine the left orientation of the molecules. Interaction energies between the ligands and the protein were calculated using MO62X with the 6-311+G* basis set. Some potential inhibitors show promising results. Mutant enzymes were also studied for their affinity for the ligands.

DFT analysis of the selectivity of Phenylalanine Hydroxylase

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Abstract: There are many molecules that act on dopamine and dopamine-like binding sites in enzymes and transport proteins. Some effects of these proteins are beneficial while others are detrimental. We are designing inhibitors for this group of proteins. Phenylalanine hydroxylase (PheOH) is a tetradydrobiopterin-dependent monooxygenase that influences the rate determining step of converting phenylalanine into tryrosine by hydroxylating phenylalanine. Both phenylalanine and tyrosine are important components in the anabolism of dopamine. A deficiency of PheOH can cause hyperphenylalaninemia, which gives rise to phenylketonuria (PKU), a severe disease that can cause mental retardation if one's diet isn't strictly monitored. A suite of dopaminergic derivatives has been developed as potential inhibitors of the PheOH enzyme. The inhibitory effectiveness of these dopaminergic derivatives has been measured via in silico models in which the strength of interaction between each substrate and the enzymatic active site was analyzed. A crystal-structure of the PheOH active site, with bound thienylalanine, was isolated from the Protein Data Bank (PDB ID: 1KW0). The positions of novel dopaminergic derivatives were optimized in the active site using M062X/6-31G with implicit solvation and with flexible amino acid side-chains. Interaction energies between the ligands and the protein were calculated using M062X and MP2 with the 6- 311+G* basis set. At present, none of the potential inhibitors examined interact as strongly as the natural substrate phenylalanine.

Electron Transfer in Organic and Biological Materials

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Charge transfer processes are ubiquitous taking a prominent role in biology and material science. While experiments give valuable information on certain kinetic and thermodynamic properties of charge transfer events, they usually do not offer a molecular-level insight into these phenomena. Adequate simulations can bridge the gap between microscopic processes and macroscopic charge transports. For instance, a combination of Marcus theory, classical molecular simulation and master equation formalism can estimate complex charge transfer processes involving multiple redox sites in large systems [1]. But such rate-based approaches usually only work for localized charge carriers and in situations where the charge transfer is slow compared to the molecular motions that couple to the charge transfer. To surpass these limitations, we have recently implemented a fast non-adiabatic molecular dynamics approach (based on Tully's surface hopping) where the wavefunction of the charge carrier is explicitly propagated in the time-dependent potential created by (classical) nuclear motion [2,3]. First applications to hole transfer in the ethylene dimer successfully reproduced exact results from the theory [3] and applications to a chain of ethylene molecules successfully predicted a crossover from activated to band-like transport [2]. Here we present a new implementation of the method into the CP2K software that enables us to model fast charge transfer in larger, application relevant organic crystals consisting of thousands of atoms. We will present applications as well as a detailed analysis of the charge transfer mechanism predicted by our surface hopping approach.

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HYDROGEN ATOM ABSTRACTION FROM ETHANOL BY ATOMIC HYDROGEN IN AQUEOUS SOLUTION

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Hydrogen abstraction from ethanol by atomic hydrogen is a well-known reaction which is one of the most important steps in ethanol decomposition.[1] Depending on temperature this reaction can proceed via three different channels resulting in three different products. It has been shown that at room temperature this reaction goes through only one pathway, however, the reaction can proceed via two transition states (gauche (g) and trans (t)) which interconvert in each other by internal rotation.[2,3] Recent computational research over this reaction is based on continuum model of solvation. In this work we expand solvation model to test the effect of specific explicit solvation on predicted kinetic isotope effects (KIEs).

Different models of aqueous solution including continuum and explicit solvation have been applied. Pure quantum mechanical calculations were used for smaller models whereas hybrid QMMM calculations were used for larger models. Kinetic isotope effects (KIEs) have been calculated for all hydrogen atoms using various theoretical approaches such as multipath variational transition state theory (MP-VTST) and path integrals methods.[3,4,5] These methods allow incorporating quantum effects such as tunneling and recrossing for multiple reaction paths with thermal rate constants determination which are further used for kinetic isotope effects calculation. The influence of environment on the obtained isotopic fractionation has been also analyzed and discussed.

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Getting ion-protein interactions right in Molecular Dynamics simulations

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Ion-biomolecules interactions are ubiquitous and play a central role in a number of fundamental biological processes, from calcium signaling to insulin storage. However, assessing the interaction of ions with biomolecules is not easy, neither experimentally nor computationally, because of the complexity of the systems involved. Indeed, quantum descriptions are too expensive to allow the study of large systems, while solvation and pairing properties of divalent cations are poorly reproduced by standard classical force fields because of polarization and charge transfer effects.

Our goal is to improve the description of divalent cations in simulations and use it to tackle biologically relevant problems. Since there is surprisingly little data available about the interaction of non transition metal divalent cations (zinc, calcium, magnesium) with typical protein groups (acetate, histidine), our strategy is first to obtain reference data on small model systems. These simple systems are studied both with *ab initio* Molecular Dynamics simulations and neutron-scattering experiments and the results are used to develop a scaled charge description of the ions, which takes into account electronic polarization in a mean field way [1-2]. This strategy allows us to design an accurate and computationally cheap description for the studied divalent cations.

The obtained force field is applied to biologically relevant systems, such as the interaction of ions with the insulin molecule, and how this changes with the multimerization state of insulin (monomer, dimer, hexamer). This question is fundamental to better understand the role of ions in insulin storage in the ion-rich secretory granules, and critically depends on a proper description of ion-protein interactions.

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Design and synthesis of novel inhibitors for the Tyrosine Hydroxylase enzyme

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Catecholamines are responsible for the fight or flight response and can be attributed to many functions within the sympathetic nervous system. Tyrosine Hydroxylase is the rate determining enzyme in the synthesis of the catecholamine, dopamine. Tyrosine Hydroxylase converts tyrosine to L-DOPA, which is administered in the treatment of Parkinson's patients. The inhibition of Tyrosine Hydroxylase allows for less feedback inhibition from catecholamines, aiding dopamine production. A crystal structure of the active site of Tyrosine Hydroxylase with a known inhibitor bound was obtained from the protein data bank (PDB ID: 2TOH) [1]. In this work, dopaminergic derivatives were inserted into the enzymatic active site *in silico* in order to test the strength of the interactions between the substrate and active site, to determine if any of these derivatives could be effective inhibitors. These derivatives were optimized with implicit solvent with M062X/6-31G and relaxed amino acid side-chains. Interaction energies between the ligands and protein were determined using M06L and MP2 with the 6- 311+G* basis set. Results shows that some of our dopaminergic derivatives show promise as inhibitors for Tyrosine Hydroxylase.

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Tricoordinate boron as donor ligand: bonding and reactivity patterns in iron pincer complexes

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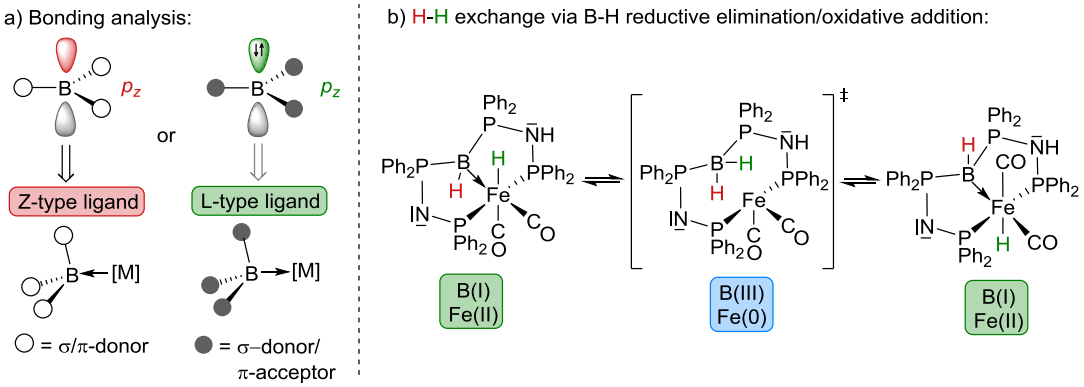
Tricoordinate boron compounds usually behave as Lewis acids, owing to their vacant p_z-orbital. If employed in transition metal complexes, they then function as electron-accepting (Z-type) ligands. Nonetheless, effort has been made recently to synthesize nucleophilic boron compounds.[1-3] This becomes possible with strong π-accepting substituents on boron, which stabilize the filled p_z-orbital. If used as ligands, these boron-compounds serve as electron-donating (L-type) ligands.

In this work we investigated an iron-PBP-pincer complex with a tricoordinate boron atom as a ligand.[4] Different methods of bonding analysis revealed that the boron atom acts as an electron-donating ligand, although it is only stabilized by phosphines. Experimental X-ray and NMR data supports this result.

The complex also shows an intramolecular H-H exchange. Possible exchange pathways were investigated with a combination of kinetic measurements and DFT calculations. A reversible reductive B-H elimination was identified as the present mechanism. (De)protonation of the ligand backbone strongly influences the exchange process, which is explained by the different stabilities of the involved species.



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Design of novel inhibitors for the aldehyde dehydrogenases I: Left Orientation

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Abstract: L-DOPA is commonly used as a xenobiotic for patients with conditions such as Parkinson's disease. L-DOPA is transformed into dopamine by DOPA-decarboxylase. Dopamine derived from L-DOPA is deactivated via metabolism by a series of enzymes including Aldehyde dehydrogenases (ALDH). The targeted inhibition of the ALDH enzyme may help to prolong the effectiveness of L-DOPA, resulting in a net increase in pharmacological efficiency. By selectively designing an inhibitor for ALDH, the effectiveness of the L-DOPA can be extended by regulating the metabolism of dopamine derived from L-DOPA. The effectiveness of a series of potential inhibitors has been measured via *in silico* models in which the strength of interaction between each substrate and the enzymatic active site was analyzed. A crystal-structure of the ALDH enzyme with an inhibitor bound in its active site (PDB ID: 4WP7) was used to create a model of the active site. Novel dopaminergic derivatives were optimized in the active site using M062X/6-31G with implicit solvation and with relaxed amino acid side-chains. Ligands can fit into the active site in a number of ways; in this work we examine the left orientation of the molecules. Interaction energies between the ligands and the protein were calculated using MO62X with the 6-311+G* basis set. Some potential inhibitors show promising results. Mutant enzymes were also studied for their affinity for the ligands.

How many water molecules does it take to dissociate the hydrogen halides?

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How many water molecules does it take to dissociate an acid? To answer this question, we systematically explored the potential energy surfaces of the hydrogen halides (HX, X= F, Cl, Br, and I) with up to seven water molecules using a modified kick algorithm called *Bilatu* [1] and Density Functional Theory (DFT) computations. The discussions are based on the B2PLYPD3/def2-TZVP results. Our conclusions indicate that hydrogen fluoride is partially dissociated with up to seven water molecules. Whereas, on the basis of ZPE-corrected electronic energies, the number of water molecules needed for HCl dissociation is four, in agreement with other reports. [2,3] However, on the basis of Gibbs free energies computed at room temperature, this number is five due to the inclusion of entropic factors. [4]. Finally, HBr and HI dissociate in the presence of four and three water molecules, respectively. Such decrease in the number of water molecules is related to the electronegativity of the halogen, and to their acidic strengths in aqueous solutions. The interactions which stabilize the clusters are: water–water and HX–water hydrogen bonds, ionic and long range X···H interactions, as well as microsolvation of H_3O^+ in the form of Eigen, quasi-Eigen cations and intermediate Zundel-Eigen-type structures. We carried out an analysis of bonding based on Wiberg Index, average dipole moments, [5] and O··· HX and H-X distances collected in Stern-Limbach plots. [6] The results provide a classification of clusters according to their non–, partially– and fully–dissociated character of the H–X bond which periodic trends are observed.

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The Reactivity of the α-O in Fe-Zeolites: a Mulitreference Aproach.

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The current commercial method to produce methanol involves a two steps procedure using syn gas and is rather energy intensive[1, 2]. Finding a direct way to oxidize methane to methanol would make this process more economical and environmentally friendly. In this respect, Fe-containing zeolites have drawn the attention of many scientists as they are able to oxidize methane to methanol under ambient conditions[3]. Only recently, the structure of the reactive intermediates in these zeolites has been ellucidated using VTVH-MCD spectroscopy and quantum chemical calculations [4]. The reactive species, called α-O, is a high spin square pyramidal Fe(IV)=O moiety. This Fe(IV) core is a common motif in nonheme iron enzymes (NHE) and in man-made model complexes[5], however not all Fe(IV)=O are as reactive as the others. In this work the reactivity of the α-O core is investigated using multirefence ab initio calculations (CASSCF/CASPT2 and DMRG-SCF/DMRG-CASPT2). The calculations identified two low lying, thermally accessible ^5E excited states. Analysis of the CASSCF wavefunction shows that that the oxyl character in the ^5E states is much higher than in the ^5A ground state. Oxyl character of Fe(IV)=O is related to its reactivity in hydrogen atom transfer (HAT) [6], this therefore indicates that the ^5E states are more reactive than the ground state. Evaluation of the reaction path with DMRG-CASPT2 shows the involvement of the ^5E and therefore proves that this reactive state is involved in HAT. The remarkable reactivity of α-O in methane hydroxylation can thus be explained by the involvement of low lying excited states. These findings may guide scientist in the synthesis of new reactive catalyst for C-H bond activation.

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Ruthenium-Xantphos catalyzed olefin hydrogenation - How well does contemporary DFT predict experimentally observed energy spans?

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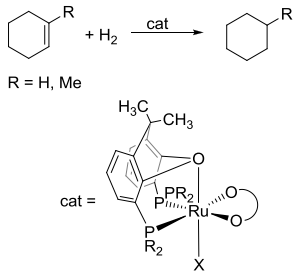
There is general consensus that DFT is the method of choice for the fast and reliable prediction of the structures of organometallic compounds. However, the use of predictive DFT computations prior to experimental work for the in-silico-design of catalyst structures has been hampered for many years by the fact that quantitative prediction of accurate overall activation barriers for typical organometallic reactions was not reliably possible. In this context the past decade has witnessed an impressive improvement with regard to the quantitative accuracy of contemporary DFT computations.[1-4] Accordingly, the question arises if DFT computations can be used for predictive catalyst design prior to experimental art. In this work we contribute to an answer by presenting accurate experimentally derived overall activation barriers (energy spans[5]) for the hydrogenation of cyclic olefins using molecularly defined ruthenium xantphos complexes (see Figure 1 below). We also show the DFT-derived underlying reaction mechanisms for these hydrogenations and also present a thorough comparison of computed energy spans obtained by state-of-the-art DFT computations. The work presented illustrates that by considering a few remaining experimental and computational boundaries DFT has reached a state which makes computational catalyst design prior to experimental work to be possible.[6]



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Theoretical Investigation on the Role of Non-Covalent Interactions in a Regioselective Aryl C(sp^2)–H Borylation Reaction

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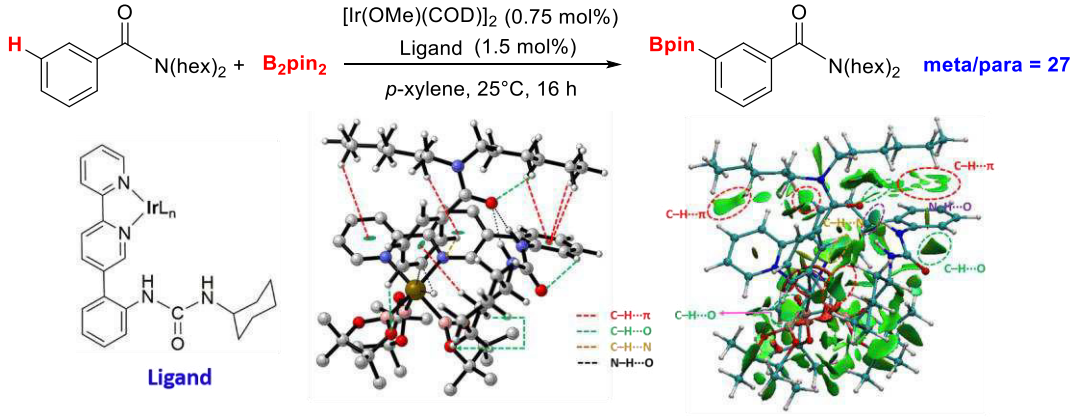
The efficient and selective activation of C−H bonds has been an important domain of development in organic chemistry. The task of achieving high activity and control in selectivity (both regio- and stereo-) in C−H activation reactions has been accomplished with the use of transition metals under homogeneous catalytic conditions. The present computational study delineates interesting mechanistic features of the first catalyst-controlled regioselective C−H borylation of aromatic compounds.[1] The important aim of this study is to examine how the *meta* selectivity is accomplished through a secondary interaction between the ligand (tethered to the catalyst framework) and the substrate (an N,N-disubstituted aryl amide). The idea of H-bond directed regioselectivity is a newer concept making use of non-covalent interactions in C–H activation reactions. DFT studies have been undertaken to address two vital issues; the mechanism and the origin of selectivity. The mechanism primarily consist of oxidative addition of Ir(III)(bpy)tris(boryl) complex (active catalyst) to the C–H bond of the substrate, reductive elimination leading to the bond formation between the aryl carbon and the boron atom of the Bpin ligand, followed by the catalyst regeneration. The oxidative addition transition state involving a C−H activation exhibits a multi-centre interaction between H, C, Ir and B atoms. Apart from the interaction between the H bonding donor (ligand) and the acceptor (substrate), several non-covalent interactions like C−H···π are also found to play a vital role in deciding the overall outcome of the reaction (Scheme 1). In line with the experimental observations, the calculations predict good selectivity of *meta* over the *para* isomer.



Scheme 1. Ir(III)-catalyzed *meta* sp^2 C–H borylation transition state with all the favorable interactions responsible for selectivity.

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DFT study of CH bond activation of Os^+, Ir^+, and Pt^+ reacting with acetylene

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Metal cations form complexes with acetylene, and can in some cases catalyze the transformation of three acetylenes into benzene[1]. Our study[2] of the complexes of Fe(+) with acetylenes revealed a number of FeCnHn (n=6) structures some of which have distinct acetylenic fragments while others contain CkHk rings including those with k=4 and 6. Fe(+)C4H4 is an intermediate in the process, while the most stable of the complexes is Fe(benzene) cation. When Fe is detached and benzene is produced the Fe(+) catalyzed process is complete. Although many states of the system are multiconfigurational, we found that DFT provides a reasonable depiction of the reaction profile.

For metals Os and Ir, M(+)C4H4 is observed[3], but further reaction with acetylene produces M(+)C6H4 and free diatomic hydrogen. Our purpose here is to explore the relative stability of M(+)benzene for M = Os, Ir, and perhaps Pt compared with the Fe(+)benzene complex. We will also establish the relative stability of the M(+)C6H4 series with Fe(+1)C6H4, and explore the reaction paths producing wither benzene or hydrogen from M(+)C4H4 + C2H2.

Acknowledgement:
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Insights on Chiral Induction using (*S*)-BINOL-Phosphoric Acids in Enantioselective Reactions through Transition State Modeling

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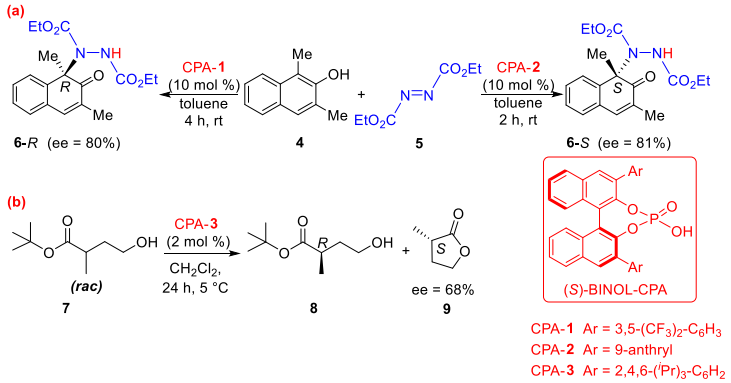
Noncovalent interactions play a ubiquitous role in asymmetric organocatalytic reactions.[1] The overall stereoselectivity of such reactions often depends on the cumulative effect of such weak noncovalent interactions. Transition state models for the stereocontrolling step developed by using DFT computations helped us to gain valuable molecular insights in the chiral BINOL-phosphoric acid (CPA) catalyzed (a) asymmetric dearomatization of *β*-naphthols through an amination reaction[2] and (b) enantioselective lactonization of *α*-substituted *γ*-hydroxy esters (Scheme 1).[3] Interesting mechanistic insights gained through the identification of various intermediates and transition states will be discussed in the poster. The differences in the preferred orientation of the substrates with respect to the 3,3′ substituents in the chiral cavity of the catalyst and the associated changes in the set of weak noncovalent interactions between CPA-**1** (predominantly C−H···F interactions between the substrates **4** and **5** and the 3,5-$(CF_3)_2$-C_6H_3 groups of CPA-**1**) and CPA-**2** (C−H···π interactions between the substrates and 9-anthryl groups of CPA-**2**) are responsible for the inversion in the sense of enantioselectivity from *R* (**6**-*R*) to *S* (**6**-*S*) (Scheme 1(a)).[4] The 3,3′-aryl groups on the BINOL framework (CPA-**3**) plays an important role in placing the substrate **7** in the chiral cavity such that lactonization occurs preferentially through one of the prochiral faces (*si*) of the ester leading to the formation of *S* lactone **9** (Scheme 1(b)). A network of favorable noncovalent interactions such as C−H···π, C−H···O, and lone pair···π between the ester and CPA-**3** is found to be the origin of enantioselectivity.[5]



Scheme 1. (*S*)-BINOL-phosphoric acid catalyzed (a) asymmetric dearomatization of *β*-naphthol through amination reaction and (b) kinetic resolution of hydroxy esters.

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Generation of Parent Phenylphosphinidene and its Oxidation to Phenyldioxophosphorane, the Elusive Phosphorous Analogue of Nitrobenzene

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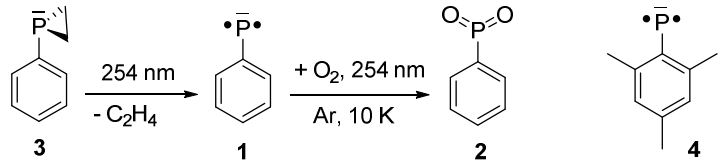
Phosphinidenes ($R–\bar{P}:$) are the phosphorus analogues of carbenes and nitrenes. While the chemistry of carbenes and nitrenes has been well established,[1] that of the phosphinides has just begun blossoming.[2] Due to their high reactivity, the chemical properties of phosphinidenes have been deduced almost exclusively from trapping or complexation experiments.[3] Several methods for their generation have been reported in the literature.[4,5] including attempts toward observation of triplet mesitylposphinidene (4) via EPR spectroscopy.[6] Phenylphosphinidene **1** is the parent of **4** and has never been observed experimentally.



Although **1** is highly reactive, its reactions with small molecules has only scarcely been studied; this would lead to several interesting novel species that have never been observed before. A prime example is the reaction of **1** with molecular oxygen (^3P-O_2) that may directly lead to phenyldioxophosphorane ($PhPO_2$, **2**), a novel compound that constitutes the phosphorous analogue of ordinary nitrobenzene.

The talk reports the first synthesis, IR, and UV-Vis spectroscopic characterization of parent phenylphosphinide (**1**) and its oxidation product phenyldioxophosphorane (**2**). Triplet phenylposhinidene **1** was characterized by IR and UV-vis spectroscopy for the first time and matching of its spectra with density functional theory (DFT) computations. Matrix isolation studies of **1** reveal an unprecedented high reactivity towards molecular oxygen, in contrast to its nitrene analogue, even at temperatures as low as 10 K.[7]

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Effects of solvents and temperature on NMR chemical shifts in hydrogen-bonded complexes

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Chemical shift in nuclear magnetic resonance (NMR) spectroscopy [1] is one of the important probes of determining the structures of chemical bonds. The shift of NMR frequency is sensitive to the variations of electronic structures around nuclei. Using NMR and UV-vis spectroscopy, Koeppe *et al.* [2] studied proton's position in a hydrogen bond of anionic complexes, $[AHX]^-$, with phenols/organic acids (AH) and carboxylic/inorganic acids (HX). They found extending (shrinking) behaviors of the distance between A (X) and H with a decrease of solvent polarity, even though the acidity of HX is stronger than that of AH in water solvents; solvent polarity allows the change of the proton donor in $[AHX]^-$.

In this paper, we theoretically study the chemical shift of H sandwiched between A and X, to understand the effect of solvent polarity and thermal vibrations on chemical shifts. Among different systems in the experiments [2], we focus on a complex composed of dichloroacedic ($A^- = CHCl_2COO^-$) and hydrochloric acids ($X^- = Cl^-$) since in this system the solvent polarity is controlled by temperature. The main calculations are performed by GAUSSIAN 09 [3]. The structural optimization is done at the MP2/6-31G** level of theory, whereas the NMR shielding tensor is calculated at four different kinds of theoretical levels, MP2/6-31G**, MP2/6-31++G**, MP2/6-311++G**, and B3LYP/aug-cc-pVTZ, with the gauge-independent atomic orbital method. First, we examine the solvent effects with the polarizable continuum model, changing the dielectric constants followed by the experimental settings. Our calculations qualitatively recover the dependence on solvents' dielectric constants in the experiments. Therefore, we claim that the behaviors of the proton chemical shifts in the experiments are attributed to the change of solvation structure. Next, we study the thermal effects, taking vibration corrections with respect to the normal modes of the complex into account. We find that the vibration corrections have impacts on a quantitative improvement of the theoretical evaluation on the chemical shifts, on three kinds of calculation levels (MP2/6-31G**, MP2/6-31++G**, and B3LYP/aug-cc-pVTZ). We will also argue the effects of anharmonic corrections from a stretching mode of the target proton, indicating a strong anharmonicity on the potential energy surface along this normal mode.

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Mechanistic Insights and Origin of Stereoinduction on NHC Catalysed Asymmetric Reactions using Transition State Modelling

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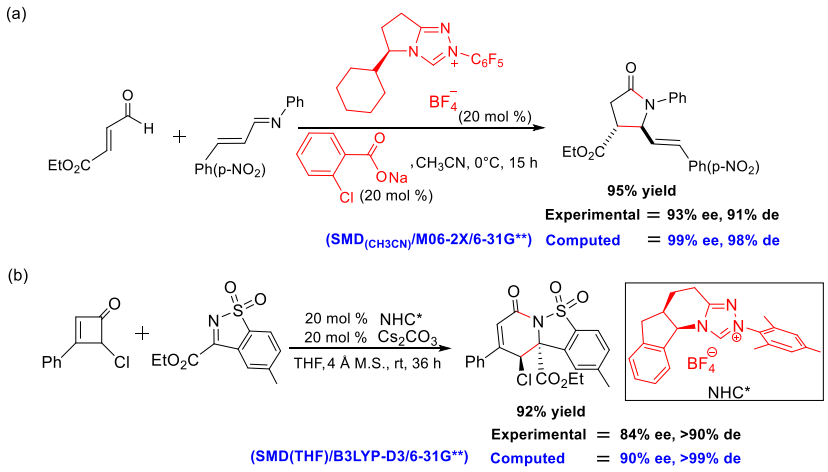
In recent years, N-heterocyclic carbenes (NHCs) have emerged as powerful nucleophilic organocatalyst and as ligands in transition metal catalysts in a wide range of asymmetric reactions. NHCs renders umpolung reactivity on reaction with aldehydes and ketones by forming different type of reactive intermediate such as acyl anion equivalent, homoenolate, enolate, or α-acylvinyl anion equivalent.[1] In this poster, we wish to present mechanistic insights and origin of stereoinduction on two such asymmetric reactions catalysed by chiral NHCs using transition state models. First asymmetric transformation involves dual cooperative catalytic reaction between enal and imine to form *trans* γ-lactam catalysed by chiral NHC and Brønsted acid (Scheme1(a)).[2] The mechanistic studies helps us to understand the role of *in situ* generated Brønsted acid, its explicit and cooperative participation with NHC lowers the energetic barrier for both the Breslow intermediate formation and in the stereocontrolling step.[3] The second reaction is C─C bond activation of cyclobutenone and subsequent reaction with sulfonyl imine to form δ-lactam with high enantio- and diastereoselectivity in the presence of chiral NHC (Scheme1(b)).[4] In both the asymmetric reactions, the stereocontrol is found to be due to an effective number of C–H···π, N–H···O, and π···π noncovalent interactions. The vital energy difference between the stereocontrolling transition states originates from the differential noncovalent interactions present in different stereochemically mode of additions.[3,5]



Scheme 1. (a) Cooperative asymmetric reaction catalysed by chiral NHC and Brønsted acid to form *trans* γ-lactam, and (b) chiral NHC catalysed C─C bond activation reaction to form δ-lactam.

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Halogen Bonding involving Aromatic acceptors

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Interest in halogen bonding (XB) has received renewed interest recently, with many theoretical studies themed on lone-pair-type XB donors. XB is also manifested in various fields such as crystal engineering, organocatalysis, functional materials, and drug design. A survey of structures within the protein data bank (PDB) revealed 33% of XB interactions involve close contacts between π-systems and a halogen (X) group.[1] Our survey of crystal structures in the Cambridge Structural Database (CSD), shows 43% of the total XB close contacts involve π...X interactions, of which 91% involve aromatic rings. Delocalization of π-electrons on the plane of the ring make the attribution of favorable XB sites on the conjugated system a difficult task, in contrast with the straightforward case in lone-pair type XBs. We report here, the locations of favorable XB binding sites involving Cl_2 as an XB donor, with different polycyclic aromatic hydrocarbons (PAHs) and heteroaromatic compounds as XB acceptors, deduced from PES scans using dispersion-corrected DFT, which in turn will provide useful insights into molecular assembly in functional material synthesis and applications.

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Mechanistic Insight into the Hydrosilylation of Alkenes Using Early Main-Group Metal Catalysts

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The key to developing highly efficient catalysts is to fully comprehend the reaction mechanism. Computational chemistry allows us to model the reactions and possible alternatives. We here present density-functional calculations for the hydrosilylation of conjugated alkenes using Ca and K-based catalysts introduced by Harder *et al.* [1]. The Markovnikov or anti-Markovnikov regiochemistry strongly depends on the catalyst and on the reaction medium. We compare the results of gas-phase and PCM solvent model calculations for the full catalytic system and model systems thereof. Our mechanistic insights are discussed within the framework of the growing number of early main group metal catalysts for alkene hydrosilylation [2].

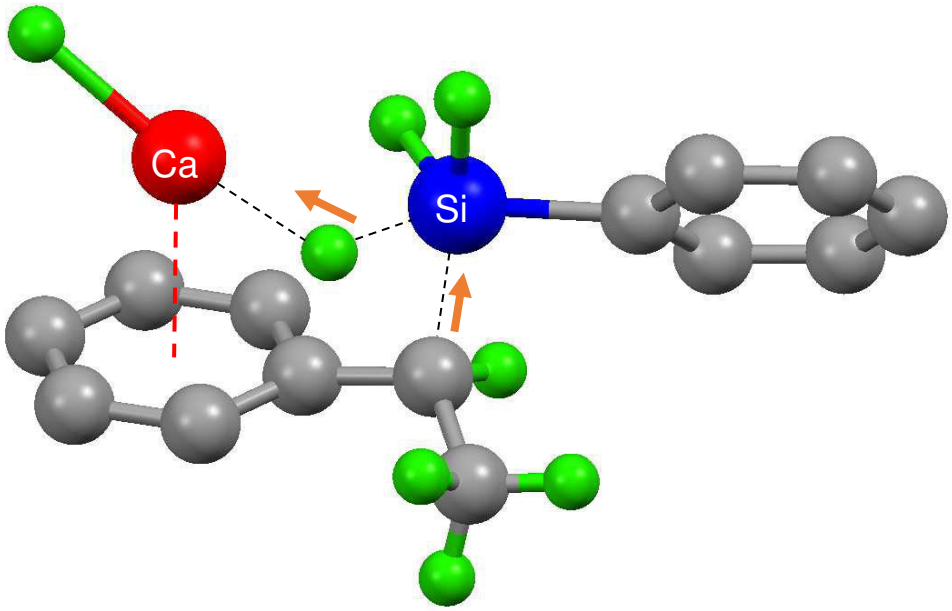

Figure 1. Transition state for the silicon-carbon bond formation with concerted hydride transfer (arrows representative of movement during the transition state)

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Mechanistic insights into aqueous methanol dehydrogenation

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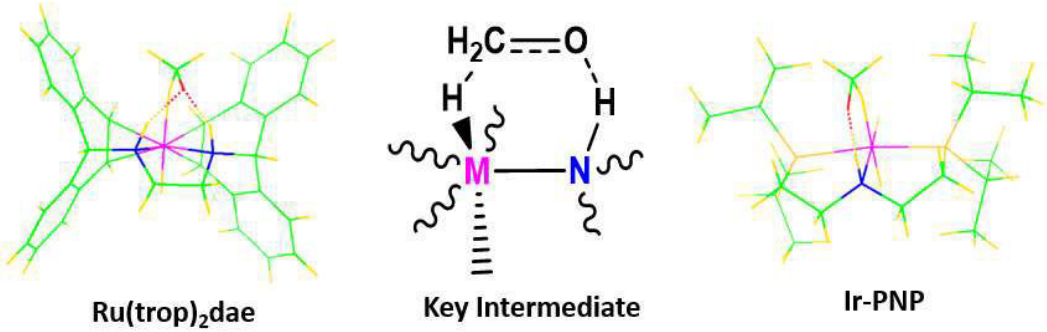
[2]Laboratorium für Anorganische Chemie, ETH, Zürich, Switzerland

Developing a Hydrogen economy can address the coupled problems of energy and environmental crises. Practical aspects like storage and production limit the use of molecular hydrogen directly as a fuel. Simple molecules like water, ammonia or methanol are carriers of hydrogen. Organometallic fuel cells [1] covered with arrays of inorganic catalysts which release the full hydrogen content of simple molecules are of particular interest. We have performed a molecular level mechanistic study of aqueous-methanol dehydrogenation over a ruthenium catalyst ($Ru(trop)_2dad$) [2]. Detailed exploration of the redox, electronic and chemical non-innocence of the ligands present in the catalytic system has been performed using DFT and CASSCF calculations. We further explore the key transition steps in alcohol dehydrogenation pathways by several other homogeneous catalysts. Our studies provide hints towards a deeper understanding of the explicit role of substrate, solvent and base concentration and how such systems can be incorporated in an OMFC device set-up.



A H-bonded methoxide-like species coordinated to the metal via alkyl hydrogen is the key intermediate in several methanol-dehydrogenation systems.

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On the Mechanism of Silver-Catalyzed Isomerization of Cubane and Homocubane.

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The attraction for polycyclic cage molecules has continued since the synthesis of the cubane skeleton by Eaton and Cole more than five decades ago.[1] Although considerable strained energy is contained within these molecules, a highly thermal stability is expected. Such behavior has been rationalized according to the Woodward-Hoffmann rules of orbital symmetry conservation.[2] However, evidence has shown that symmetry-disallowed isomerizations of several strained cage molecules are catalyzed by transition metal ions. Such is the case of cubane and homocubane, which are readily isomerized to cuneane structures under the presence of silver (I) ions, similar pathways have been observed for the homocubyl cation.[3] Despite the arguments that support a non-concerted mechanism for the valence isomerization of these systems, the possibility of a intervening concerted mechanism remains to be fully elucidated.[4] In the present work, we studied the silver-catalyzed isomerization for cubane and homocubane systems by means of ab-initio computations. Our results indicate that a silver ion reduces significantly the activation energies (ca. 3.0 kcal/mol) and that a stepwise mechanism is involved.

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Effect of an external electric field on the structure and dynamics of CaO films

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Oxide films play a key role in a broad range of economically relevant fields due to the thickness-dependent properties. The recent scanning tunneling microscopy (STM) study suggested that carrier transport in CaO films deposited on Mo support proceeds via strong phonon excitations with a signal depending on the film thickness [1]. To check the assumption about phonon-assisted transport, we present a density functional theory (DFT) study of a detailed investigation of the phonons together with structural and electronic properties of freestanding and Mo(100)-supported CaO films as functions of the film thickness and intensity of the external electric field [2]. Calculations were carried out by using CRYSTAL14 code within the framework of the PWGGA functional with 10% of the exact part. Phonon eigenvalues and eigenvectors were subsequently calculated for optimized freestanding and Mo-supported CaO films. The external electric field was applied along a non-periodic direction to reproduce experimental sample bias in the STM setup. Our study demonstrates that phonon frequencies negligibly depend on the applied electric field; a small increase in the energy of CaO phonons was detected upon increase of the film thickness that is in line with experimental findings. Effect of Mo support was found to be in the systematic decrease of the energy of phonons that is known as the phonon softening. Even though structural properties were negligibly affected by the electric field, significant effect on the electronic structure of CaO films was observed. Particularly, reduction of the band gap of CaO films was found under the applied electric field with more pronounced effect on thicker films. It is explained by the band dispersion that comes from the loss of the symmetry of oxide films in the presence of electric field.

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Coordination chemistry of Zn2+: Tetrahedral coordination or penta-coordination? A DFT analysis and review.

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The coordination chemistry of the Zn^{2+} cation is mainly dominated by a tetrahedral geometry which agrees well with the 18 electrons rule. However, several compounds exhibit a penta-coordination which would lead to a 20 electrons environment in which an axial ligand is added to a quasi-square planar geometry, but no octahedral geometry exists. The purpose of this work is to rationalize this situation, using conceptual density descriptors and to see how all the known Zn^{2+} complexes fit into these two optional geometries, and predict the geometries of any Zn^{2+} complexes.

In a first approach the properties of the $[ZnCl_4]^{2-}$ cluster will be studied, and some general rules will be extracted. These results prompted us to extend these studies also to other known Zn(II)- complexes based on sal(ph)en ligand recognized by their self-assembled behavior and in which the Zinc metal center can adopt either tetrahedral [1], or penta-coordination [2], hence depending on the nature of the bridging diamine. The properties and structures of these moieties are analyzed and rationalized.

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Synthetic nitrogen fixation with mononuclear molybdenum complexes: Electronic-structural and mechanistic insights from DFT

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The fixation of molecular dinitrogen from the atmosphere performed by the enzyme nitrogenase has drawn considerable interest, and although large advancements have been made towards understanding the involved processes, many questions yet remain.[1]
So far various model systems for synthetic nitrogen fixation have been presented some of which exhibit catalytic ammonia formation. Recently our group identified and synthesized a promising model complex featuring a new pentadentate ligand systems that was designed to envelop the metal center completely and thus minimize spurious side reactions (cf. Fig. 1).[2]

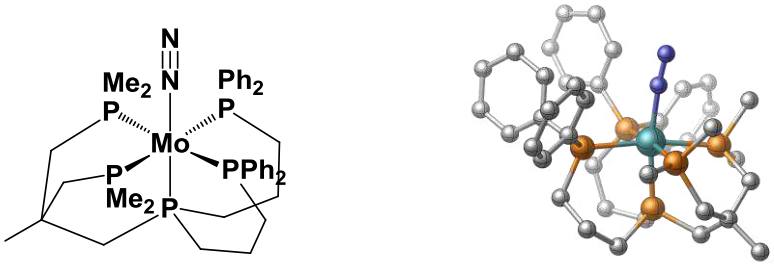

Fig. 1: Schematic and optimized structure of the Mo(0)-N_2 pentaPod complex. Hydrogen atoms are omitted for clarity.

An in-depth study of this [Mo(N_2)(pentaPod)] complex was conducted including spectroscopic characterization, evaluation of the activation towards protonation and an extensive DFT study of the reactive pathway leading from N_2 to NH_3. The latter provided a useful comparison to previously synthesized complexes and demonstrated the potential of this complex for a catalytic nitrogen fixation cycle.[3]

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Effects of External Electric Field and Anisotropic Long-Range Reactivity on Charge Separation Probability

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The recombination of geminate charge pairs generated by radiation has been investigated intensively, especially in an effort to design more efficient solar cells. In this work, we employ the recently proposed solution method for Fredholm integral equations of the second kind to treat the effects of external electric field and anisotropic long-range reactivity on the recomination dynamics of a geminate charge pair. A closed-form analytic expression for the ultimate separation probability of the pair is presented. In previous theories, analytic expressions for the separation probability were obtained only for the case where the recombination reaction can be assumed to occur at a contact separation. For this case, Noolandi and Hong obtained an exact expression for the separation probability. However, the solution was expressed as an infinite series of two complicated functions, each of which is also expressed as an infinite series, and involved expansion coefficients that need to be determined by solving a set of linear equations containing infinite sums. As such, an approximate analytic expression proposed by Braun has been widely used. However, Braun's expression overestimates the separation probability when the electric field is large. Very recently, Seki and Wojcik obtained an approximate expression for separtion probability that is very accurate when the Onsager distance is large, so that the expression is useful for low permittivity materials. However, when the Onsager distance is small, their expression fails. In this work, we have derived an approximate analytic expression that is accurate enough for all parameter values. In addition the expression is applicable also when the interaction between the geminate charge pair is described by screened Coulombic potential, and the recombination reaction has an anisotropic and long-range reactivity. We also provide the expression for the separation probability when the initial separation between the geminate charge pair is larger than the contact distance.

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Activation Strain Analyses for copper-free click reactions of alkyl azides with cyclooctynes and dibenzocyclooctynes

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The copper-free click chemistry reactions known as strain-promoted azide-alkyne cycloaddition (SPAAC) [1] have gained a wide range of applications for coupling reactants *in vivo*. In this work we explored through DFT at B3LYP/6-311++G(d,p) level 1,3-dipolar cycloaddition reactions of alkyl azides with cyclooctynes and dibenzocyclooctynes. We used activation strain model (ASM) [2] and the molecular orbital (MO) [3] to investigate the steric and electronic factors that govern the reactivity and regioselectivity in these reactions.

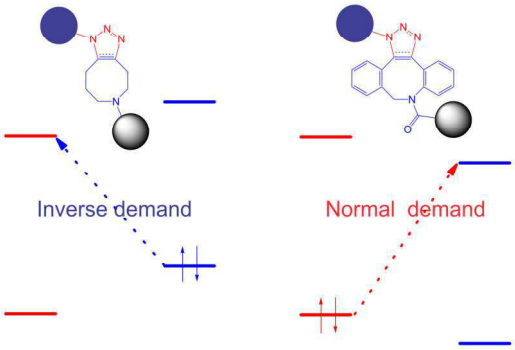

Figure 1. Frontier molecular interactions in 1,3-dipolar cycloaddition.

Three concepts arise for the 1,3-dipolar cycloadditions of alkyl azides: (i) cyclooctynes leads to an inverse electron-demand; (ii) dibenzocyclooctynes favor the normal electron-demand; (iii) the *anti* regiochemistry preference is observed. The higher reactivity of dibenzocyclooctynes than corresponding cyclooctynes is the result of a more stabilizing interaction energy and not so much a low strain energy. The *anti* regiochemistry preference is favoured by a normal electron-demand interaction which also goes with less distortion of the dipole.

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Computational study of the electrochemical reduction of [(dpp-bian)Re(CO)$_3$Br]^0: mechanism and EPR spectroscopy of intermediates.

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The [(dpp-bian)Re(CO)$_3$Br]^0 complex belongs to well-known family of rhenium(I) tricarbonyl diimine complexes. Usually, this type of complexes exhibit phosphorescence characterized by high quantum yields and very large Stokes shifts and is prone to catalyze the CO_2 photo- and electrochemical reduction to produce energy-rich compounds. This makes these complexes promising candidates for a variety of applications.

Recently [1], a mechanistic study of the CO_2 reduction in the presence of 2,2′-bipyridyl-based Re(I) and Mn(I) *fac*-tricarbonyl electrocatalysts has been performed using IR spectroscopy and a series of intermediates has been proposed. For electrochemical reduction of complex **1**, our collaborators were able to register the EPR spectra of two intermediates. However, the electronic structure of proposed intermediates in the reduction of Re(I) tricarbonyl diimine complexes has never been verified using quantum chemistry. It should be noted that the calculation of both the electronic structure and spin-Hamiltonian parameters (HFC constants, g-factors etc.) for complexes of 5d elements especially with open-shell ligands is a non-trivial task, and at least, full-electron calculations with scalar relativistic Hamiltonian are required [2].

The report will present results of our theoretical study on the mechanism of complex **1** electrochemical reduction. To calculate Gibbs free energy of the elementary reactions, the structures of proposed intermediates were optimized at the B97-D3/def2-TZVP level in DMF solution using the COSMO solvation model. The optimized geometries of primary reduced complex **1**$^{-\bullet}$ and other reduced paramagnetic complexes were used for the calculations of their g-tensors and hyperfine coupling (HFC) constants on Re, Br and N atoms of the ligand. All-electron DFT with scalar relativistic Hamiltonian (DKH2 or ZORA) and a number of functionals have been used in these calculations. It was found that application of BHandHLYP hybrid functional and WTBS basis set for Re leads to most reliable values of HFC constants.

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Non-analytical functionals – A new strategy in density functional theory

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Non-analytical functionals provide the functional values at a given point of interest rather than an analytical correspondence between the functional values and all possible input functions. In contrast to conventional functional design, where a certain ansatz for the energy of the system has to be chosen, non-analytical functionals are constructed with the help of exact functional properties, and as such yield the exact energy provided the corresponding input potential is exact. This offers a new strategy for a systematic development of potential-functionals applicable in the computation of molecular complexes and material design.

Numerical Nuclear Second Derivatives on a Grid: A Faster and Enabling Method for Hessian Calculations

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The computation of nuclear second derivatives (NSD) is an essential routine in quantum chemical investigations. Previous work has contributed to the analytical evaluation of NSD (aNSD)[1] and to the improvement of integral evaluation[2] and storage to enable NSD evaluations for larger systems within a manageable wall clock time in a less demanding hardware framework. Another facet of NSD computations focuses on hardware-enabled faster and more capable integral evaluations based on specialized processors such as graphic processing units (GPUs).[3] This facet of NSD computation is complimentary to the continuing development of theory and mathematical approximations.

Herein, we describe another facet of improving NSD computations focusing on the utilization of grid computing to enable numerical differentiations of analytical first derivatives (aNFD) to calculate NSD (nNSD). The advantage of nNSD over aNSD is that it circumvents the costly evaluation of the coupled-perturbed Hartree-Fock or Kohn-Sham equations. Hence, the scaling of nNSD is on the same order as aNFD. The unfavorable pre-scaling factor, which is twice of the degrees of freedom in central differences, of the nNSD is reduced to unity by distributing each differentiation to a remote computer. In our case, $C_{22}H_{14}$ with 626 basis functions (BFs) and 1764 density fitting functions (DFFs) using RIJCOSX-B3LYP-D3 took 22±5 min using the nNSD-on-grid method *vs* 52 min using aNSD on 16 processors (total CPU time = 848 min). In addition, the nNSD-on-grid method allows NSD readily tractable for macromolecules. NSD can be evaluated for an insulin molecule ($C_{253}H_{374}N_{76}O_{76}S_6$; 12266 BFs and 33956 DFFs) using nNSD-on-grid while I/O bottleneck forbids aNSD. Lastly, nNSD-on-grid enables NSD using correlated wave-functions on larger molecules (> 50 atoms). NSD of a molecular dichromium complex with 62 atoms, 1138 BFs, and 3012 DFFs can be evaluated using NEVPT2:CAS(2,2).

Grid computing on numerical methods can outperform analytical methods in terms of wall clock time and the size of systems treatable. The nNSD-on-grid method presented in this abstract is one example of this concept and a pioneer for future implementations.

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A Study of the Global and Local Aromaticity of Hetero[8]circulenes

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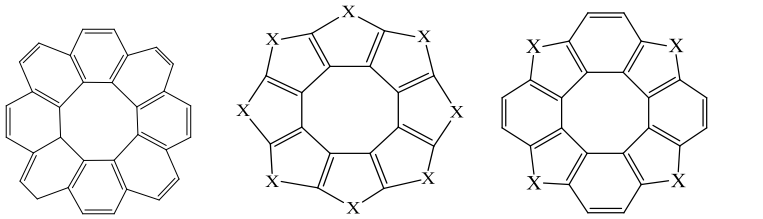
Abstract

The global aromaticity of the hetero[8]circulenes and their double charged ions was investigated using the topological resonance energy (TRE) method[1]. The bond resonance energy (BRE) and circuit resonance energy (CRE) methods were used to evaluate local aromaticity[1-3]. Analysis was made of the effects of the types and the arrangement of heteroatoms on the global and local aromaticity of the molecules under consideration. The local aromaticity results obtained here using the CRE and BRE methods were compared with the nucleus independent chemical shift values (NICS (0) and NICS (1)) as reported in the literature [4-5]. With respect to local aromaticity, discrepancies arose between results we obtained using the CRE and BRE methods and those predicted by the NICS (0) and NICS (1) methods. We found that increases in the local aromaticity of the cyclooctatetraene rings have a significant effect in increasing the global aromaticity of the molecule as a whole. Both in the neutral and double charged states, the benzene, thiophene, furan, and pyrrole rings, which are fused to the cyclooctatetraene ring, retain their local aromaticity. Finally, the ring current results were analyzed.



1 **2** X=O; **3** X=S; **4** X=NH **5** X=O; **6** X=S; **7** X=NH

Fig.1. The structure of the compounds in this study

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A Study of the Global and Local Antiaromaticity of 1, 4-Diazapentalene Derivatives

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Abstract

The global antiaromaticity of several types of heteroacenes bearing the 1,4-diazapentalene core was investigated using the topological resonance energy and magnetic resonance energy methods[1]. The bond resonance energy (BRE) and circuit resonance energy (CRE) methods were used to evaluate local antiaromaticity[1,2]. Analysis was made of the effects of the number and the arrangement of heteroatoms on the global and local antiaromaticity of the molecules under consideration. The local antiaromaticity results obtained here using the CRE and BRE methods were compared with the nucleus independent chemical shift values (NICS(1)zz) as reported in the literature[3]. Regarding local aromaticity, discrepancies arose between results we obtained using the CRE and BRE methods and those predicted by the (NICS(1)zz) method. We found that the fusion of aromatic rings to the 1,4-diazapentalene core may dilute its antiaromatic character. Ring current results show that when aromatic rings are fused to the 1,4-diazapentalene cores, the cores maintain strong paratropic ring currents; the aromatic ring sections however, maintain diamagnetic currents flows around their molecular perimeter.

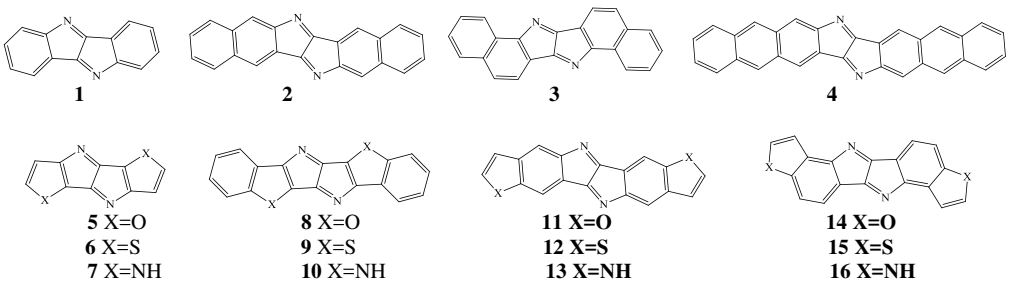

Fig.1. The structure of the compounds in this study

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Time-dependent coupled-cluster method for laser-driven multielectron dynamics

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Ab initio description of light-matter interaction is a long-standing challenge for theoreticians, and recently gathering practical attention in the context of rapidly developing high-field physics and ultrafast science[1]. The time-dependent Schrödinger equation (TDSE) rigorously describes such electron dynamics. However, the exact solution of TDSE for an interesting chemical system is far beyond the reach, therefore, as an approximate but reasonably accurate solution to the TDSE, multiconfiguration time-dependent Hartree-Fock (MCTDHF) method has been developed for intense-laser driven multielectron dynamics[2]. Though powerful, the MCTDHF method suffers from exponential scaling of the computational cost with respect to the number of electrons. Attempts have been made by partitioning the orbital subspace to reduce the computational cost [3, 4, 5]. However, a problem with these approaches, except for the full configuration-interaction based MCTDHF and time-dependent complete-active-space self-consistent-field (TD-CASSCF) methods [3], is the lack of size-extensivity. An alternative method allowing size-extensive description of intense-laser driven multielectron dynamics with a moderate computational cost is strongly desired. The coupled-cluster (CC) method is an attractive candidate to fullfil this purpose, in viewing spectacular success of the method in the stationary theory[6]. Recently, Kvaal [7] has proposed a time-dependent version of the CC (TD-CC) method using adaptive bi-orthogonal orbitals and applied to a collision problem, which clearly requires further theoretical refinement. In the present contribution, we survey the theoretical background of the TD-CC method and present our recent development of real-time/real-space version of the TD-CC with numerical applications.

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From G4(MP2)-6X to W3X-L: A Range of Efficient and Accurate Thermochemical Composite Protocols

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The continuous development of quantum chemistry composite protocols has provided chemists with some powerful tools for quantitative computation of thermochemical quantities. Notably, the G*n* and W*n* series of composite methods are nowadays "household names" within the (computational) chemistry community. These two lines of methods have been designed with distinct philosophies, which result in their different capabilities that are often complementary with one another. The G*n* procedures provide good and efficient approximations to CCSD(T) and are currently applicable to systems as large as C_{60}, whereas W*n* employ more rigorous formulations to produce even better accuracies but at the expense of computational efficiency. Over the last few years, we have constructed variants of G*n* and W*n* with the aim of combining their advantageous characteristics [1–6]. In this presentation, we will provide a synopsis on this collection of methodologies, with a focus on our more recent investigations.

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Theoretical study of anatase (101) and rutile (110) TiO_2 nanotubes

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Experimental and theoretical studies of nanotubes have increased over the last decades [1-2]. Simulations, molecular modeling and theoretical investigations were performed for different conformation of materials (nanotubes, surfaces, crystals) formed by various compounds (TiO_2, ZnO, SnO_2, GaAs), using quantum chemistry calculations in order to point out important structural and electronics properties of these materials.

Anatase and rutile nanotubes showed the same trend for the stability. It was noticed that a decrease in the value of the energy variation occurred dependent on the growth of the diameter, forming more stable structures. Increasing the length of the nanotubes did not influence the behavior change, that is, the smaller diameter structures remained more unstable than the larger diameter ones. Among the clusters obtained, we highlighted the nanotube anatase using large cluster that presented the lowest value of ΔE, while rutile nanotubes showed smaller nanotubes for the lowest values of ΔE.

The analysis of the energy variation of anatase and rutile nanotubes showed the stability is dependent on the growth of the diameter and consequently the decrease of the curvature. There were small variations in the results of *ab initio* calculations between the bases used in the study (6-31G and 6-311G).

Acknowledgment: CNPQ, CAPES, FAPEG, FAPDF

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Ab initio construction of phase diagrams for molecular crystals.

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Due to the complex interplay of non-covalent interactions and an immense number of packing motives available, molecular crystals exhibit polymorphism. Considering its ubiquity, it seems there is no direct link between the complexity of a molecule and the number of its existing polymorphs. Polymorph screening and the determination of phase stability have long been experimentally challenging and expensive due to the difficulties of crystallization and the laborious calorimetric and spectroscopy experiments required to characterize polymorphs over broad ranges of pressures (p) and temperatures (T). However, the advent of reliable quantum chemistry calculations of cohesive energies and phonons creates new opportunities to predict phase stabilities *in silico*. Such a development should find many uses in pharmaceutical industry or modelling of processes in solid phase. [1]
Ab initio construction of a phase diagram consists in calculating the equilibrium curves of coexistence of the phases in the $p - T$ coordinates. [2] In this work, many-body expansion [3, 4] and periodic quantum calculations [5] are used to obtain cohesive energies and phonon properties of the crystalline phases. Such data are processed by the quasi-harmonic approximation [6, 7] to yield the thermodynamic properties. The relevant criterion for assessing the phase stability at given p and T is the minimum molar Gibbs energy. Sublimation equilibrium is included in the phase diagrams in a relatively straightforward way since the vapor phases are assumed to be the ideal gas which can be treated by a combination of quantum calculations of molecular degrees of freedom and statistical-thermodynamics rules.
This work studies polymorphism on a test set of four simple molecules – methanol, ethane, benzene and imidazole, and seeks to determine how reliably phase stability and sublimation equilibrium can be predicted. Since the energy differences among various polymorphs usually range to a few kJ mol^{-1}, and the sublimation pressure depends exponentially on T, the highest accessible ab initio levels of theory need to be used for evaluation of cohesive energies. Vibration-based terms are calculated within the cheaper density functional theory framework. Several quantum chemistry methods are compared in this work and their effect on the resulting phase diagram is studied. Calculated data are confronted with their experimental counterparts so that the computational uncertainty can be estimated.

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Quantum Chemical Exploration of Transition Metal Mediated CO_2 Disproportionation and Hydrogenation

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Biological carbon fixation into organic matter occurs predominantly during the Calvin-Benson-Bassham Cycle (dark Photosynthetic cycle) that converts millions of tons of CO_2 into biomass with the intermediacy of the enzyme, RuBisCo. The key role here is played by the Mg^{+2} centre at the active site of the metalloenzyme that promotes CO_2 fixation and feasible C-O bond cleavage to yield the desired product, phosphoglycerate. However chemical reduction of CO_2 is very challenging and involves high energetic requirement ($E^{o'}$ = -1.9 V vs NHE) for the large structural rearrangement from linear CO_2 to bent $CO_2^{\bullet-}$. Nevertheless, coupled multi-electron and multi-proton reactions occur at relatively modest potentials ($E^{o'}$ = -0.52 V to -0.43 V). This signifies that two-electron reduction of CO_2 requires efficient bi-functional catalyst.[1] Here, we have studied the mechanistic possibilities of two electron reduction of CO_2 primarily involving the following processes: (a) CO_2 Reductive Disproportionation ($2CO_2 + 2e^- \rightarrow CO + CO_3^{2-}$) which is promoted by $\kappa N,\eta^6$-arene-ligated $L^{tBu}Co$, where L^{tBu} = 2,2,6,6-tetramethyl-3,5-bis(2,4,6-tri-isopropylphenylimido)hept-4-yl. Our computational investigations reveal that a second metal-ligand complex is involved as a Lewis acid to polarize the target C-O bond and effectuate facile C-O bond cleavage involving a lower-barrier kinetic process than the monometallic pathway. (b) CO_2 hydrogenation by Hydride Transfer ($CO_2 + H^+ + 2e^- \rightarrow HCOO^-$) studied with a series of phosphine-based metal-hydride complexes (from Group 8 and 9).[2] Our analysis shows that it is the stability of the Metal-Hydride complex derived from H_2-Splitting that determines the rate determining step. This is an experimentally measured property called hydricity (or hydride affinity) which increases down a group and makes hydride transfer difficult for heavier metals (like Iridium).[3]

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Molecular dynamics simulation reveals how phosphorylation of tyrosine 26 of PGAM1 upregulate glycolysis

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Phosphoglycerate mutase 1 (PGAM1) catalyzes the eighth step of glycolysis and is often found upregulated in cancer cells. To test the hypothesis that the phosphorylation of tyrosine 26 residue of PGAM1 greatly enhances its activity, we performed both conventional and steered molecular dynamics simulations on the binding and unbinding of PGAM1 to its substrates, with tyrosine 26 either phosphorylated or not. We analyzed the simulated data in terms of structural stability, hydrogen bond formation, binding free energy, etc. We found that tyrosine 26 phosphorylation enhances the binding of PGAM1 to its substrates through generating electrostatic environment and structural features that are advantageous to the binding. Our studies have revealed considerable atomistic details of PGAM1, its substrates, and their interactions, which may provide valuable insights into computeraided design of drugs that specifically target cancer cells. Through virtual screening of chemical libraries, for example, small drug molecules may be found that can greatly weaken or even block the binding between PGAM1 phos and its substrates, while having little effects on PGAM1 wt. Our results may provide valuable insights into computer-aided design of drugs that specifically target cancer cells with PGAM1 tyrosine 26 phosphorylated.

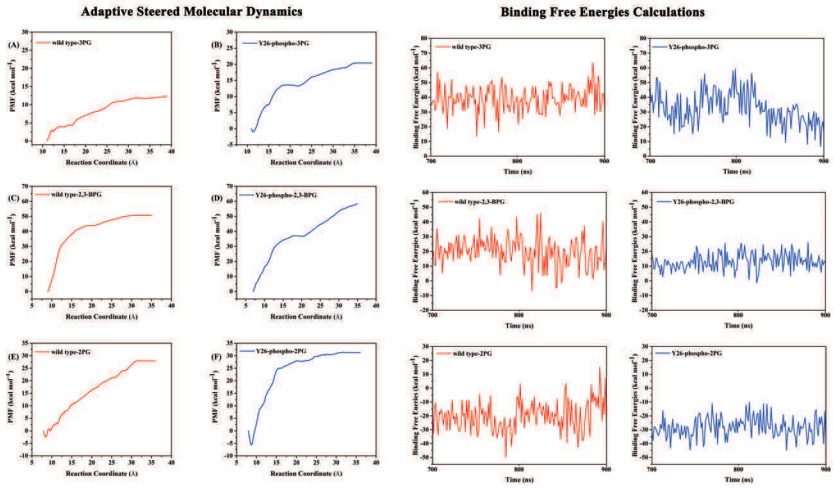

Figure 1: Left panel: The 3-Phosphoglyceric acid, 2-Phosphoglyceric acid and 2,3-Bisphosphoglyceric acid molecules were pulled out of the binding pocket of PGAM1, by using the Adaptive Steered Molecular Dynamics method. The results of PMF were shown in the left panel; Right panel: The results of calculations of binding free energies. All the energy unit is kcal/mol.

Purely relativistic electric dipole moment interactions of the electron from quasi-relativistic calculations

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A permanent electric dipole moment of the electron (eEDM) would violate parity $\mathcal{P}$ and time-reversal $\mathcal{T}$ symmetry simultaneously.[1, 2] By $\mathcal{CPT}$-theorem[3] this is directly connected to $\mathcal{CP}$-violation. Thus experiments that search for an eEDM provide sensitive tests of physics beyond the Standard Model of particle physics.[4] The best tests for the existence of an eEDM are provided from high-precision spectroscopy of molecules.[5] Due to enhancement effects of the electronic structure these measurements are sensitive to an energy regime of TeV.[1, 5] A theoretical prediction of interactions of the eEDM in molecules is indispensable for the interpretation and design of experiments. However, interactions of an eEDM in molecular systems are purely relativistic, i.e. they depend only on the lower component of the Dirac bi-spinor:[6]

$$\hat{H}_{\mathrm{eEDM}} = -d_{\mathrm{e}} \begin{pmatrix} \mathbf{0}_{2\times2} & \mathbf{0}_{2\times2} \\ \mathbf{0}_{2\times2} & \vec{\boldsymbol{\sigma}} \cdot \vec{\mathcal{E}} \end{pmatrix}, \tag{1}$$

where $\hat{H}_{\mathrm{eEDM}}$ is the eEDM interaction Hamiltonian, d_{e} is the eEDM, $\vec{\boldsymbol{\sigma}}$ is the vector of the Pauli spin matrices and $\vec{\mathcal{E}}$ is the internal electrical field of the molecule. Thus costly relativistic four-component electron correlation calculations are mostly employed for the description of eEDM interactions.

We present efficient quasi-relativistic methods in a zeroth order regular approximation (ZORA) framework for the calculation of purely relativistic eEDM interactions.[7] Thereby electron correlation is addressed via complex generalized Hartree-Fock (cGHF) or Kohn-Sham (cGKS) schemes. By comparisons of these numerical studies with analytical models a deeper understanding of $\mathcal{P},\mathcal{T}$-odd effects in molecules is provided.

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STEEPLECHASE FOR 2-RDM APPROXIMATIONS

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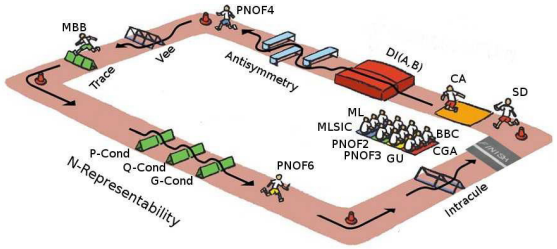
In this work, we will present some tests that we have performed to analize the goodness of second-order reduced density matrices approximations (2-RDM) when the effects of correlation become important. The approximations studied are used to construct functionals in natural orbital functional theory(NOFT)[1]. The battery of tests presented here include: the delocalization index, the fulfillment of the sum rule, termwise error for the diagonal elements and for the whole matrix, the fulfillment of some N-representability[2, 3] conditions, the attainment of symmetry properties and some quantities related to the intracule density. The energy is usually the guiding star for the validation of NOFT functionals, therefore this battery of tests offers a wide variety of assessments that permit to check relevant features of the approximated 2-RDMs that are normally not put into test

To tune the correlation effects, we have chosen the Harmonium atom (HA) model[4] as our reference system. In HA, the effects of correlation are driven by one single parameter called the confinement strength. This model systems provides a realistic description of electron correlation effects and renders itself to analytic solutions for some values of the confinement strength. Harmonium has been used to calibrate DFT functionals[5] and third-order reduced density matrices[6].



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Excited States Insight to Assess Phototoxicity of Non-Steroidal Anti-Inflammatory Drugs.

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The assessment of the photosensitivity of pharmaceuticals is essential to predict a loss of potency or production of toxic reactive species induced by an electronic excitation, as outlined in the International Council of Harminization (ICH) S10 guidance. Our research aims of understanding the photophysical processes, including the deactivation mechanisms, initiated after light absorption of an UV-visible photon.

We have modelled the absorption spectra of non-steroidal anti-inflammatory drugs (NSAIDs), such as aspirin and ibuprofen in gas phase as well as in solvent. Multistate second order perturbation theory on state average complete active space self-consistent field wavefunctions MS-CASPT2//SA-CASSCF[1,2,3] and time dependent density functional theory (TD-DFT)[4] were the computational protocols for this purpose.

Starting from the spectroscopic state, we have mapped the topology of the potential energy surface relevant to the deactivation of these systems by performing minimum energy path calculations and locating the main stationary and crossing points along the singlet manifold. Some of these crossings involve a change of spin, allowing the transfer of populations to other manifolds with multiplicity different than that of the ground state (intersystem crossing, ISC).

These calculations provide an idea of the photophysical deactivation mechanisms that will next serve as a reference to obtain a time resolved picture of the evolution of the system upon its electronic excitation by means of non-adiabatic molecular dynamic simulations.

Our ultimate goal with these results is to design a model that would translate the main features of the deactivation mechanisms into a phototoxicity alert that can be introduced at early stages of the drug discovery process and help mitigate risks associated with photon absorption.

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New porphyrin for application in Dye-Sensitized Solar Cells

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A possible renewable energy source are the Dye-Sensitizes Solar Cells (DSSC) [1]. The choice of the dye plays an important role in the solar cell's efficiency and to employ D-π-A dyes have shown promising results. This type of dye is formed by an electron donor group (D) and an acceptor group (A), both connected by a π-conjugated system, e.g. porphyrins, since they a formed by an extended conjugated system [2]. In this work, we propose new porphyrinic derivatives and performed density functional theory (DFT) calculations for geometry optimization, as well as to obtain the vibrational frequencies. To study the electronic properties, time dependent DFT (TD-DFT) calculations were performed. M06 functional and 6-311G(d,p) basis set were used in all calculations. Solvent effects (THF) were included with IEFPCM continuum model. All calculations were made using Gaussian09 package. Our studies [3] showed that porphyrin with secondary amines bonded in *meso* position presents promising absorption spectra and Kohn-Sham molecular orbitals with a significant push-pull effect. There is also a noticeable influence of linker's dihedral angle (indicated in Figure 1) in the increase of push-pull effect. We have observed that when the set formed by porphyrin's ring and the acceptor group loses its planar structure this effect increase. In this sense, we have decided to propose a structure with secondary amines in *meso* position and propane groups in β position to create a steric hindrance in order to make dye loses its planar structure. In fact, the obtained compound has adequate absorption spectrum and Kohn-Sham orbitals what enable this molecule as a possible dye to be applied in more efficient DSSC.

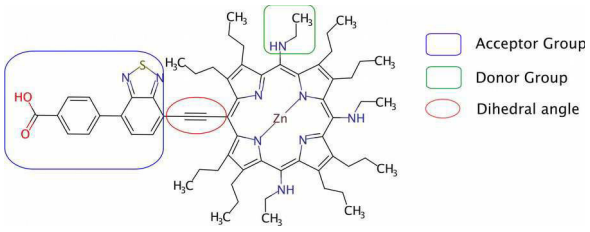

Figure 1: Porphyrin's structure

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Systematic search for chemical reactions in gas-phase contributing to methanol formation in the interstellar medium.

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Methanol is among the molecules found in the Interstellar medium (ISM) considered as a potential precursor of more complex, prebiotic species, like sugars and aminoacids.[1,2] Observed mainly in very low density and extremely cold places, called molecular clouds, their chemistry is dominated by the following features to be viable: (i) the reactions must involve at most two reactants, (ii) they must be significantly exergonic, and (iii) they must be very fast (with very small or no activation energy).[3-6] There are numerous studies proposing possible chemical routes yielding methanol in the ISM, with or without involving interstellar grain mantles.[7-10] Unfortunately, the existent approaches fail to reproduce the observed fractional abundance of methanol in molecular clouds.[5]

The goal of this work is to perform a systematic search for reactions that yield methanol (exclusively on the gas-phase). The strategy included 82 molecules identified in the ISM, and 7 proposed intermediates. The search engine combines the molecules with the minimum number of atoms necessary to form methanol. The search led to 678 reactions involved in chemical routes toward molecular complexity. For each one, several selection criteria were applied: i) thermochemical viability ii) high exergonicity, iii) free radicals and/or ionic reactants, iv) maximum number of necessary elementary steps, v) lower energy isomers and vi) reaction barriers. After applying all of them, 15 reactions are proposed as potential candidates to contribute to methanol formation in the ISM. It is expected that including them into the models would improve the agreement with the observed methanol abundance in molecular clouds.

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Modeling of ions in aqueous environments: from the gas to the condensed phase

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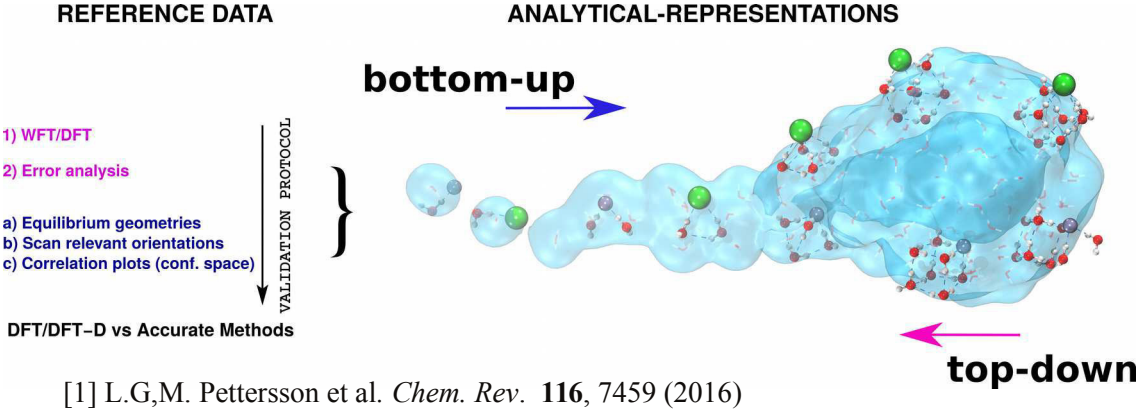
Much effort have been made to understand the influence of solutes on the HB network of aqueous environments [1,2], however there is still a lot of debate regarding its dynamic heterogeneity and a integral picture of the involved molecular mechanisms, as well as, the underlying interactions is still missing. In this contribution, we present a family of *ab-initio* polarizable interaction potentials [3,4] and we provide a systematic route for the development of transferable interactions able to describe properties in clusters, ionic solutions (in the infinite dilute or concentrated regimes) and in surfaces of aqueous electrolytes. By construction, these effective many-body potentials are compatible with any TTM-based model and could be parametrized for any general water potential. They include an explicit treatment of 2B short and long range interactions adjusted to electronic structure data coming from energies, forces, polarizabilities and dipoles (for both bottom-up and top-down approaches, see Fig 1), while many-body effects are taken into account through damped polarization schemes. Additionally, we further compare with currently available semiempirical and ab initio-based potential surfaces and we provide a systematic protocol to validate and assess the accuracy-performance of modern DFT approximations [5] (including the effect of semilocal approach, exact-exchange/correlation admixture, range-separation, as well as dispersion-correction terms) for alkali and halide water systems, with respect to reference CCSD(T)-F12/DF-MP2 calculations on a representative set of configurations [6]. Further investigations of statical and dynamical response properties in gas and condensed-phase environments are currently in progress.



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A Study of the Global and Local Aromaticity of Azaacepentalenes

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Abstract

The global aromaticity of the azaacepentalenes was investigated using the topological resonance energy (TRE) and magnetic resonance energy (MRE) methods[1]. The bond resonance energy (BRE) and circuit resonance energy (CRE) methods were used to evaluate local aromaticity[1,2]. Analysis was made of the effects of the types, number, and arrangement of nitrogen atoms on the global and local aromaticity of the molecules under consideration. Our TRE results show that acepentalene (**1**) is antiaromatic with negative TRE energy. However, the azaacepentalenes (**2-16**) are aromatic with positive TREs. Peripheral nitrogen substitution causes a decrease in aromaticity. The local aromaticity results obtained here using the CRE and BRE methods were compared with the nucleus independent chemical shift values (NICS(1)) as reported in the literature[3]. Our CRE and BRE results show that azaacepentalenes (**2-16**) are stabilized primarily by the 6π electronic system. Ring current results predict that a strong diamagnetic current flows around the whole molecular perimeter.

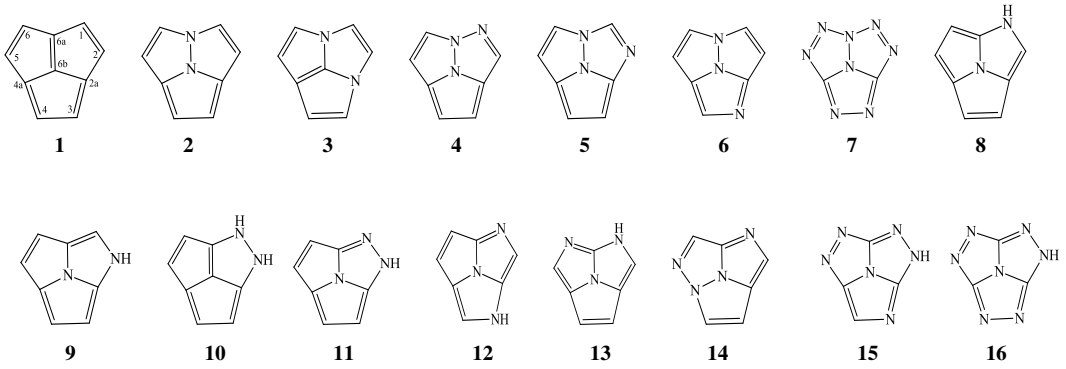

Fig.1. The structure of the compounds in this study

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Recent Advances in Approximate Excited State Calculations in the ADF Modeling Suite

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We present recent advances in the approximate calculation of excited states that have recently been implemented in the ADF modeling suite:

1. Intensity selection as a technique for the accelerated calculation of UV/Vis absorption spectra for large systems.

2. The calculation of vibrationally resolved absorption and emission spectra with density functional based tight binding (DFTB) and its linear response extension (TD-DFTB).

3. A new method named TD-DFT+TB that combines ideas from TD-DFTB excited state calculations with a ground state from DFT. We show that the new method is an excellent approximation to full TD-DFT calculations while being computationally very efficient. Furthermore the new method does not require the availability of DFTB parameters for the studied system.

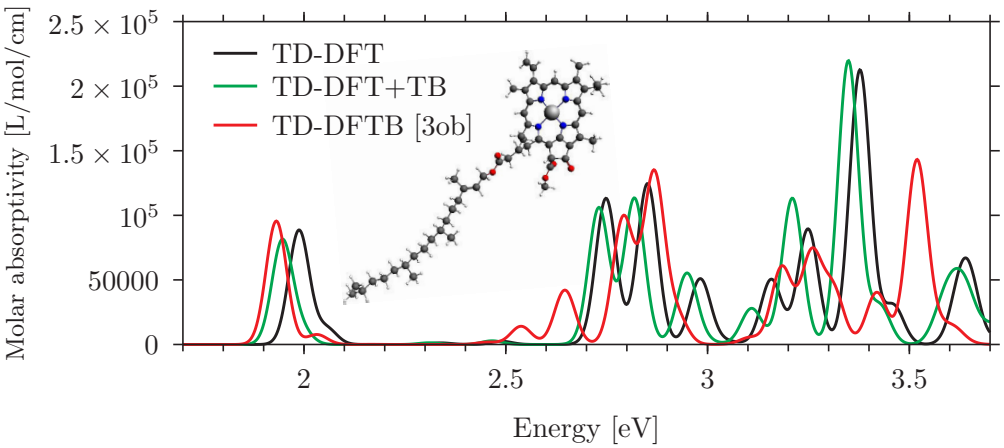

Figure 1: UV/Vis absorption spectrum of chlorophyll A calculated with different methods.

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Combined Theoretical and Experimental Studies on Polymer and Plasticizer Interactions

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Assessment of interactions among polymer and plasticizer molecules is important criterion for design and development of composite propellant formulations. The objective of this study is to screen plasticizers for selected polymers viz, hydroxyl terminated polybutadiene (HTPB), nitrile butadiene rubber (NBR) and glycidylazide polymer (GAP) which are used in the advanced propellant formulations. The solubility parameter is a measure of non-bonded interactions and it can be a quantitative tool for assessing the interactions. It is evaluated by Gee's equilibrium swelling experiments for cross-linked polymers and intrinsic viscosity measurements for linear polymers. The solubility parameter determined from swelling studies for partially cross-linked HTPB and GAP is 17.97 and 23.62 $J^{1/2}cm^{-3/2}$ respectively. Further, solubility parameter of HTPB achieved from intrinsic viscosity measurements is also comparable with swelling study data which reveals that there is no significant change in solubility parameter of linear and cross-linked HTPB. Classical mechanics based molecular dynamics simulations employing COMPASS force field are also used to evaluate solubility parameter of polymers viz, HTPB, NBR, GAP, and plasticizers, NG, DOA, DEGDN, BTTN, TEGDN, BuNENA, and TMETN. Experimental data of studied systems overall matched well with the simulation results. Flory-Huggins interaction parameter (χ) is also calculated for identifying the suitable pair of plasticizer and polymer based on the enthalpy contributions. It is inferred from predicted solubility parameter data that energetic plasticizers are not compatible with HTPB; while n-Butyl-nitratoethylnitramine(Bu-NENA) is found to be the most suitable plasticizer for NBR and GAP. Overall, this study finds its importance in identifying an appropriate plasticizer for any specific polymer, which is the foremost critical step for achieving successful propellant formulations with desired characteristics.

Keywords: Modeling and Simulation, Molecular Dynamics, Solubility parameter, Miscibility, Energetic materials.

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CO, NO, and NO_2 Adsorptions on Boron Antisite (B_N) in Boron-Rich Boron Nitride Nanotube (BNNT)

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Carbon and nitrogen oxides (CO, NO, and NO_2) released during the combustion of fossil fuels, contribute to both smog and acid precipitation and affect both terrestrial and aquatic ecosystems.[1] Additionally, they are central to the formation of fine particles (PM) resulting in a variety of breathing problems, of which are associated with adverse health effects. Sequestration of these gases emitted from coal-fired power stations or motor vehicles is thus one of the most pressing issues in the environmental protection. Due to their intrinsic high surface areas and polarity, boron nitride nanotube (BNNT) could be a good candidate as chemical gas adsorbent.[2-4] However, the pristine BNNT with a large band gap has been widely known to be almost inert to gas molecules. In this study, we chose BNNT with boron antisite (B_N) as CO, NO, and NO_2 adsorbents, based on our previous work presenting that B_N in BNNT can capture CO_2 strongly enough to the ambient-condition sequestration.[5] In this congress, let us report that CO, NO, and NO_2 are strongly adsorbed on B_N in BNNT almost regardless of tube diameter. The geometrical, energetic, and electronic properties of gas-adsorbed B_N-BNNTs were analyzed via ab initio calculations using plane waves [PAW-PBE] and localized atomic orbitals [ONIOM(ωB97X-D/6-31G*:AM1)].

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Structural analysis of phthalocyanines dimers using computational methods

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Phthalocyanines (Pc's) compounds have widely application in nanotechnology and photodynamic therapy of cancer, besides their common use as dye [1,2]. In phthalocyanines dimers with a face-to-face stacking it is possible to observe π—π interaction between the two Pc rings [3] affecting their photophysical and photochemical properties. In order to see how phthalocyanines and naphthalocyanines (Nc's) complexed with Zn(II) have their optical properties changed when stacked in dimers, we have conducted computational studies, as well as verifying the tert-butyl substituent influence.

The computational method employed was based on Density Functional Theory (DFT). The geometry optimization and the TD-DFT were carried out by using the BLYP functional and 6-31G basis set and the dispersion correction was included with the Grimme`s approach (D3-BJ). We have evaluated 4 molecules: ZnPc and ZnNc without substituents and both compounds with tert-butyl as substituent. For each optimized molecule, we performed conformational analysis with molecular mechanics approach (using UFF force field) and found 3 to 4 dimers conformations that were more probable. After this procedure, all conformations found were submitted to DFT calculations (geometry optimization and TD-DFT calculations).

The optimized dimers of ZnPc and ZnNc without substituents converged to conformations where monomers were rotated 45º or 90º. The only exception was ZnPc with tert-butyl, whose conformation presented the rings eclipsed, with a torsion angle about 20º. The distances between the Zn-Zn in the dimers with 90º were smaller than their distance in the dimers with 45º, because the Zn(II) from one monomer complex to nitrogen atoms of the other monomer. So, besides π-interaction, aggregation is also driven by complexation.

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Density Functional Study of [2+1] Radical Cation Cycloaddition

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Radical cation intermediates have been implicated in the oxidation-promoted, electron-transfer catalyzed cycloaddition of two electron-rich alkenes experimentally[1, 2, 3]. Herein, we performed a detailed study of the hetereodimeric cycloaddition between two unsymmetrical alkenes using density functional theory (DFT) M062X functional. Concerted [2+1] cycloaddition is ruled out based on our calculations. We found that the first C-C bond formation in the stepwise mechanism is the rate-determining step of the whole reaction. Both 4-membered and 6-membered rings can be accessible under suitable reaction conditions. Conformational effects have been fully explored and it is found that the positive-gauche addition proceeds with the lowest energy barrier. Anti-cyclobutyl ring is found to be the most thermodynamically stable, in accordance with experimental findings. The effects of solvents on the reaction have also been investigated.

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Configurational Bias Monte Carlo method to sample molecular flexibility: The case of octane and 1,2-dichloroethane

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Several processes in physics, chemistry and biology are affected by the molecular structure. In computer simulations, structures are usually sampled through either Molecular Dynamics (MD) or Monte Carlo (MC). The method of choice usually depends on the properties of interest. However, to study flexible molecules usually MD is applied, since several efficient implementations are available and MC lacks a standard and established method to sample the molecular internal degrees of freedom of a molecule. This problem arises since the standard Cartesian coordinates atomistic displacements usually applied within MC are very inefficient to generate structures with large conformational changes. In this work we implemented and improved a Configurational Bias Monte Carlo (CBMC) method used to sample molecular conformations in solvent. Based on the work of Shah and Maginn[1, 2] we implemented in the DICE package[3] a CBMC strategy that separates hard and soft degrees of freedom within a fragment scheme. We guarantee that the correct ensemble is sampled by enforcing the detailed balance to obtain the acceptance criteria. We checked and benchmarked our implementation[4] by applying it to octane and 1,2-dicholoroethane in different solvents. The trans and gauche populations were compared with experimental data and results from MD simulations. In both cases the results had an excellent agreement. We observe that at least for those systems, the correct population is achieved faster with our CBMC implementation than with MD, being the CBMC less likely to get trapped in local minima.

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DFT Calculations on Enantioselective Pd-Catalyzed Diboration of 1,1-Disubstituted Allenes: Dispersion-Drive Eantioselectivity

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Tang, Ding and coworkers developed the first enantioselective Pd-catalyzed diboration of 1,1-disubstituted allenes to form chiral alkene products with a quaternary carbon (Fig.1(a)).[1] We carried out DFT calculations to study the reaction mechanism and the origin of the enantioselectivity. Our results indicate that the enantioselectivity is dictated by oxidative addition of diboron concerted with allene insertion (Fig.1(b)). Distortion/interaction analysis reveals that a larger interaction energy especially dispersion interaction between the phenyl group on the allene and the two boryl groups in **TS1**$_{Re}$ than **TS1**$_{Si,}$ is the key factor for the enantioselectivity. Exclusion of the dispersion contribution could reverse the enantioselectivity. Dispersion-drive enantioselectivity is unusual, compared to the common steric-hindrance-driven manner.

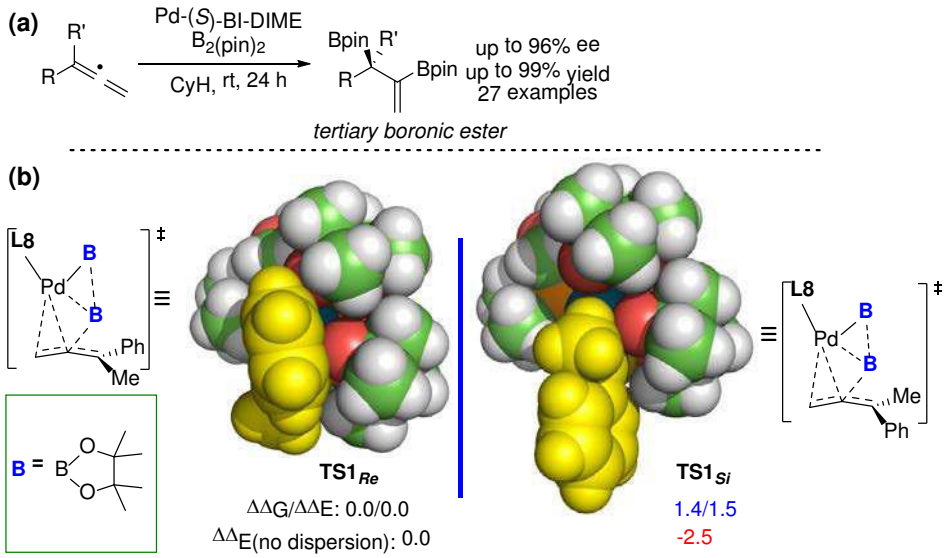

Fig.1 (a). Enantioselective Pd-catalyzed diboration of 1,1-disubstituted allenes. (b) Our key B3LYP-D3 results.

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Aluminum interaction with serine and O-phosphoserine

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Although, aluminum is the most abundant metal and the third most abundant element in the Earth's crust it has no essential role in any biochemical system in any extant organism[1]. In the last century, human intervention has made aluminum so available for biological systems. Unfortunately, there is increasing evidence that aluminum could be behind of a variety of toxic effects, with significant risks for human health[2].

The toxicity of aluminum is greatly affected by its bioavailability. Additionally, partly independently of the chemical form in which it is absorbed, it will interact with many potential Al binders in the various biofluids and tissues. Accordingly, speciation studies[3] are fundamental to understand the effects of Aluminum in biological systems.

In addition, phosphorylation of proteins is thought to increase their affinity for aluminum[5] and could be a key aspect in understanding the Al promotion of the NFT aggregation process[6]. The alcoholic-OH of Ser and Thr and the phenolic-OH of Tyr are the phosphorylation sites of proteins. Thus, phosphoserine (Pser) molecule serves as a model of phosphorylated protein residues.

The aim of this work is to give insight into the increase in the binding affinity of aluminum to phosphorylated proteins in general. As a first step of this goal, we characterize and compare the binding affinity of aluminum cation to Ser and PSer, by Density Functional Theory studies combined with polarizable continuum models to account for bulk solvent effects. This allows us to estimate the increase in aluminum binding affinity expected by phosphorylation of Ser in peptides.

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Preparing a computational database of surface structures for investigating catalytic reactions

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There is constant need for discovering new materials to yield better solutions of global issues in environment, renewable energy, and human health. To efficiently find candidates of new materials, data-driven researches were proposed in several perspectives. Materials screening based on a huge database can be more important in the future as more computational results are accumulated in both private and public databases with the advances in computational and theoretical methods. Nowadays, physical properties of bulk materials can be found in some open-databases and surface structures and their surface energies are available for elemental crystals. Here, we present our strategy of preparing a new database for studying chemical reactions on catalytic surfaces. Starting from structures in existing databases of elemental crystals, we performed first-principles calculations to generate our database. We will also discuss possible applications of our database for understanding reaction mechanisms on catalytic surfaces.

Experimental and theoretical investigations of spectroscopic properties of azobenzene derivatives

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A series of azobenzenes was studied using ab initio and DFT methods to determine the substituent effects on the ground and electronically excited states. Azobenzene molecule is known to undergo a photoisomerization from trans to cis conformation upon irradiation by light. The aim of the presentation is twofold. Firstly, we analyze different methods of calculations of electronic excitations of azobenzene molecule by comparing the results with experimental data. Secondly, we present the results of calculations of the UV-Visible spectra of azobenzene derivatives (e.g. Figure 1) and analyze the nature of the experimentally observed excitations.

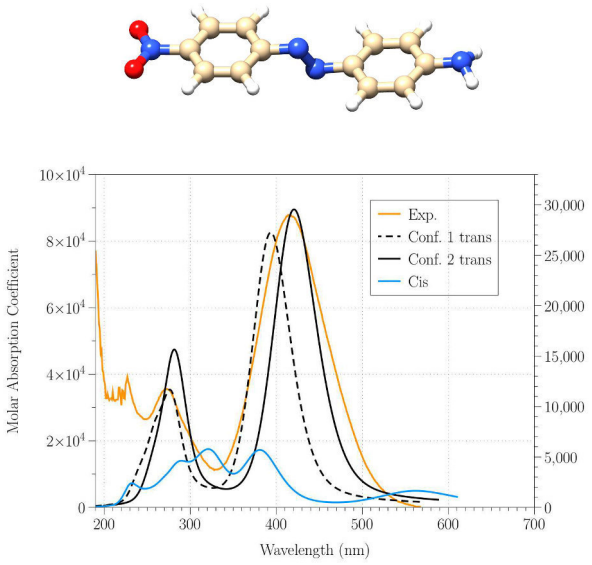

Figure 1: Disperse Orange 3 TD-DFT/CAM-B3LYP vs. experimental UV-Visible spectra

Computational Thermochemistry of Carbamic Acid and Related Compounds

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Carbamic acid (H2N-COOH, "CA") has been implicated in the equilibrium between solid ammonium carbamate and gas phase carbon dioxide and ammonia [1], as an intermediate in the production of urea from carbon dioxide and ammonia [2]; and as a participant in processes occurring in ammonia-carbon dioxide ices on interstellar grains [3]. Monomeric CA is not observed in the gas phase but existence of the dimer (CA)2 and perhaps higher-order clusters is suggested by IR studies [3,4].

Computational modeling of CA and associated species has relied primarily on density functional theory evaluations of molecular structures and harmonic frequencies, and has only rarely [2] been directed toward estimation of thermochemical quantities. Chemical accuracy (ca. 1 kcal/mol) is essential to the evaluation of mechanistic proposals for processes in which carbamic CA or related species may participate [1] . Here we report vibrational frequencies corrected for anharmonicity and estimates of thermochemical quantities of high accuracy derived from CBS-QB3 and Wn calculations. These results can guide experimental studies of kinetics and aid in the search for new species in the interstellar medium.

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The effect of the environment on the photodynamics of biological chromophores

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The key step in activation of many photoreceptor proteins is photoisomerization of a conjugated chromophore. Interactions between these chromophores and the protein matrix control the outcome and efficiency of these photoreactions. Understanding how proteins have evolved to mediate those excited state dynamics might be important to controlling photochemistry in artificial systems. As the required time and spatial resolution are notoriously difficult to access experimentally, we use excited-state molecular dynamics simulations with quantum-mechanical description (QM/MD) to simulate the photo-isomerization of the chromophore of the prototypical photoreceptor photoactive yellow protein (pCK). Whereas a single isomerization pathway was found in the protein [1], multiple pathways were observed in solution. Our simulations provide a detailed understanding of how solvent viscosity and hydrogen bonding control the isomerization process, which we a currently validating by means of time-resolved spectroscopy measurements.

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A QM/MM Study of the Catalytic Mechanism of Human β–ketoacyl Reductase

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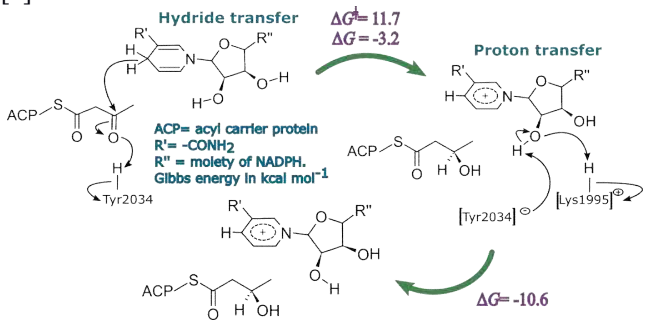
The β-ketoreductase (KR) is a catalytic domain in the human fatty acid synthase (hFAS) enzyme that catalyzes the reduction of β–ketoacyl to β–hydroxyacyl through a NADPH cofactor. The hFAS is a citosolic enzyme involved in the synthesis of palmitic acid, and is generally overexpressed in cancer cells. Thus, the catalysis by KR is an intermediate step in the cycle of reactions that elongate the substrate's carbon chain until the final product (palmitic acid) is obtained [1-2].

We conducted hybrid QM/MM calculation to propose the catalytic mechanism of the KR domain, at the ONIOM(B3LYP/6-311+G(2d,2p):AMBER) level of theory [3]. The QM/MM results have shown that the reduction step occurs in two stages; i) nucleophilic attack by the hydrogen in NADPH to the β–carbon of the substrate, with an asynchronous deprotonation of the Tyr2034 to hold the final alcohol product; and ii) an asynchronous deprotonation of the hydroxyl in the $NADP^+$'s ribose by Tyr, and of the Lys1995 by the resulting alkoxide in the former ribose. The Gibbs energy barrier for the rate-limiting steps in the first steps was found to be 11.7 $kcal \cdot mol^{-1}$ and the Gibbs reactions energy was -10.6 $kcal \cdot mol^{-1}$. These results seem to lead a suitable description of the catalysis by KR. In addition, we found that the oxyanion hole contributes for the TS stabilization through the hydrogen bond formation with the catalytic residues identified as essential for the reduction reaction [4].



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Sightseeing in the Electronic Structure: Topological Analysis of $|\Psi|^2$

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Local properties of a chemical system (e.g. partial charges, interaction energies) are expressed in its electronic wave function but the perception of the relations is lost with an increasing number of particles due to the high dimensionality. To retrieve these relations and derive chemical concepts and descriptors from them, usually, effective one-electron methods are employed and can be broadly categorized into orbital localization methods (e.g. natural bond orbitals analysis) and electron density methods (e.g. electron localization function, quantum theory of atoms in molecules).
In this work, we present a complementary approach considering the full, $3N$-dimensional, electronic wave function Ψ: A topological analysis of the probability density $|\Psi|^2$. By drawing $|\Psi|^2$-distributed samples and following the gradient of $|\Psi|^2$, we identify statistically significant and highly probable maxima constituting interesting sights in the electronic wave function. The associated electron arrangements, which we exemplarily show for the ethane molecule, exhibit highly ordered motifs that can be rationalized by means of Coulomb interaction and Pauli repulsion and show correlation effects [1]. We show that maxima are interconnected by maximum probability density paths and provide a natural, spatial partitioning of $|\Psi|^2$ into $3N$-dimensional attractor domains, which can be utilized for the definition of local properties. In future works, the results obtained from topological analyses of $|\Psi|^2$ can be employed to retrieve relations and derive chemical concepts and descriptors from the electronic wave function.

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Mechanistic studies and bonding situation on organometallic chemistry of gold(III) complexes.

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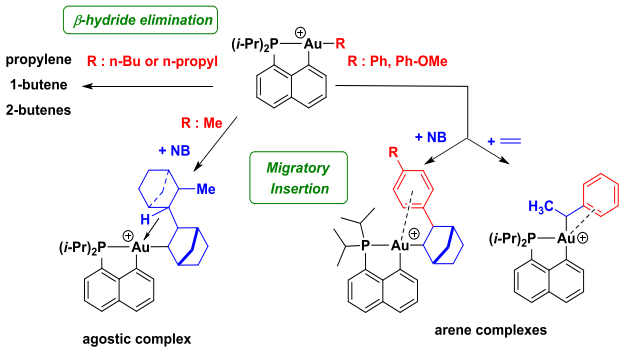
The organometallic chemistry of gold(III) compounds remained for a long time much less developed than that of their isolobal Pt(II) and Pd(II) counterparts.[1] Very little was known about the structure, stability and reactivity of gold(III) complexes because of the intrinsic instability of gold species in high oxidation state and the challenges associated with their synthesis. However, thanks to the recent development of new synthetic routes, a variety of new organometallic gold(III) compounds have been isolated and important insights have been gained into their intrinsic properties. Reductive elimination, transmetallation, and C–H activation, have been progressively documented. However, two last important elementary reactions were unknown and remained to be highlighted and described : the migratory insertion of unsaturated substrates into gold–carbon bonds and β-hydride elimination at low gold (III) center.

In the frame of our research program on the reactivity of gold complexes, we have obtained by a joint experimental / theoretical approach, precise insights into these unprecedented processes, demonstrating the ability of gold(III) complexes to undergo these two key organometallic transformations, [2] which comprise most of the important catalytic cycles.



This communication will report a detailed picture of the migratory insertion mechanism as well as the comprehensive study of β-hydride elimination at gold(III) by joint DFT and NMR studies. A particular attention will also devote to the description of new bonding situations (agostic interaction, π-complexes with gold(III)) in some intermediates by NBO and AIM analyses and calculations of specific NMR data.

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Impact of chosen DFT functionals on one- and two-photon absorption properties of fluorescent proteins chromophores

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Fluorescent proteins (FPs) belong to versatile and modern markers for visualization of various processes taking place *in vivo*. The chromophore – "the heart" of every fluorescent protein – is created in a series of autocatalyzed reactions without a need of external cofactors except for molecular oxygen. The mutagenesis of amino acids residues surrounding the chromophore brings the possibility of constructing novel FPs. In fact since mid-90s, a pallete of FPs has been obtained with absorption and emission spectra covering the whole visual spectrum as well as near ultraviolet and near infrared.

One of the most recent and rapidly developing directions of engineering FPs is searching for markers with high two-photon absorption (TPA) cross-section values for TPA-based visualization techniques possessing many advantages over one-photon absorption (OPA) based ones, including lower phototoxicity, higher resolution of images and deeper penetration of living tissues. Due to various drawbacks of experimental techniques for TPA measurements, it seems that theoretical chemistry methods will play a leading role in explaining mechanisms by which the protein environment influences chromophore's TPA spectrum, ultimately allowing for rational and directed design of FPs for TPA-based visualization techniques.

Such investigations will, however, require costly hybrid (QM/MM) calculations with polarizable force fields. Performing such calculations with wavefunction based methods, e.g. within coupled cluster ansatz although possible is extremely costly. For this reason, a computationally cheap yet reliable QM methodology is required. Currently, time-dependent density functional theory (TDDFT) seems to be the method of choice. However, the question remains which DFT functional should be used? In our present contribution, we analyse the gas phase excitation energies, OPA oscillator strengths and TPA cross-sections, calculated with the TDDFT methodology employing the BLYP (0 % of HF exchange), B3LYP (20 %), B1LYP (25 %), BHandHLYP (50 %) and CAM-B3LYP (19 % + 65 %) functionals for a variety of FPs' chromophores in reference to CC2 results. Our choice of DFT functionals is dictated by increasing percentage of the HF exchange energy, providing systematic assessment of this parameter impact on investigated spectral properties. We show a dramatic importance of the HF exchange energy for a qualitative recovery of TPA intensities in reference to *ab initio* CC2 results, while OPA oscillator strengths seem to be less affected. We believe that our work provides a missing, although important, assessment of TDDFT functionals for TPA and OPA properties calculations that also finds its applications for further calculations including protein environment.

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Nitrogen doping strategies for modulating the biradicaloid nature of acenes: insights from multireference calculations

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Acenes are fascinating polyaromatic compounds that combine impressive semiconductor properties with an open-shell character by varying their molecular size. However, the increasing chemical instability related to their biradicaloid structure poses a great challenge for synthetic chemistry [1, 2]. Modifying the π-bond topology through chemical doping allows modulating the electronic, optical, and physico-chemical properties of graphene-related materials [3, 4]. In spite of the practical importance of these techniques, remarkably little is known about basic question - the extent of the radical character created or quenched thereby. From a theoretical point of view, high-level *multireference methods* (MR) formally provide an adequate approach to address such a question [5]. In this work, we report a computational MR study on two acene oligomers chemically modified with different types of nitrogen defects. Moving the dopants from the terminal rings to the central ones leads to a remarkable variation in the biradicaloid character (and thereby also in the chemical stability). This effect is related to a π-charge transfer involving the dopants and the radical carbon centers at the zigzag edges. Our findings also provide specific guidelines to a rational design of large polyaromatic compounds with enhanced chemical stability.

Acknowledgments: Brazilian funding agencies CNPq, CAPES-ITA and FAPESP.

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Computation of Atom-Atom Electrostatic Energy in RNA Based on Multipolar Electrostatics

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Abstract: Empirical force field calculations on biological molecules (RNA) represent an effective method to obtain atomic detail information on the relationship of their structure to their function. Results from those calculations depend on the quality of the force field. Although state-of-the-art Molecular Dynamics (MD) force fields have been applied widely to simulate the structure and compute the stable free-energy of biological molecules (RNA), the results suggest yet not accuracy enough compared with the experimental results. In this manuscript, optimization of the atom-atom electrostatic energy for force fields is presented. The optimization procedure is based on small molecules from quantum mechanical studies. These small molecules are cut from the pilot RNA (2MVY), including phosphate, pentose, base, phosphate-pentose, pentose-base, or nucleotide, and are then capped by mimicking structure environment in RNA. The atoms in the small molecules are defined though Quantum Chemical Topology (QCT) as finite volume electron density fragments, each endowed with multipole moments. The minimum internuclear distance in the convergent region of all the 15 possible types of atom-atom interactions in RNA (2MVY) that were calculated based on phosphate, pentose and base are close to the values calculated from phosphate-pentose, pentose-base and from nucleotide. Calculations are completed at HF/6-31G(d,p), B3LYP/aug-cc-pVTZ, and MP2/aug-cc-pVTZ levels. Values obtained at these three levels are quite similar and are tested through another RNA (1ELH) which demonstrated the transferable of the convergence behavior. Furthermore, the change of the multipole moments for a selected central atom by varying the system it exists, and how far away this influence can be ignored is determined as well.

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A Computational Study of the Diels-Alder Reaction between 2,3-dibromo-1,3-butadiene and Maleic Anhydride

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The Diels-Alder reaction is one of the most important reactions in organic chemistry. It has been extensively studied in order to elucidate whether or not it is a concerted process and, if so, whether it happens in a synchronous or an asynchronous manner. The general picture has emerged that neutral reactions usually occur in a concerted fashion while cationic systems react in a non-concerted way [1, 2]. However, the border between asynchronous, concerted and stepwise mechanisms is not yet clear [3, 4].
Recent advances in molecular-beam experiments allow now conformational separation of isomers by electrostatic deflection of a molecular beam based on their different dipole moments [5]. Hence, the separation of the s-cis and s-trans conformers of a diene is possible as long as they meet the experimental requirements for this technique.
We aim to experimentally and computationally explore the detailed mechanism of the Diels-Alder reaction between conformationally selected 2,3-dibromo-1,3-butadiene and supersonically cooled maleic anhydride both in its neutral and cationic states. Here, we present computational results on this particular reaction. Density functional theory calculations show that the neutral reaction is concerted while the cationic reaction can be either concerted or stepwise. Further isomerizations of the Diels-Alder products have been explored in order to predict possible fragmentation routes that would be important for the interpretation of the experimental results. Rice-Ramsperger-Kassel-Marcus (RRKM) calculations suggest that under typical single-collision experimental conditions the neutral product may reform the reactants and the cationic product will most likely eliminate CO_2 [6]. We are currently working on the parametrization of a force field that will allow us to run reactive dynamics in this system [7].

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Improved partitioning of biomolecules for quantum-chemical embedding calculations based on graph theory

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Quantum-chemical subsystem methods [1] allow for the efficient calculations of local molecular properties, such as local excitation energies in biomolecular systems. To this end, the system is partitioned into a subsystem of interest (e.g., the chromophore) and its environment. This environment is usually further partitioned into smaller fragments.[2] For protein environments, a partitioning into fragments containing a fixed number of amino acids has so far been employed.[3]

Here, we employ methods from graph theory to determine the partitioning of protein environments for quantum-chemical embedding calculations of local molecular properties. The main challenge is to map the protein structure onto a graph in which the nodes are the amino acid residues connected by edges. Depending on the strength of interaction and distance to the subsystem of interest, weighting factors are assigned to the edges. These have to be chosen in a way that they estimate the error in the property of interest that is expected when assigning its two nodes to different subsystems. To obtain these weighting factors, we employed DFT calculations for all pairs of amino acids in small proteins. Based on these graphs we use heuristics and cut-offs for larger protein test cases where the direct calculation becomes computationally unfeasible.[4]

We then apply graph partitioning algorithms for partitioning the protein graphs into clusters with the lowest cut weights, i.e., the partitioning for which the estimated error in the local molecular property is low for a given number of fragments. Established graph partitioning tools had to be modified to be applied directly to such protein graphs, as some additional constraints had to be introduced due to chemical idiosyncracies.[5]

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PEGylation of Temozolomide (TMZ): A Molecular Dynamics study

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There has been a great interest in PEGylation of small drugs, mainly antitumor agents because of their low solubility, high toxicity, rapid excretion or untargeted biodistribution [1]. PEGylation can increase the circulating half-life of the drugs and also lead to a continued drug release [2]. However, the exact interaction between small drug molecules and PEG is still not clearly understood.
Imidazotetrazine compounds presented promising results as antitumor agents, but, only temozolomide is currently used [3]. However, there are some limitations, namely poor uptake and tumour cell resistance. PEGylation can help overcome these constraints by promoting drug delivery *in situ*, protecting against proteolytic enzymes and reticuloendothelial system (RES) uptake, leading to an increase in the circulating half-life.
In this study we performed several all atom molecular dynamic simulations with systems containing different poly(ethylene) glycol (PEG) molecules, the active form of an imidazotetrazine drug, temozolomide (TMZ) and salt at physiological conditions.
Based on the results we are able to evaluate the influence of type of functional group, molecular weight, presence of drug molecules and Na^+ and Cl^- ion concentration in the behaviour of PEG as well as provide atomic-scale insight into its interaction with other molecules and complement experimental findings. This is an on-going work and we plan to expand this study to other drugs, proteins and nanocarries such as dendrimers and liposomes.

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Decoherence of Electron Dynamics upon Ionization of Polyatomic Molecules

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Knowledge about the electronic motion in molecules is essential for our understanding of chemical reactions. The advent of attosecond techniques opens up the possibility to induce electronic motion, observe it in real time, and potentially steer it. Many theoretical studies so far treated molecular electron dynamics upon ionisation as a purely electronic process: by neglecting the nuclear coordinates, long-lived oscillations in the electronic density are then predicted. There has been an enormous experimental effort dedicated to observe the predicted oscillations in the electronic density of molecules [1], unsuccessful so far. But what does the oscillatory electronic motion actually become when the nuclear coordinates are taken into account? Here, we simulate the dynamics upon ionization of paraxylene (Figure 1a) and modified bis-methylene-adamantane, with a quantum mechanical treatment of both electron and nuclear dynamics using the direct dynamics variational multiconfigurational Gaussian method [2]. Our simulations give new important physical insights about the expected decoherence process. In particular, we show that the decoherence of electron dynamics happens on the time scale of a few femtoseconds (Figure 1b), with the interplay of different mechanisms [3].

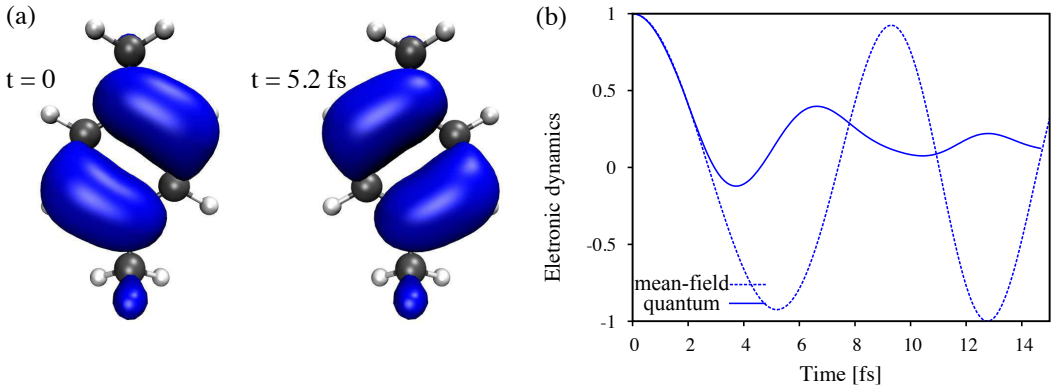

Figure 1: (a) Time-dependent hole density in paraxylene cation. (b) Electron dynamics with a mean-field nuclear motion (dashed line) and with quantum nuclear motion (solid line).

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Investigation of the degradation process of chlorhexidine using Density Functional Theory calculations

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Chlorhexidine (CHD) is a germicidal drug which has hemotoxic and carcinogenic degradation products. Although the descriptions of the main degradation products have been reported through experimental studies [1, 2, 3], there is no consensus either about the degradation pathway, or the molecule's structure in its neutral form. In order to shed light on that mechanism, we have employed Density Functional Theory calculations to study reactants (both conformers), in different protonation states, its degradation products and some intermediates involved in the different pathways. Based on free energy values comparison and frontier molecular orbital analysis in terms of energy and form/localization, we have obtained the most stable structures in each protonation state. CHD in saturated form was found as the most stable: it has HOMO localized in one *p*-chloroaniline, and, due to molecule's symmetry, HOMO-1 has contributions from the other side of the molecule, but mainly from the biguanide portion of the molecule, instead of from the *p*-chloroaniline. Also, for the saturated form we have studied two possible degradation pathways, starting from the monoprotonated structure, and three pathways starting from the neutral structure. We found out that the mechanisms proposed in literature, whose pathways lead to *p*-chloroaniline (PCA) formation in a smaller number of steps, are more likely than the mechanisms with more intermediate steps or pathways that do not predict PCA formation. Also, based on free energy results, we have found that the formation of another sub-product (PBG-AU) is favorable as well, being it our main result.

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Deep Eutectic Solvents: The Effect of the Hydrogen Bond Donor on Structure

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Deep Eutectic Solvents (DES) are a relatively new class of solvent, formed from mixtures of a salt and molecular hydrogen bond donor (HBD). At a certain molar ratio, the mixture of these two components exhibits a melting temperature far reduced compared to the pure components themselves. The archetypal DES is a 1:2 molar ratio mixture of choline chloride (ChCl, mp: 302 °C) and urea (mp: 133 °C), which is liquid at room temperature.[1]

The temperature depression in DES is thought to be the result of the intercalation of the HBD in the ionic salt lattice. However, this qualitative picture does not explain why different HBD species lead to different temperature depressions. Recently, we have presented the first structural model of bulk DES, based on QM/MD simulations,[2] which demonstrated that the structural ordering of the urea HBD determines the melting point depression. In this work, we present ab initio calculations of DES formed between ChCl and four HBDs - urea, thiourea, acetamide, and 2,2,2-trifluoroacetamide, to systematically probe the relationship between the HBD and the bulk DES structure. Analysis of non-covalent interactions (via the reduced density gradient[3] analyses) within $(ChCl)_xHBD_{2x}$ (x=1…5) clusters reveals for the first time the dominant intermolecular forces acting in DES, and how the HBD controls these interactions. Our results provide a new and fundamental understanding of the origins of solvation in this interesting class of solvents.

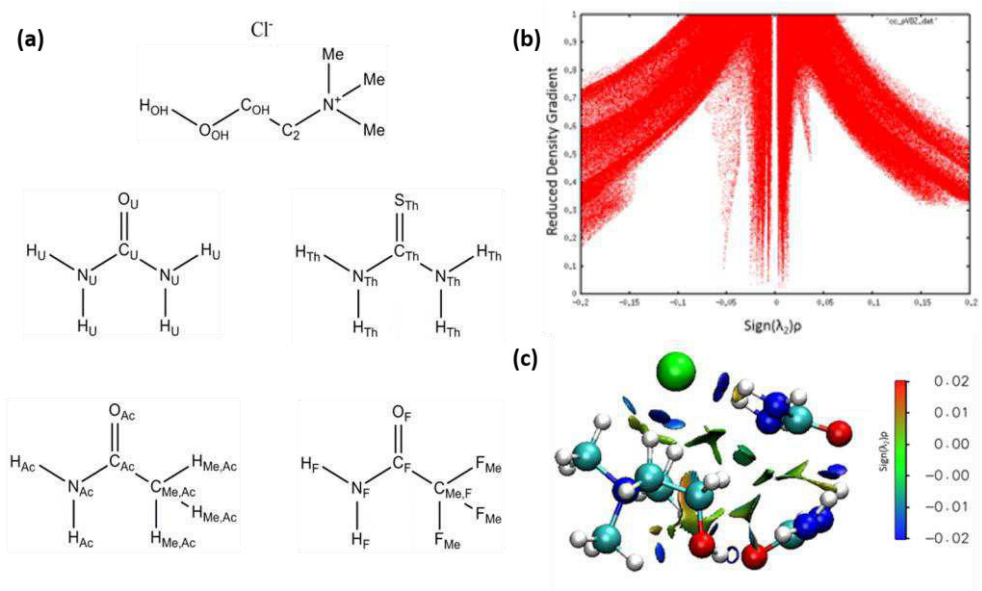

Figure 1. (a) Structure of parent salt (choline chloride, top) and HBDs studied (clockwise from top left; urea, thiourea, 2,2,2-trifluoroacetamide, and acetamide), (b) plot of reduced density gradient vs. electron density for ChCl:$Urea_2$ produced using NCIPLOT,[4] and (c) the graphical representation of structure and RDG isosurface (right).

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How does Nitrogen Change Carbon Nanotube Chirality? Insights from Quantum Chemistry.

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The chirality (*n, m*)-controlled growth of carbon nanotubes (CNTs) on a commercial scale is an ongoing challenge. Chemical vapour deposition (CVD) is the preferred method for the synthesis of CNTs though (*n, m*) product mixtures are obtained. Recent studies have shown that the addition of an etchant to the feedstock gas can alter the chirality and diameter during CVD [1]. However, the mechanism explaining how nitrogen changes CNT chirality during growth remains largely unexplored. Here, we present first principles denisty functional theory (DFT) calculations and non-equilibrium density functional tight binding molecular dynamics (DFTB/MD) simulations that reveal how nitrogen etchants, e.g. ammonia and acetonitrile, influence the CVD mechanism and change CNT nucleation during growth [2, 3]. We propose that particular chirality CNTs can be removed from CVD-produced distributions via "chirality-selective etching" [2]. DFTB/MD simulations additionally show that ammonia is selectively activated by the CVD catalyst, providing a sustained source of hydrogen during growth. These simulations reveal for the first time that nitrogenous species influence CNT nucleation and growth in new, unexpected ways.

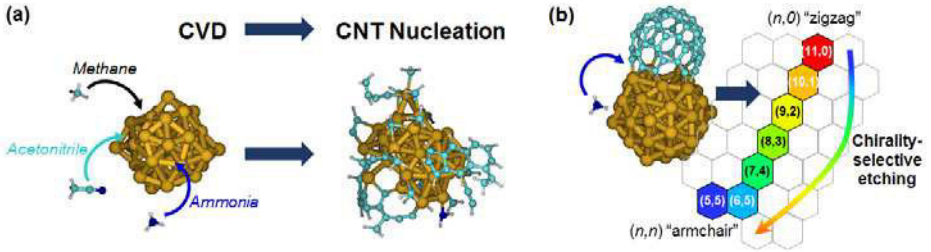

Figure 1. (a) DFTB/MD simulations show how ammonia and acetonitrile influence CNT nucleation on transition metal nanoparticles, (b) DFT calculations demonstrate CNT reactive selectivity is a function of (*n,m*) chirality.

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Development and Application of ReaxFF for Describing Catalytic Boron Nitride Nanotube Growth

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Boron nitride nanotubes (BNNTs), first predicted in 1994 [1] and experimentally realised in 1995 [2], are structural analogues to carbon nanotubes (CNTs). Unlike CNTs, BNNTs exhibit the same physical properties independent of the tube chirality, with a wide band gap of 5-6 eV [3]. Among other techniques [4], BNNTs can be synthesised effectively via boron oxide chemical vapour deposition (BOCVD) [5-8]:

$$B_2O_2(g) + 2NH_3(g) \rightarrow 2BN(s) + 2H_2O(g) + H_2(g)$$

The mechanism explaining this self-assembly process remains essentially unexplored. Here we report an atomistic mechanism to explain BOCVD and BNNT growth, using nonequilibrium ReaxFF molecular dynamics simulations [9]. ReaxFF parameters to describe B/N-transition metal interactions have additionally been developed for transition metals including Co, Cu, Fe and Ni. These simulations reveal, for the first time, the fundamental steps towards BN nanomaterial nucleation from B_2O_2 and NH_3 precursors during catalytic CVD and the process of B nanoparticle autocatalysis.

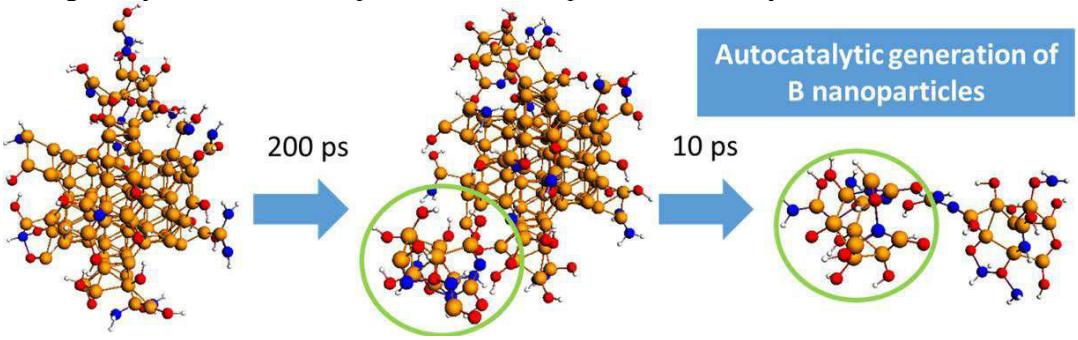

Figure: Non-equilibrium ReaxFF MD simulations reveal autocatalytic generation of boron nanoparticles during simulated CVD

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The electronic structure of the $[C_{20}X_{20}]^{-}$, $[C_{20}X_{20}]^{-2}$, $[Si_{20}F_{20}]^{-}$, $[Si_{20}F_{20}]^{-2}$ (X= F, Cl, Br, I) anions.

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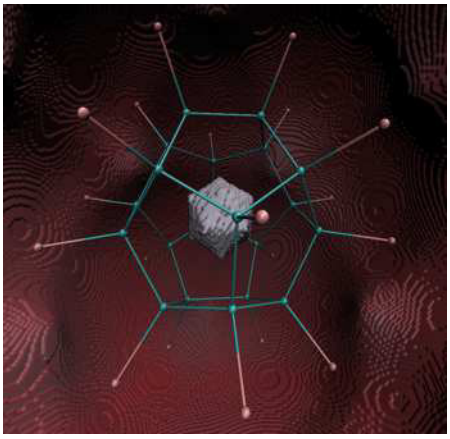
Following the strategy of Irikura [1] for design of electron boxes on the basis of fluorocarbon cages, we have studied three problems related to the localisation of electron density inside atomic cages: 1) a possibility to increase an amount of electron density inside the cage going from the $[C_{20}X_{20}]^{-}$ to $[C_{20}X_{20}]^{-2}$ anion 2) how the decreasing electronegativity of halogen in $[C_{20}X_{20}]^{-}$ and $[C_{20}X_{20}]^{-2}$ cages influences properties of electron density localised inside the cage and local electronic nature of C-C and C-X bonds, 3) a possibility of electron localisation inside the cage, where carbon is replaced by silicon for $[Si_{20}F_{20}]^{-}$and $[Si_{20}F_{20}]^{-2}$ clusters. The analysis of molecular electronic structure is performed in real space using topological analysis of Electron Localisation Function (ELF) [2]. Above methodology is free from the arbirtrary selection of molecular orbitals. This study is a continuation of our previous research [3] where we have shown that among the following radical anions: C_4F_4, C_8F_8, $C_{10}F_{16}$, $C_{20}F_{20}$, the local maximum of ELF inside the cage is observed only for the $[C_{20}F_{20}]^{-}$ cage. We believe that our results will contribute to the synthesis of new materials from molecular electrides group.



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From functional mechanism to new therapeutic tools: reaction modelling and computational design of PDC inhibitors.

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Pyruvate (PYR) dehydrogenase complex (PDC) is a multi-subunits molecular machine responsible of the conversion of PYR into acetyl-CoA by a process known as pyruvate decarboxylation. From the biochemical point of view PDC is the gatekeeper controlling the entry of carbon in the TCA cycle (also known as Krebs cycle) from two main sources: carbohydrates and gluconeogenic amino acids.
Metabolic modifications of cancer cells were firstly described by Otto Warburg in 1930, and subsequently confirmed by several studies. In particular, cancer cells have a higher rate of glycolysis than normal cells, however, according to the Warburg interpretation, this is mainly followed by lactic fermentation rather than mitochondrial PYR oxidation, as it happens in normal cellular conditions. In spite of this, recent investigations pointed out the importance of oxidative phosphorylation in some specific cancers [1-2]. Other studies, also carried out by some of us, highlighted a key role for the PDC activity in the progression of prostate cancer and glioblastoma. These observations confirmed that PDC inhibition, for a long time scarcely considered as target for the development of new anti-cancer drugs, could be a viable strategy for the design of new antineoplastic molecules.
In our studies, starting from the available structural information, we used multiple computational techniques to (1) improve our knowledge about the functional mechanisms of PDC and (2) identify new drug-like inhibitors.
These efforts lead to the identification of one lead compound able to inhibit both the enzyme and the prostate cancer cellular growth.
Moreover, applying different QM/MM calculations (geometrical optimization of relevant intermediates or Umbrella Sampling calculations) on specific structural models, we were able to estimate a free energy profile of the enzymatic reaction fully consistent with the available experimental data.
In strict collaboration with synthetic organic chemists and molecular oncologists, we are using the acquired knowledge about the PDC functional mechanism and computer simulations to design new molecules with improved affinity and bioavailability with respect to identified lead compound, obtaining encouraging results.

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Towards the description of non-covalent interactions in AP1roG model

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Geminal-based methods are a promising alternative to standard multireference methods because they allow us to efficiently model strongly-correlated systems, like bond-breaking processes and heavy-element chemistry [1–3]. One example is the Antisymmetric Product of 1-reference orbital Geminals (AP1roG) [1–4]. However, in order to reach chemical accuracy when predicting molecular properties, the missing correlation effects that cannot be described by electron-pair states have to be included in the electronic wave function. Different a posteriori corrections with an AP1roG reference function have been developed that aim at including dynamic electron correlation effects (see for instance Refs. [5, 6]).
In this work, we discuss a different approach to account for dynamic correlation on top of AP1roG in weakly interacting dimers that will allow us to model dispersion energies. Specifically, we apply Symmetry Adapted Perturbation Theory (SAPT)[7] to approximate the dispersion energy between two interacting monomers.

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CO_2 Hydrogenation using Earth Abundant Metal Catalysts: Role of Ligand

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Abstract: The catalytic conversion of CO_2 into useful products is highly desirable as CO_2 is a promising feedstock for one-carbon building block based organic products. In the CO_2 hydrogenation reaction, heterolytic H_2 cleavage and hydride transfer are usually the rate-determining steps. Using the density functional theory (DFT) calculations, earth abundant metal (Mn and Fe) based complexes (Figure 1) have been studied for CO_2 hydrogenation reaction. We show that the role of σ and π acceptor ligands is important to improve the rate determining steps. A base free CO_2 hydrogenation mechanism is possible in the presence of flexible ligands. Here, we will present a series of earth abundant metal-based catalysts with different set of ligands to show that earth abundant metal-based catalysts are very promising for CO_2 hydrogenation reaction.

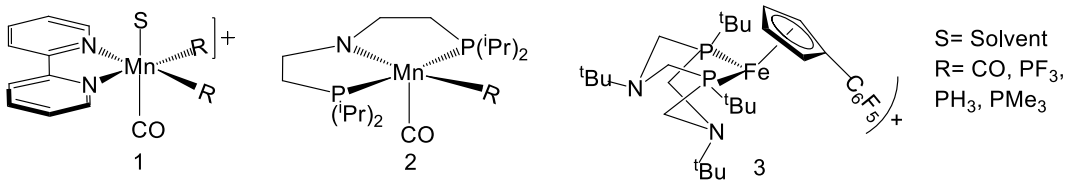

Figure 1. Different types of metal Catalysts have been studied for the CO_2 hydrogenation using different nature of the ligands.

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Instantaneous absorption spectra of firefly oxyluciferin using the first principle molecular dynamics simulations

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The spectroscopic characteristics of oxyluciferin and its conjugate bases, the emitters of firefly bioluminescence, are critical for understanding firefly bioluminescence. In our studies, first, we elucidated the vibronic effect on the absorption and fluorescence spectra of the firefly oxyluciferin and its conjugate bases. While the energies of the excited states were calculated with the time-dependent density functional theory (TD-DFT), the solvent effect was incorporated using the polarized continuum model (PCM). The calculated absorption energies are slightly lower than the experimental ones. The calculated spectral shapes well reproduce the experimental shapes except for the case of keto type of oxyluciferin anion of which theoretical spectra peak is very sharp, different from the experimental broad shape. Then, the effects of hydrogen bonding interactions were clarified through a theoretical study on the stability of the oxyluciferin anions with explicit water molecules using the first-principles molecular dynamics (FPMD) simulations [1]. These simulations showed that enol type of anion is more stable than keto type because of the unique features of the static and dynamical hydration structures, which are difficult to capture using the PCM solvation model. Next, the absorption spectra of aqueous oxyluciferin anions were derived using the structures obtained from the FPMD simulations at room temperature for each isomeric form, in order to account for the effects of vibrations of oxyluciferin anions and dynamical fluctuations of their hydration structures [2].

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Low-lying excited states and diradical nature of conjugated dicarbonyl compounds

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The open-shell electronic structure of certain organic systems has demonstrated to be fundamental for the comprehension of their remarkable physico-chemical properties, leading to applications in a broad range of fields of materials science.[1] As a general observation, this kind of systems are usually characterized by a small energy gap between the open-shell singlet ground state and the lowest triplet state. Thus, these systems are promising candidates to host the singlet fission (SF) process, a mechanism that may enhance the efficiency of conventional solar cells, by which a singlet excited state splits into two triplets, following the condition $E(S_1) \geq 2E(T_1)$. Despite the scientific effort carried out, additional molecular design protocols are required to achieve a system with real application. In such a way, diradicals has been proposed as a class of promising SF sensitizers.[2] As a representative part of a larger investigation, in this communication we present an analysis of the diradical character and the low-lying excited states of 19 quinone-like molecules, classified as benzoquinones (BQ), pentaloquinones (PQ), naphtoquinones (NQ) and anthraquinones (AQ), in the pursuit of new efficient SF molecules.

Due to the inherent difficulties in the proper description of diradicaloids, a previous benchmark has been performed assessing TDDFT and spin-flip TDDFT (SF-TDDFT) methods. The diradical character is evaluated by means of the spin-projected UHF (PUHF) method. While the diradical character ranges between 0 and 0.8, the optimal structures are characterized by a moderate diradical character (0.1-0.4). Both TDDFT and SF-TDDFT demonstrate to work well depending on the diradical character. Several molecules fulfill the aforementioned conditions, and those labeled as 1,4-PQ, 1,6-PQ, 1,5-NQ, 1,7-NQ, 2,6-AQ, 1,10-AQ, and 2,9-AQ seem to be promising for their application as singlet fission sensitizers.

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Energetics and dynamics of a light-driven sodium-pumping rhodopsin

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The conversion of light energy into ion gradients across biological membranes is one of the most fundamental reactions in primary biological energy transduction. Recently, the structure of the first light-activated Na^+ pump, *Krokinobacter eikastus* rhodopsin 2 (KR2), was resolved at atomic resolution [2]. In order to elucidate its molecular mechanism for Na^+ pumping, we perform extensive classical molecular dynamics (MD) simulations and hybrid quantum mechanics/molecular mechanics (QM/MM) calculations of transient photocycle states. Our simulations show how the dynamics of key residues regulate water and ion access between the bulk and the buried light-triggered retinal site. We identify putative Na^+ binding sites and show how protonation and conformational changes gate the ion through these sites toward the extracellular side. We further show by correlated *ab initio* quantum chemical calculations that the obtained putative photocycle intermediates are in close agreement with experimental transient optical spectroscopic data. The combined results of the ion translocation and gating mechanisms in KR2 may provide a basis for the rational design of novel light-driven ion pumps with optogenetic applications.

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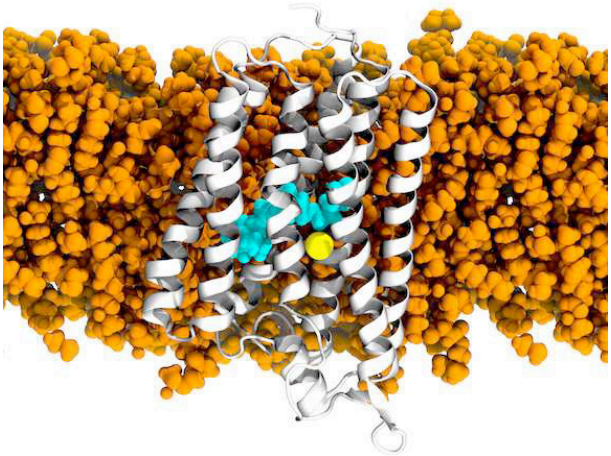

Mechanistic Study on Photocatalytic Water Splitting with Carbon Nitride Materials

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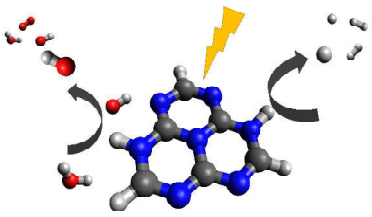
Impressive progress has recently been achieved in photocatalytic water splitting with so-called graphitic carbon nitride materials consisting of heptazine (tri-*s*-triazine) building blocks [1]. In addition to efficient hydrogen evolution in the presence of sacrificial electron donors, stoichiometric splitting of pure water with doped C_3N_4 materials has been reported [2,3]. However, the fundamental mechanistic principles of the photoinduced reaction and the catalytic cycle are, as yet, poorly understood.

We provide first-principles computational evidence that water splitting with carbon-nitride based materials can be understood as a molecular photochemical reaction taking place in hydrogen-bonded chromophore-water complexes. The oxidation of water occurs homolytically via a light-driven concerted electron/proton transfer from water to heptazine. Via a conical intersection of the potential-energy surface of the charge transfer state with the electronic ground state, ground-state heptazinyl and OH radicals are generated. It is shown that the excess hydrogen atom of the chromophore radical can be photodetached by a second photon, which regenerates the chromophore. A water molecule is thus catalytically split into H and OH radicals by the sequential absorption of two photons. Alternatively to the photodetachment reaction, two heptazinyl radicals can recombine in an exothermic dark reaction to form H_2 and two heptazine molecules. The recombination of OH radicals is also exothermic and may yield H_2O_2 and eventually O_2 and H_2O in catalyzed dark reactions. The proposed photochemical reaction scheme within hydrogen-bonded chromophore-water complexes is complementary to the traditional paradigm of photocatalytic water splitting, which requires the separation of electrons and holes over substantial time scales (microseconds) and distances (micrometers).



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Fluorescent markers for the dection of amyloid-β in Alzheimer's disease

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Alzheimer's disease is a progressive disorder of the central nervous system showing several pathological hallmarks, including plaques caused by aggregation of the peptide amyloid-β (Aβ) into fibrils. According to the amyloid cascade hypothesis, deposition of Aβ in the brain is the central event of Alzheimer's pathology and thus, detection of these deposits is crucial to monitor the evolution of this disease.[1]

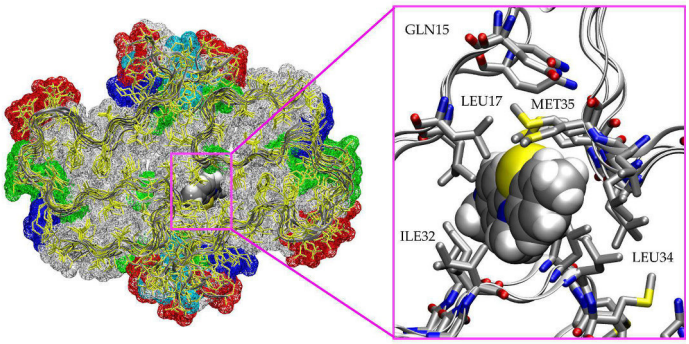

Figure 1: Binding pose of a marker on a model of Aβ42 fibril.

Several Aβ fluorescent markers have been studied with TDDFT and fit-induced docking techniques with the aim of optimizing their optical properties and affinity for Aβ fibrils. Results indicate that Aβ fibrils affect the fluorescence properties of these markers through a number of mechanisms, such as reducing the efficiency of non-radiative decay pathways through hindering of molecular flexibility and disaggregation of quenched aggregates spontaneously forming in aqueous solution. Additionally, the binding of these markers to Aβ fibrils has been shown to be aspecific and driven by geometric complementarity and weak interactions.[2,3]

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DFT Study of Cp*Co^{III}-Catalyzed C−H Alkenylation/Annulation Reactions of Indoles with Alkynes

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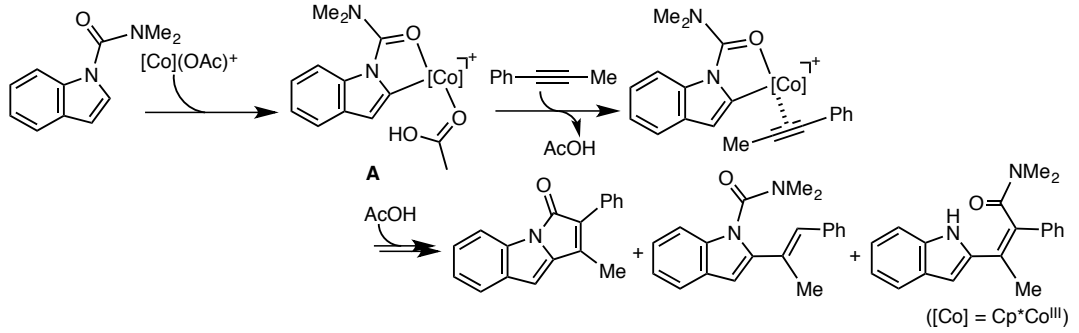
In Cp*Co^{III}-catalyzed C−H functionalization reaction of indoles with alkynes, pyrroloindolone synthesis as well as C2-selective C−H alkenylation of indoles has been reported [1]. In this study, the reaction pathways were examined by using M06-level DFT calculations. After the C≡C bond in the alkyne is inserted into the Co−C bond at an intermediate alkenyl-Co complex (**A**) given by the C−H bond activation step, the reaction pathway bifurcates into alkenylation and annulation pathways (**Scheme 1**). When AcOH coordinates to the Co atom, alkenylation proceeds via proton transfer. On the other hand, the annulation pathway to give pyrroloindolone proceeds in the case where the ring-closure C−C bond formation is followed by the attachment of AcOH. At a high temperature (393K), the difference in the Gibbs free energy between the transition state for proton transfer in the alkenylation pathway and that for the attack of the alkenyl carbon to the carbamoyl carbon in the annulation pathway is relatively small, so both pathways are significant. We further found another pathway to provide the directing-group migration on the way to annulation. This finding well elucidates the recent experimental report that tetrasubstituted alkenes were obtained as the major product under different conditions [2].

Scheme 1



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Ab Initio Crystal Orbital Calculation of Electronic Structure of B-type model-DNA

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Abstract: As an attempts at the electronic structure calculations of the B-type model-DNA, the double helix polymers including sodium atoms as counter cation are performed by means of *ab initio* Hartree-Fock crystal orbital method adapting the screw axis-symmetry[1-3]. All sugar backbones and ions are included in the calculations. The calculation levels are at 3-21G and 6-31G levels.

The simplest DNA model is polymononucleotide, just using guanine and cytosine (or adenine and thymine) base pair. The dG and dC pair repeats with 3.38 angstrom translation and 36 degrees rotation becoming a double helix polymer. The base sequences of two polymononucleotides and four polydinucleotides are shown in Fig. 1. We hereafter use the abbreviations AT, AC, AG, and GC for poly-(dA-T)poly-(dA-T), poly-(dA-C)poly-(dG-T), poly-(dA-G)poly-(dC-T), and poly-(dG-C)poly-(dG-C) in Figure 1, respectively. In addition we use GG and AA for poly-(dG-G)poly-(dC-C) and poly-(dA-A)poly-(dT-T), respectively. These are really polymononucleotides, however, for the comparison of the results of polymononucleotides with those of polydinucleotides, a double-sized unit cell is applied for polymononucleotide for easy comparison with the results of polydinucleotides.

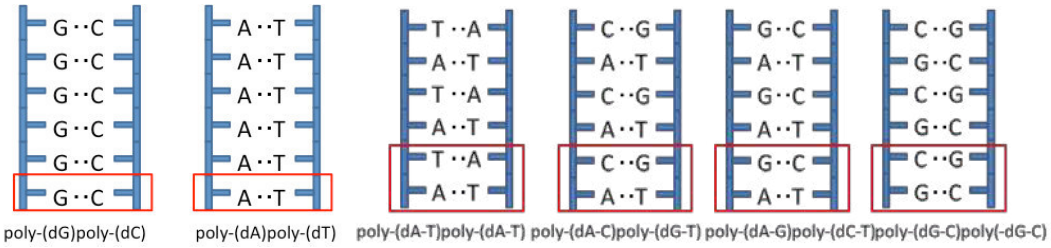

FIGURE 1. The structures of base sequences of polymononucleotides and polydinucleotides.

Hole conductions could be expected better in the G-C pair rich environment, while electron conductions could be expected for all the environments. The next step of the present work are; (1) re-calculate with more larger N values, the convergence of properties would not be sufficient, (2) calculate all poly-mononucleotide and di-nucleotide with and without ions, and (3) calculations of poly-trinucleotide. Such a calculation is in progress and will be published elsewhere.

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COMPUTATIONAL MODELING OF VERSATILE PHOTOSENSITIZERS

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Nowadays, the most available renewable energy source on the planet is sunlight. Therefore, one of the most prolific chemical research lines in photovoltaics cells consists in the search for dyes, molecules to be used in the so-called Dye-Sensitized Solar Cells (DSSC). Solar cells are a promising alternative to the silicon photovoltaic cells because they are easier to build and very economical. The challenge today is to improve the yield of DSSC in the transformation of sunlight into electricity.[1] Dyes used in DSSC can also be used in Organic Light Emitting Diodes (OLEDs) devices and in the water splitting process.[2]

In this project, we have studied the electronic structure of sixteen copper photosensitizers (three have been synthetized and characterized in the lab) using different density functionals in the framework of Time-Dependent Density Functional Theory (TDDFT).[3] We have analyzed LC-ωPBE functional by optimizing the attenuating parameter (ω).[4] Our results show the importance of the improvement of several properties upon optimization of ω, such as the simulation of UV-Vis absorption spectra and REDOX potentials. Research is underway in our laboratories to improve the adjustment of the computationally simulated absorption spectra and find new molecules that present a wider range of absorption.

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Multistructural microiteration technique for geometry optimization and reaction path calculation in large systems

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To efficiently explore reaction paths accompanied by a large scale structural transition in the surrounding part of large systems, we have proposed a multistructural microiteration (MSM) technique [1]. In the MSM method, the surrounding part is described as the weighted sum of multiple structures to account for a large-scale structural change along the reaction path. Each surrounding structure is independently optimized with fixing atoms in the reaction center part, and then, geometrical displacements of the reaction-center atoms are compute in the mean field generated by the weighted sum of the multiple surrounding structures. In this study, the MSM technique combined with the ONIOM method [2] was applied to organic reactions in water solution and also to enzyme reactions.

Figs. 1a) and 1b) show relative energy and weight factors of surrounding structures along the AFIR path [3]. Relative energy found by the MSM method was lower than that by ONIOM-microiteration, showing that favorable surrounding structures changed along the AFIR path. In Fig 1b), the weight factor of "Surrounding 1" was the largest among the five surrounding structures for both reactant and product, while that of "Surrounding 2" was the largest around the highest-energy point on the AFIR path. From Fig1c), energy barriers of ONIOM-microiteration and MSM were 41.4 and 32.3 kcal/mol, respectively, where the total energies of the reactant structure by the ONIOM-microiteration and MSM methods were −293.89394 and −293.89670 (a.u.), respectively. The energy profile determined by the MSM method was lower in absolute energy over the entire IRC profile than that determined by the ONIOM-microiteration method.

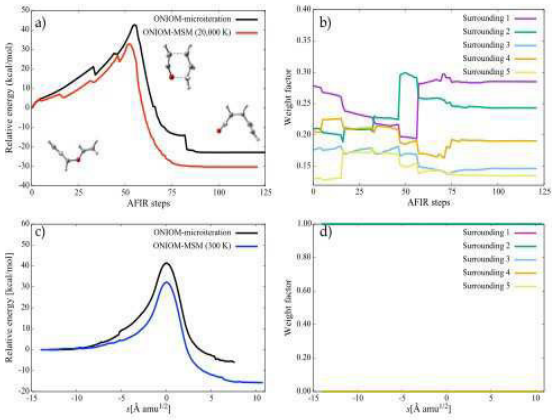

Figure 1. Relative energy (a) and weight factors of the ONIOM-MSM method at T^{MSM} = 20,000 K (b) along the AFIR paths, and relative energy (c) and weight factors at T^{MSM} = 300 K along the IRC paths, for Claisen rearrangement in aqueous solution.

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Nuclear motion is classical

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The Born-Oppenheimer approximation can be replaced by a better approximation in a very simple way. The consideration starts from the notion that it is problematic to describe the nuclei and the electronic cloud in a similar way, hoping that quantum mechanics will somehow generate meaningful results for these two different types of objects. This is not the case. In the end one wants to have well localized nuclei, eventually smeared out a bit due to temperature. The only consistent way to achieve this is by treating the motion of the nuclei classically right from the beginning. The result is the ab-initio molecular dynamics (AIMD) energy expression. Movies of chemical reactions generated with AIMD show clearly that this approach is working well. Failures of the Born-Oppenheimer approximation are reduced to a technical problem.

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Heavy Atom Secondary Kinetic Isotope Effect on Tunneling

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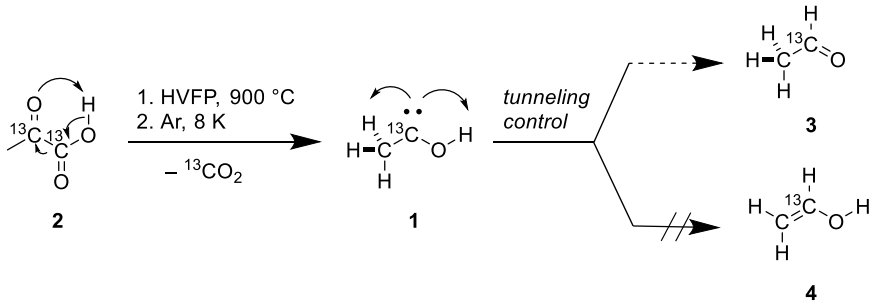
Methylhydroxycarbene **1** can be generated by high-vacuum flash pyrolysis (HVFP) of pyruvic acid **2** and trapped in a solid noble gas matrix at 3 K.[1] The hydroxycarbene rearranges through a tunneling controlled [1,2]H-shift reaction to the thermodynamic product acetaldehyde **3** with a half-life τ of 1 h in argon. The expected kinetic product vinyl alcohol **4** does not form under matrix isolation conditions.



Here we investigate the effect of heavy atom ^{13}C labelling of the carbene center on the rate of H-tunneling experimentally and computationally. Isotope substituted 1-^{13}C-**1** was prepared by HVFP of 1,2-^{13}C-**2** and the tunneling half-life determined in noble gases (Ne, Ar, Kr, and Xe). The secondary tunneling kinetic isotope effect (KIE) was determined and compared with the computations. The latter utilized the one-dimensional WKB[2-4] approach as well as the multidimensional instanton[5-7] and CVT/SCT[8] tunneling models.

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Why Lead(II) Hydride Complex Would be Better for CO_2 Activation than Its 14 Group Analogues?

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A low valent $Pb^{(II)}$ hydride complex with NacNac ligand (NacNac = $[ArNC(Me)CHC(Me)NAr]^-$ with Ar = 2,6-$iPr_2C_6H_3$) is predicted to be the best catalyst for CO_2 activation compared to its $Ge^{(II)}$ and $Sn^{(II)}$ analogues, which have been experimentally reported[1, 2]. The CO_2 activation mechanism was studied in toluene using density functional theory calculations mediated by $Ge^{(II)}$, $Sn^{(II)}$ and $Pb^{(II)}$ catalysts. The results show that the activation can be carried out through two reaction pathways, giving rise to two different conformers which have been computationally predicted for the first time. In all the cases, the activation process was thermodynamically favored, in addition, the $Pb^{(II)}$ catalyst exhibited the lowest activation energy compared with $Ge^{(II)}$, $Sn^{(II)}$, and even $Si^{(II)}$. Thus, it was found that, going down in group 14, the reactivity of the NacNac based complexes toward CO_2 activation increases considerably. Additionally, a detailed characterization of possible interconversions between the products of activation helps to explain the X-ray structures obtained to date. Our calculations suggest that the CO_2 activation catalyzed by $Pb^{(II)}$NacNac hydride complex would be both thermodynamically and kinetically viable. The reactivity trend found in this work contributes to the growing development of CO_2 activation by transition metal-free catalysts.

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Ab initio Molecular Dynamics Simulations of the Ion Irradiation on CH_4 Ice

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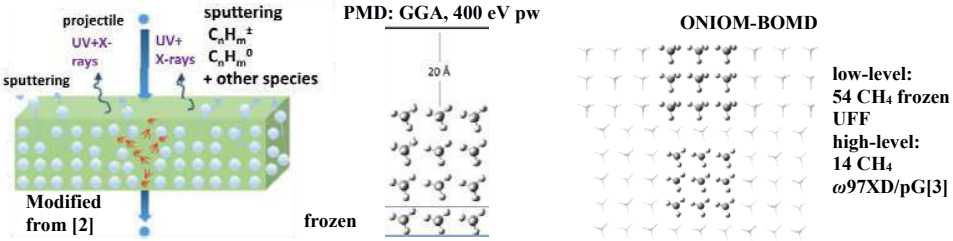
The occurrence of methane (CH_4) in the solar system and interstellar medium is of particular significance: interstellar body surfaces containing condensed CH_4 are continuously modified by physicochemical processes, such as: heating, radiolysis (cosmic rays and stellar winds) and photolysis (UV and X-rays). Laboratory simulations of ices bombarded with MeV heavy ions (projectiles) may help to understand the formation and destruction of molecular species in interstellar icy mantles. It is well established that ions, radicals, and atomic species are released, generating new molecular species. In this work, the temporal behavior of the fcc-CH_4 under the influence of projectile impacts is modeled. The projectile effect is considered in two ways: i) by including an initial velocity (corresponding to 0.02 eV [1]) in various H atoms, or ii) by increasing the sample temperature (298 K, 600 K and 900 K); in a neutral, cationic and anionic potential energy surface (PES). DFT molecular dynamics (MD) implemented in G09 [Born−Oppenheimer MD (BOMD)] and VASP [Periodical MD (PMD)] programs are employed. In the case of BOMD simulations the ONIOM-BOMD variation is utilized, while in the PMD approach, the 001 surface is employed. The trajectories were analyzed until 1*ps*.



Only CH_4 desorption from the sample is obtained with PMD, irrespectively of the temperature used or the PES considered. In the ONIOM-BOMD no desorption is observed, and the amorphization of the sample is predicted. In the cationic PES, one of the C-H bond increased its length in two CH_4 molecules, triggering the H-H interaction to form the H_3C---H---H---CH_3 complex. Repetition of this process may generate the desorption of H_2 and C_nH_m molecules in concordance with experimental results [4].

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Second-Order Perturbation Theory Based on Density Matrix Renormalization Group: Applications for Transition Metal Complexes

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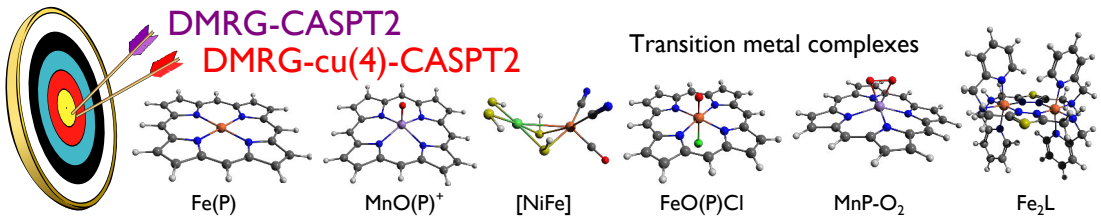
The density matrix renormalization group (DMRG) [1] is considered one of the most promising methods to study strongly correlated molecular systems (e.g. transition metal complexes) because of its compact parametrization of the wave function. However, DMRG only includes static correlation and inefficiently treats dynamic correlation, hindering its applications for quantitatively studying transition metal (TM) complexes. To circumvent this biggest problem of DMRG, perturbative approaches on top of DMRG [2, 3, 4, 5] have been used to account for dynamic correlation.

In this work, we demonstrate the applications of DMRG-CASPT2 [5] to study a series of important chemical properties in TM complexes. We first discuss the accuracy and limitations of an approximation of DMRG-CASPT2, in which calculations of the 4-particle reduced density matrix 4-RDM is avoided (DMRG-cu(4)-CASPT2 [2]), to study spin state energetics of iron porphyrin Fe(P), NiFe hydrogenase, and manganese-oxo porphyrin $MnO(P)^+$ [6]. More challenging problems were studied with the exact solution of DMRG-CASPT2, as implemented in our recent Molcas-CheMPS2 interface. Employing an efficient contraction of the generalized Fock matrix with the 4-RDM, reliable DMRG-CASPT2 calculations with an active space of ~30 active orbitals can be performed. We employed DMRG-CASPT2 to study spin state energetics of a model for compound I (FeO(P)Cl), new families of dinuclear Fe(II) spin-crossover compounds, and binding energy of O_2 to metal porphyrin anions.



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XMCQDPT2 calculations elucidated the origin of red to far-red spectral tuning in light-sensitive proteins phytochromes

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Photoswitchable photoreceptor proteins phytochromes reversibly photoconvert between two thermally stable Pr (red light absorbing) and Pfr (far-red light absorbing) forms. The interconversion is driven by the photochemical isomerization of the tetrapyrrole chromophore covalently bound to the protein via its pyrrole ring A. Upon the C15=C16 double-bond isomerization [1], the pyrrole ring D changes its hydrogen bonding; it interacts with the conserved histidine in the Pr form [2] and with the conserved aspartate in the Pfr form [3]. Because of the rather large molecular size of the chromophore, the origin of the spectral tuning in phytochromes has not yet been investigated using quantum-chemical calculations. For the first time, we performed excited-state calculations of the phytochrome models using the state of the art multi-configurational multi-reference XMCQDPT2 method [4]. These calculations allowed identifying intermolecular interactions of the chromophore with the protein that induce the red shift in the Pfr form as compared to the Pr form [5]. We demonstrated that interactions between ring D and the carboxylate group of the conserved aspartate lead to bond-length alternation of the tetrapyrrole. The geometry change reflects on the change in the electronic structure, which translates to the red shift of the absorption spectrum of the Pfr form. Further, we tested performance of the widely used TD-DFT method in the calculations of the phytochrome color tuning. Understanding the role of hydrogen bonding in control of the tetrapyrrole color provided by our calculations and analysis may facilitate engineering of phytochromes and other tetrapyrrole binding proteins as photoswitches and fluorescent proteins operating in the red spectral region.

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How do oxidised phospholipids affect the properties of a lipid bilayer?

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Oxidative stress continues to be associated with aging and disease. It is known to affect the pathophysiology of lipids in conditions including, but not limited to, Alzheimer's disease, cycstic fibrosis, atherosclerosis, cardiovascular disease and cancer. Lipid peroxidation has a wide and varied impact on cells, and little is know about the effects of oxidative stress on the integrity and biophysical properties of the cell plasma membrane. To address this, we performed a series of microsecond-timescale atomistic molecular dynamics simulations of bilayers containing standard and oxidised phospholipids. We studied the following bilayers: 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC), POPC + cholesterol, POPC + oxidised POPC (1-palmitoyl-2-(9'-oxononanoyl)-*sn*-glycero-3-phosphocholine (PoxnoPC) or 1-palmitoyl-2-azelaoyl-*sn*-glycero-3-phosphocholine (PazePC)) and POPC + cholesterol + oxidised POPC (PoxnoPC or PazePC). Our results suggest that membrane composition influences the basic biophysical properties of bilayer systems, including bilayer thickness, permeability to water, area per lipid, bilayer phase and ordering. This is fundamental to our understanding of the effect of lipid peroxidation on biological membranes.

Computational study of hydrogen shift reaction catalysed by sulphuric acid in Criegee intermediate

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Abstract: The Criegee intermediates (CIs) are formed during ozonolysis of unsaturated hydrocarbons in the troposphere. The fate of the CIs is of critical importance to troposphere oxidation chemistry, particularly in the context of secondary aerosol formation. Using the high-level G4(MP2) ab initio method, we investigate the 1,4 hydrogen shift reaction in all CIs of two common biogenic hydrocarbons: isoprene and α-pinene. We consider the uncatalyzed reaction as well as the reaction catalyzed by a single water molecule and by sulphuric acid. We find that sulphuric acid is a very effective catalyst leading to a barrierless process relative to the free reactants. In contrast, the water-catalyzed mechanism is associated with a significantly higher reaction barrier. The present findings provide insights into the reaction mechanisms by which larger and less volatile organic compounds are generated in the troposphere from smaller components as required for aerosol growth.

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On-the-fly Kinetic Monte Carlo based on Global Reaction Route Mapping

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Molecular dynamics simulations of chemical systems and reactivity are plagued by the timescale issue: very small timesteps require prohibitively long simulations to achieve experimentally relevant timescales, even for classical force fields. This problem is exacerbated for systems characterized by infrequent state-to-state transitions (i.e. "rare events"). Kinetic Monte Carlo (KMC) [1-3] can overcome this problem, however is based on the assumption that the complete set of the state-to-state transitions and associated rate constants (the "move table") is known *a priori*. Ideally, the move table should be constructed "on-the-fly" at each successive equilibrium point as the system evolves [4-6]. Here, we describe a new on-the-fly KMC algorithm [10] that uses global reaction route mapping (GRRM) [7-9] to determine all possible reactive pathways around an equilibrium point, and demonstrated its capabilities in describing intramolecular proton transfer, nanoscale surface diffusion and intramolecular rearrangement.

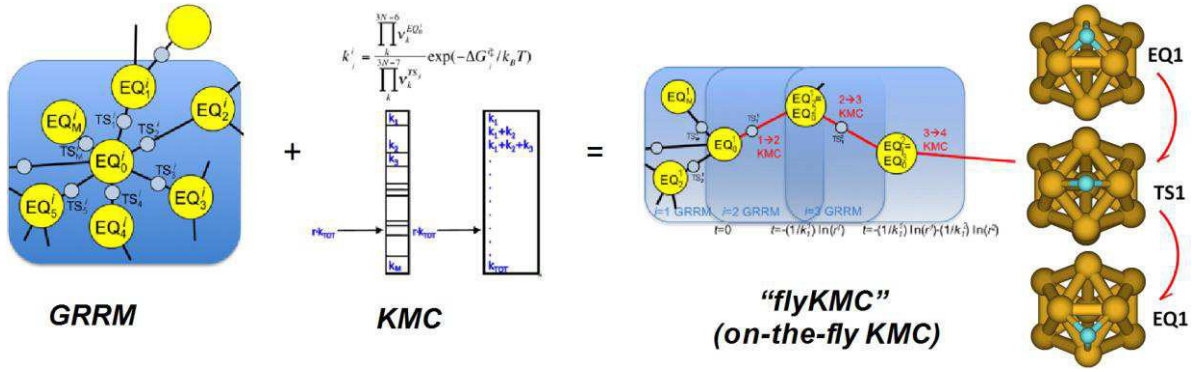

Figure 1: GRRM-KMC algorithm for determining the KMC move table on-the-fly. This can allow us to simulate diffusion

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Serenity: A Subsystem Quantum Chemistry Program

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We present key features of our new quantum chemistry program SERENITY. It implements a wide variety of functionalities with a focus on subsystem methodology. The modular code structure in combination with publicly available external tools and particular design concepts ensures extensibility and robustness with a focus on the needs of a subsystem program.

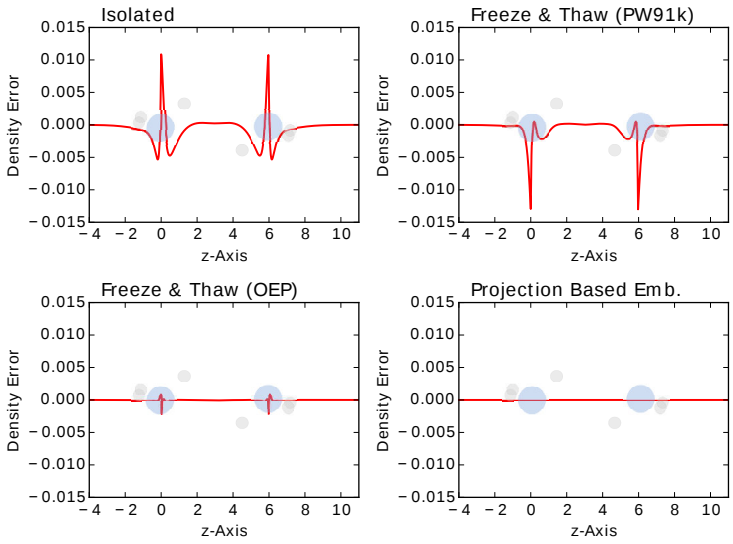

Figure 1: Comparison of different embedding techniques w.r.t. a supersystem calculation in terms of the density error.

Several important features of the program are exemplified with sample calculations using subsystem density functional theory, potential reconstruction techniques, a projection-based embedding approach and combinations thereof. Further features as well as motivation and implementation details are highlighted on the poster.

Towards laser pulse control of molecular symmetry breaking and restoration

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Symmetry breaking is a fundamental process in chemistry. Fascinating examples of molecular symmetry breaking by laser pulses have already been demonstrated, both experimentally and theoretically, see Refs. [1, 2, 3, 4]. Here we show that laser pulses can also achieve the opposite effect, symmetry restoration. For this purpose, the laser pulse for symmetry restoration must be designed as the time-reverse of the pulse that broke the symmetry, and the time of time-reversal must coincide with the instant when the molecule with broken symmetry is represented by a real wave function. As a proof-of-principle, quantum dynamics simulations demonstrate restoration of D_{6h} symmetry of benzene, after laser induced $D_{6h} \rightarrow C_{2v}$ symmetry breaking[3, 4]. Experimentally, one may allow marginal deviations from the theoretical results. Accordinglly, the laser pulse for symmetry restoration has to be applied with 10 as precision. This challenge reminds of analogous requirements for control of the laser pulses' carrier envelope phase (CEP) for various tasks such as high harmonic generation (HHG)[5]. Gratifyingly, the present experimental state-of-the-art allows to control the time delay between two laser pulses with the required resolution.[6]

ACKNOWLEDGMENTS
Generous financial support by the Deutsche Forschungsgemeinschaft (projects Ma 515/26-1 and Tr 1109/2-1) and China Scholarship Council are gratefully acknowledged.

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Combining AIMD and Neutron Scattering Data based EPSR Simulations to uncover Water Participation in Catalysis

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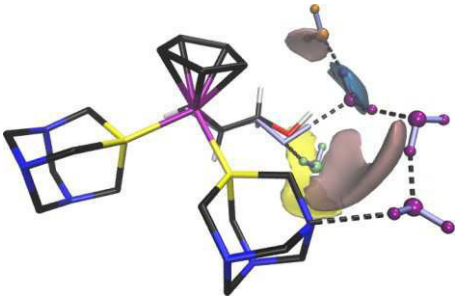
The advantages of using water as a solvent in catalysis are obvious: it is abundantly available, cheap and easily recyclable. However, the majority of homogeneous catalytic processes mediated by metal complexes take place in organic solvents which is due to the insolubility of many complexes and the easy decomposition of most of the catalytically active metal complexes in water. In order to shed light on the reaction mechanism of catalytic processes in water two things are of key interest: the complex/substrate conformation and the interaction with water. Aqueous solutions pose a challenge for many classical analytic methods. Experimental techniques like NMR or theoretical approaches like DFT can give some indications on complex conformation. By taking into account the electronic structure, AIMD (*ab inito* molecular dynamics) simulations with explicitly described water are able to give a detailed picture of coordination of single water molecules, their influence on solute conformation and their evolution over time. Small angle neutron scattering is capable of detecting hydrogens and is predestined to examine molecules in water. The EPSR (Empirical Potential Structure Refinement) simulations use data from the neutron scattering measurements to refine structure and determine probabilities of water distribution.



Overlay of AIMD snapshot and EPSR spatial density functions of water

On the example of the water soluble complex $[RuCp(H_2O\text{-}\kappa O)(PTA)_2]^+$ (PTA = 1,3,5-triaza-7-phosphaadamantane) that catalyses the isomerization of allylic alcohols to aldehydes or ketones and that shows increased catalytic efficiency in the presence of more than a stoichiometric amount of water[1,2], we herein present the combination of AIMD and EPSR simulations that can aid identifying catalyst and substrate conformation and water participation in aqueous solutions.

Acknowledgement: European Commission FEDER program (CTQ2015-67384-R MINECO), Junta de Andalucía PAI FQM-317, COST Action CM1302 (WG1, WG2).

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MD Simulation Analysis on Asynchronous Solute-Solvent Coupling Magnitude in Ring Closing Reaction of Chromene

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Chemical reaction kinetics in condensed phase normally obey Transition State Theory (TST) under thermal equilibrium of whole system. However, the rate constant behaviour deviate from Arrhenius plot (dynamic solvent effect) when the coupling between solute and solvent become unsynchronous under TST breakdown.

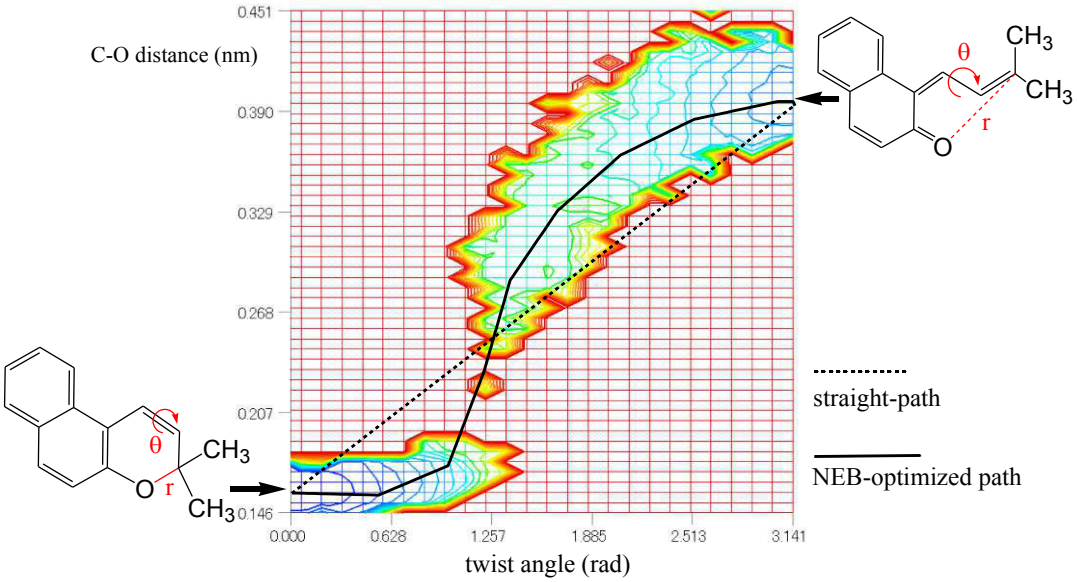

Fig. 1 Schematic 2D-FES for two CVs (θ, r) reaction path

In the present study, the non-TST behavior of reaction rate constants of thermally slow cyclization of chromene is computationally analyzed based on topological characteristics of Free energy surface (FES). FES are constructed by metadynamics sampling along the reaction path opmimized Nudged Elastic Band (Fig.1). MD simulations are carried out using REAX-FF [1] which is a special form of force field describable for bond generation/fission. The asynchronous solute-solvent coupling magnitude is estimated by the ratio between FES(θ_TS,0)/FES(θ_TS, r_TS), which qualitatively correspond to the solvent contribution ΔG realtive to the whole reaction ΔG.

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Theoretical description of excitations and excitonic couplings of perfluoropentacene

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Organic solids consisting of π-conjugated molecules play an important role for the design of different electronic or optoelectronic devices. Perfluoropentacene is a typical example for these organic π-conjugated systems, which are used for instance as organic field-effect transistors.

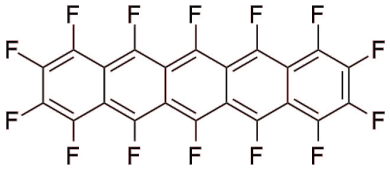

Figure 1: Structural formula of perfluoropentacene

This compound has been chosen as model systems to describe the formation of excitons and the vibrationally assisted transitions between different electronic states. The electronic and vibrational structures are calculated with DFT and CC2 methods, the vibronic transitions are described by Franck-Condon and Herzberg-Teller profiles.
To describe the excitonic coupling in the solid state, an effective model Hamiltonian is used, which is parametrized according to the crystal structure and to the results from the electronic calculations of the molecule.

$$\hat{H}_{\text{eff}} = \hat{H}_{\text{ex}} + \hat{H}_{\text{vib}} + \hat{H}_{\text{ex-vib}}$$

With this, a model description of aggregates is achieved which can be used to compare to experiment and identify the relevant vibronically excited states.

Lowest electronic states of alkali (Li, Na, K, Rb) – alkaline-earth (Ca, Sr) diatomic molecules

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Alkali and alkaline-earth atoms are well under control in ultracold physics and are good candidates to form ultracold molecules with a permanent electric and magnetic dipole moment[1]. In contrast to heteronuclear alkali diatomics, which are already under investigation in ultracold physics, allows the combination of an alkali atom with an alkaline-earth atom to produce a molecule with an unpaired electron and due to this a corresponding magnetic moment. This opens up new possibilities to manipulate these molecules and to make use of intermolecular interactions[2]. In the current work the lowest excited states of eight such molecules were determined by a multiconfigurational self-consistent field calculation followed by multireference configuration interaction[3]. This approach yielded reliable potentials in previous studies, where the results were compared to experiments of our group[4, 5, 6]. In order to estimate the methodological uncertainty of the results we also performed coupled cluster and perturbation theory computations. For the four heavier compounds also spin-orbit interaction was considered by two different approaches. The resulting potential energy curves were then used to determine the vibronic states. The Franck-Condon factors in combination with the electronic transition dipole moments were applied to obtain the Einstein A factors between different vibronic states. These results will be presented and trends as well as the influence of uncertainties of the computed properties will be discussed.

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Global Search for Periodic Structures of Carbon by Artificial Force Induced Reaction Method

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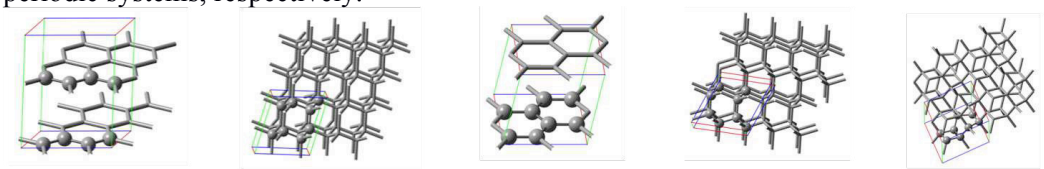
[Introduction] Properties of materials depend not only on their composition but also on their crystal structure. For example, carbon has various allotropes [1] such as graphite, diamond, etc. Furthermore, many crystal structures have been predicted theoretically. *M*-carbon and Cco-C_8 (or *Z*-carbon), etc. are those predicted recently. Prediction of their structures has been a great challenge in computational science. One- or two-dimensional periodic structures such as carbon nanotube and graphene have also been attracted attention as novel materials and catalysts. In our group, an efficient method, artificial force induced reaction (AFIR),[2] has been developed for automated exploration of chemical reaction pathways. This method has been applied to various chemical reactions in the gas phase and in the solution phase. In this study, we extended the AFIR method for periodic system by combining this method with periodic boundary conditions (PBCs). This approach is tested for searches of periodic structures of carbon, not only crystal but also one- and two-dimensional structures. [3]

[Method] All calculations were carried out by utilizing a local developmental version of the GRRM program. Energies, gradients, and lattice stresses were computed by density functional theory (DFT) using the PBE functional and DZP basis sets as implemented in the SIESTA program. Grimme's dispersion is also considered.

[Results and Discussion] As a case study, the SC-AFIR was applied to carbon with a very small unit-cell which includes eight carbon atoms (C_8/unit-cell). The search was initiated from one random structure. Then, we obtained 274 structures of carbon crystals including famous structures such as graphite and diamond. Fig. 1 shows some of local structures. The obtained structures include not only known structures but also a lot of unreported ones. In addition, the searches for one- or two-dimensional periodic structures were also performed. The search found 49 and 122 local structures for the one- and two-dimensional periodic systems, respectively.



3D-min0 graphite $P6_3/mmc$ 0.0 kJ/mol·atoms | 3D-min1 diamond $Fd\bar{3}m$ 0.1 kJ/mol ·atoms | 3D-min2 graphite $R3m$ 0.9 kJ/mol·atoms | 3D-min3 lonsdaleite $P6_3/mmc$ 2.8 kJ/mol ·atoms | 3D-min4 Cco-C_8 $Cmmm$ 12.7 kJ/mol·atoms

Fig.1 Five most stable structures of the C_8/unit-cell among 274 structures obtained by the automated search. Name of structure, space group, and relative energy are shown in labels.

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Decoherence correction and trivial crossing detection in fragment-orbital based surface hopping.

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Simulations of charge transport in large pi-conjugated systems (e.g. organic semiconductors or biological molecules) are paramount to a better understanding of their carrier mobilities and to improve the performance of low-cost and promising opto-electronic devices. While hopping and wide band theories have proved inappropriate to study this kind of systems in most situations [1, 2], polaronic band theories based on Holstein-Peierl-Hamiltonians have shown to give a better transport description [3]. Going beyond model Hamiltonian approaches, the development of direct charge propagation schemes, such as non-adiabatic molecular dynamics is of great importance. In this respect, Tully's surface hopping approach [4] can aid to deal with these large and complex systems. Within this strategy, the nuclei evolve on a single potential energy surface and nonadiabatic effects are included by allowing hopping from one surface to another according to the fewest switches algorithm. Nevertheless, this method requires the calculation of the Hamiltonian and the nonadiabatic coupling elements at each time step, making the procedure still computationally very demanding.

Our fragment-orbital based surface hopping method (FOB-SH) has been specifically designed to overcome this difficulty. In particular, the ultrafast calculation of Hamiltonian and forces of the system allows us to treat fundamental charge transfer properties in large molecular assemblies without assuming any specific charge transport model [5].

Here, we present the results obtained by applying this strategy to chains of organic molecules. We consider particularly fundamental requirements (e.g. total energy conservation, detailed balance and internal consistency) that the surface hopping algorithm should fulfil. We show how solving well-known limitations of the SH approach for instance the overcoherence of the electronic wavefunction or the trivial crossing problem improves the quality of our simulations. In particular, we investigate different decoherence methods that could be used to reach the internal consistency and also the trivial crossings correction, proposed by Prezhdo *et al.* [6], to deal with finite MD timesteps. We find that damping the wavefunction coefficients at each time step massively improves on internal consistency and the trivial crossing correction gives more accurate Boltzmann population and/or allows for larger time steps.

The results presented in this work will serve as starting point for studying even larger systems (e.g. organic crystal and proteins).

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Adsorption and dissociation of water on tungsten trioxide (001) from first principles

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Photocatalytic water splitting is a cutting-edge topic nowadays since there is no environmental friendly and efficient way known for hydrogen production. This reaction can be catalyzed by metal oxides, which are stable, cheap, non-toxic and abundant in nature. Unfortunately, the frequently investigated material titanium dioxide [1] has a too large band gap in order to use the spectrum of visible light efficiently for water splitting. A more promising material in this context is tungsten trioxide, which has on the one hand a more suitable band gap and an appropriate valence band position for oxygen production, but on the other hand an unsuitable conduction band position for hydrogen evolution [2].
At this point, a deeper understanding of the water splitting mechanism is crucial in order to make this reaction more efficient. Calculations with periodic boundary conditions offer a powerful tool regarding the modelling and understanding of adsorption processes and reactions on solid surfaces.
In this work, we present results of the interaction of water in its molecular and its dissociative form on the perfect tungsten trioxide (001) surface. We used hybrid density functional theory as implemented in the CRYSTAL14 [3] program package. These results are useful in order to perform *ab initio* cluster calculations for ground and excited states.

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Water adsorption on tantalum(V) nitride (100): favourite adsorption sites and surface behaviour

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The efficient splitting of water into its elementary components hydrogen and oxygen represents one of the most studied reactions in nowadays society. A promising approach consists of using an appropriate photocatalyst that harvests the sun light as an energy source to initiate this reaction. Although many oxide semiconductors were already investigated, no feasible catalyst is available yet.[1] However, non-oxide, nitride-based semiconductors gained much attention recently. One candidate is tantalum(V) nitride (Ta_3N_5) due to its suitable band gap of about 2.1 eV and its band edges.[2] Experimentally, its ability to split water is being improved by controlling its morphology and employ nanostructuring.[3] From a theoretical point of view, the interaction of water with the Ta_3N_5 surface represents the key to understand the initial step of the water dissociation reaction and may aid in further improving the design of an efficient Ta-based photocatalyst.
In this contribution, we therefore want to investigate the influence of water adsorption on Ta_3N_5 by quantum chemical density functional theory calculations. As a versatile program package to model such adsorbate-surface systems, we use the CRYSTAL14 program code with periodic boundary conditions based on linear combinations of atom centered Gaussian functions.[4] As a first step, we thoroughly analyse the structure and energetics of the (100) surface, which represents the thermodynamically most stable surface.[5] Subsequently, an adequate model system will be utilised for the adsorption of water in its molecular and dissociative form. Our results will be directly comparable to previously published plane-wave based calculations [6] and will constitute the basis for an embedded cluster approach to address the electronically excited state during the water photodissociation process.

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Towards efficient coupled-cluster theories for periodic systems

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Over the last few years, quantum-chemical correlation methods have been increasingly often applied to extended systems. In this work we explore canonical coupled-cluster theory within the projector-augmented-wave method using a plane-wave basis as implemented in the VASP code. A combination of Gaussian basis-functions with plane-waves [1], as well as a low-rank factorization of the Coulomb integrals [2] results in an effective quantum-chemical scheme for extended systems. We demonstrate the capabilities of the methods by benchmarking water adsorption on two-dimensional or quasi two-dimensional periodic surfaces [3, 4]. Our findings show that quantum chemical approaches are becoming a robust and reliable tool for solid state electronic structure calculations, providing an additional tool that can further improve widely-used van der Waals density-functionals.

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Intramolecular electronic flux during adiabatic attosecond charge migration

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We develop the quantum theory of the electronic flux that drives the time dependent motions of electrons during charge migration. Applications to model systems reveal the following fundamental aspects (A-J).

H_2^+ can be prepared in a superposition state of the electronic ground (σ_g) and first excited (σ_u) states such that the charge is localized on one nucleus. From this initial condition, the charge migrates periodically between the nuclei, with the period $\tau = 550$ as [1]. The model of Eyring, Walter and Kimball allows to derive analytical expressions for time evolutions of the electron density, flux density, axial electron density, and axial flux. Accordingly: (A) the flux is a simple product of the axial electronic yield times a sinusoidal temporal factor; (B) the flux satisfies various symmetry rules; (C) the absolute value of the axial flux is maximal at $t = \tau/4$, at the nuclear center of mass where the axial electron density has its local minimum; (D) Charge migration is depleted by decoherence between the bound electronic ground state and dissociative excited state; (E) Charge migration proceeds without electron correlation. [2,3]

Recently, quasi-field-free charge migration in $HCCI^+$ was investigated [4]. Experimentally, the initial ($t = 0$) state is found to be a superposition state of the electronic ground and first excited state of the cation. We show that: (F) this initial state can be prepared by ultrafast ionization of HCCI [4] or by electronic excitation of $HCCI^+$.[5] The excess electronic charge then migrates periodically between the acetylenic and ionic moieties, with period $\tau = 1.85$ fs; (G) the maximum axial electronic flux occurs between the two moieties where the axial density has its local minimum; (H) the electronic flux is launched already during the laser pulse that prepares the initial state; (I) we can design electric fields to optimize the electronic flux.[6]

Finally, we show (J) how to control the angular electronic flux during charge migration in non-aromatic excited benzene, by means of linearly and circularly polarized laser pulses.[7-9]

Financial support by Deutsche Forschungsgemeinschaft (projects Ma 515/26-1 and Tr1109/2-1) and by the talent program of Shanxi is gratefully acknowledged.

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[2,3,5-9] see our recent work – will be presented at WATOC 2017

In-Silico Homovalent Screening of Hybrid Halide Perovskite Materials for Tandem Solar Cells

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Solar cells based on hybrid organic-inorganic lead-halide perovskites are among the most promising emerging photovoltaic materials of the past decade. Within only a very short research time span, record efficiencies were achieved with solar cells based on methylammonium lead iodide ($CH_3NH_3PbI_3$). Despite these notable achievements, many of the basic properties of hybrid perovskite materials are not yet fully understood.

The presence of Pb in the currently most efficient perovskite solar cells has raised questions over the possible toxicity of these devices and the extent of their environmental impact. Therefore, a lot of research has been devoted to finding alternative perovskite materials with similar or even better optoelectronic properties. A flipside strategy to improve the efficiency of thin-film solar cells is to build efficient tandem cells by combining materials with specifically tailored band-gaps. The prospect of building thin-film tandem cells made of two or more layers of different hybrid perovskites, however, yet needs to be explored.

The first step towards the development of perovskite-only tandem solar cells is to identify complementary hybrid perovskite materials with specifically tailored band gaps to maximize the efficiency of the tandem cell. The optimal set of optical gaps for a tandem structure made of two different materials is 1.9 eV and 1.0 eV. Since the electronic properties of hybrid perovskites are known to be strongly dependent on the composition and the distortion of the crystal lattice, we start our search by focusing both on the band gap and the perovskite crystal structure calculated from density functional theory (DFT). As a first step, geometrical and electronic structure of the different candidate structures for application in tandem cells are calculated using semilocal (PBE) and hybrid DFT functionals (HSE) with relativistic corrections. To assess the error in the band-gap predicted by the DFT calculations, quasi-particle energy band gaps of some reference structures are calculated using the first principles G_0W_0 approach.

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A Quasi-Diabatization Scheme on the Study of Vibronic Coupling of Chlorophylls Excited States

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Radiationless relaxation in molecular excited states plays significant roles in many photophysical and photochemical processes, such as light harvesting in photosynthesis and photoprotection in skin. In particular, the ultrafast dynamics of internal conversion of Q_x to Q_y in chlorophylls is crucial to the high efficiency of light harvesting in photosynthesis. In this work, we explored the internal conversion processes of chlorophyll a (Chl a) and bacteriochlorophyll a (BChl a) theoretically by evaluating the vibronic couplings and electronic couplings to construct effective Hamiltonians in diabatic basis describing non-adiabatic phenomena. The first principle study of radiationless relaxation of Q_x to Q_y was achieved by combining time dependent density functional theory (TD-DFT) and diabatization method through enforcement of configuration uniformity [1]. The parameters are obtained using harmonic approximations and TD-DFT calculations, leading to excellent agreement between experimental and simulated absorption and high-resolution fluorescence line narrowing (ΔFLN) spectra [2, 3]. Our results successfully predict ultrafast Q_x to Q_y relaxation in both chlorophyll systems and indicate that the relatively strongly-coupled modes in high frequency region matching the electronic energy gap facilitate the internal conversion process in the chlorophyll systems. The model we proposed enables detailed dynamical study of the energy relaxation in the chlorophyll systems, allowing us to gain insights into the nature's design of the most important chromophore in photosynthesis. Furthermore, the general methodology shown in this work could be applied to other radiationless relaxation processes, which could find broad applications in the study of photoactive materials used in photovoltaic and photocatalysis.

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Evaluation of the Cohesive Energy of a Solid via Lattice Sums

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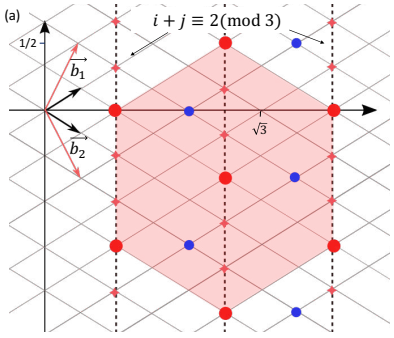
The main contribution to the cohesive (binding) energy of a solid comes from the interaction energies between all possible atom pairs in the extended system. Using an extended Lennard Jones functional form, $\sum_{n>3} c_n x^{-n}$, to describe the dimer interaction one arrives at an analytical expression for the (two-body) cohesive energy per atom [1]: $E_{\mathrm{ELJ}}^{\mathrm{coh}} = \frac{1}{2} \sum_{n>3} c_n L_n r_s^{-n}$. The beauty of this formula is that it only depends on the dimer potential parameters c_n, the next-nearest neighbour distance r_s and the so-called Lennard-Jones-Ingham, LJI, coefficients L_n. Analytical expressions for other solid-state properties like pressure, bulk moduli and zero-point energy follow directly.

The LJI coefficients only depend on the underlying symmetry of the lattice and thus, have only be computed once for every lattice structure, but they present very slowly converging sums. For cubic lattices, several expressions for the LJI have already been derived and techniques for a fast evaluation developed [2]. Here, we will give a visual interpretation of these cubic lattice sums. This visualisation allowed us to find alternative representation for the cubic LJI coefficients and most importantly, a new formula for the hexagonal closed packed structure was found (see figure). This formula allows us to use the same techniques as in the cubic cases. Therefore an efficient and accurate evaluation of the LJI coefficients is now possible.



The B layer (red atoms) of the 'ABAB' hcp structure forms a 2D hexagonal lattice shifted against the A layer (containing the reference atom at the origin). By scaling the basis vectors and mirroring the atoms from the left (blue atoms) one recovers the unshifted lattice again.

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Molecular dynamics simulation studies of structure and dynamics of poly(acrylic) acid in semidilute concentration regime

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A detailed fully atomistic molecular dynamics (MD) simulation study was carried out with the aid of explicit specification of solvent molecules on poly(acrylic) acid (PAA) in salt free aqueous solution from dilute to semidilute concentration region at different degree of ionization (*f*) values viz. f = 0.2, 0.4, 0.7 and 1.0. The structural properties viz. Radius of gyration (R_g), end-to-end distance (R), hydrogen bonding (interchain, intrachain and intermolecular), intermolecular structure, bound water ratio, scattering structure factor, interchain distance, interchain contacts and dihedral angle distribution have been elucidated. The dynamic properties viz. hydrogen-bond dynamics and self diffusion coefficient of PAA and counterions have been reported and compared with experimental and model studies. The results have revealed that, conformation size (R_g and R) decreases with increase in polymer volume fraction (ϕ_P) which is in qualitative agreement with the experimental studies where, ionized PAA particle length decreases with increase in PAA concentration in the semidilute region [1]. Moreover, this behavior is in agreement with the model studies [2] that, demonstrated a decrease in conformational R_g with polymer concentration. The number of interchain and intrachain H-bonds show an increase with increase in ϕ_P. The self diffusion coefficient of PAA and sodium counterions showed a non-monotonic and monotonic decrease with increase in ϕ_P which, is in good agreement with the bead – spring polyelectrolyte model studies under fully ionized conditions [3]. The details of analysis of properties will be presented.

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Quantum chemical investigation of the incorporation of Uranium(V) into Magnetite

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Thorough characterization of the chemical states and redox kinetics of uranium in contact with magnetite are of substantial importance for understanding uranium transport and retention mechanisms in the near and far fields of nuclear waste repositories. Uranium has two main environmentally relevant redox states, highly mobile U(VI) and sparingly soluble U(IV). U(V) is frequently believed to form as an intermediate species in redox processes. It exhibits a so far poorly investigated geochemical behavior, although from a chemical perspective a close analogy with Np(V) is to be expected. Recent experimental studies at KIT-INE applying high-energy resolution X-ray absorption spectroscopy and EXAFS found that uranium(V) incorporated in octahedral magnetite sites remains stable over 226 days under ambient conditions as unambiguously shown for the magnetite nanoparticles containing 1000 ppm uranium [1] .

Magnetite has Fe^{3+} at octahedral as well as tetrahedral sites and Fe^{2+} at octahedral sites. Fe^{3+} is a high spin case and the occupation of the five d-orbitals in the ligand field is obvious. This is not so clear anymore for Fe^{2+} where two important questions arise: (i) what is the occupation pattern for Fe^{2+} and, (ii) is the ground state nondegenerate? These questions were addressed with the multireference complete active space self consistent field (CASSCF) calculations. This is not only of theoretical interest but a major issue because DFT require a nondegenerate ground state. This system was in a first step characterized with CASSCF. Based on these results we further performed plane wave density functional (DFT+U) calculations with periodic boundary conditions on pure magnetite accounting for the strong on-site coulomb repulsion of the 3d electrons by means of the additional U term. We tested this methodology and compared with available structural information and magnetic properties.

In view of the excellent agreement of our theoretical data with available experimental observations for pure magnetite we proceeded to perform calculations of the incorporation of uranium(V) into magnetite. Uranium(V) is a $5f^1$ system and hence, theoretical, a fairly easy system to be studied with theoretical methods. Still we accompanied these DFT calculations with CASSCF calculations identifying the ground state of uranium(V) in the tetrahedral and octahedral ligand field. For the determination of the changes implied on magnetite upon the incorporation of uranium(V) we employed DFT+U. We probed different incorporation and charge compensation schemes of the incorporation of uranium(V) into magnetite. Overall we found a very good agreement of our theoretical determined structures with the experimental data provided by Pidchenko and Vitova *et al.* [1] and strongly support the characterization of the incorporation site.

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Quantum Chemical Spin Densities for Radical Cations of Photosynthetic Pigment Models

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The spin-density distribution plays an important role in EPR and NMR measurements. Accurate calculations of this property may shed light on various biophysical processes including photoionization or charge transfer. However, DFT often faces the problem of charge overdelocalization due to self-interaction error and leads to qualitatively wrong spin densities [1].

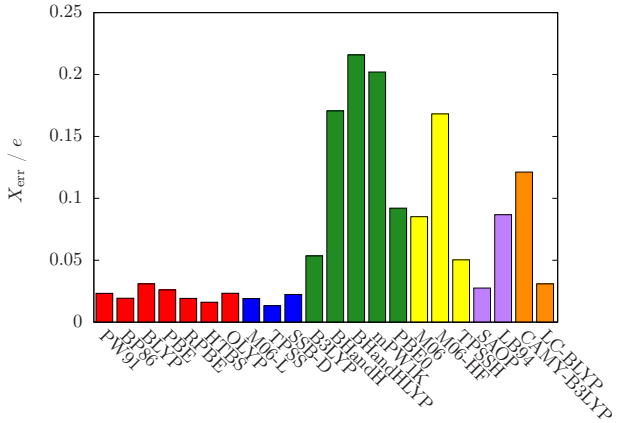

Figure 1: Errors X_{err} of DFT spin populations for the $^2A_{1u}$ of the Mg-porphyrin radical cation.

We present multireference quantum chemical spin-density calculations for radical cations of Mg-porphyrin, Mg-chlorine and a truncated chlorophyll *a* model [2]. Because CASSCF spin densities do not converge in certain critical cases w.r.t. the active space size, we suggest to use DMRG [3]. Based on these reference data, we assess the accuracy of different density-functional approximations. Our results provide a starting point for investigations of spin densities of more complex systems such as the hinge model for the primary electron donor in photosystem II [4].

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Benchmarking Structures and Vibrational Frequencies from Subsystem DFT

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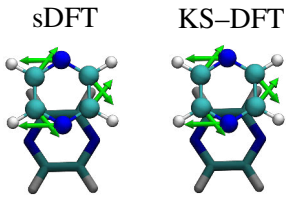
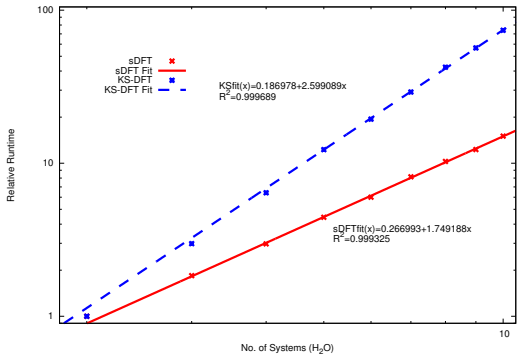
Describing reaction pathways with computational methods can be a demanding task even for Kohn-Sham density functional theory (KS–DFT), especially if explicit solvation needs to be considered. Subsystem DFT (sDFT), a fragment-based approach to density functional theory, is an efficient alternative to KS-DFT [1–4]. By partitioning the total electron density $\rho_{\mathrm{tot}}(\boldsymbol{r})$ into a set of smaller subsystem densities, the ansatz introduces linear scaling with the number of subsystems.



Sample mode from S22 stacked pyrazine dimer structure at 1303.85 cm^{-1} (sDFT) / 1306.12 cm^{-1} (KS–DFT).



Comparison of relative run times from sDFT and KS–DFT supersystem gradient calculations for H_2O clusters with increasing system size.

Here, we discuss a benchmark study of our analytical sDFT gradient implementation into our group's quantum chemistry program Serenity [5]. In addition, a first benchmark of vibrational frequencies based on semi-numerical differentiation is presented.

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Optimization of optical properties:

Inverse Design of dye-sensitized solar cells

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The search for new materials with interesting optical properties is a challenging task. To study all possible systems by pure experimental research is very cost- and time-consuming. A pre-screening of these large pools of systems by theoretical techniques can be one solution to this problem.

Alternatively, in this paper we report an extension of our previous inverse design method[1] that automatically optimizes materials regarding their optical properties for solar cell applications. Instead of varying atom types at predefined positions in SiGe clusters as was done in our proof-of-principle study[1] we will have a fixed organic backbone and vary the functional groups attached to this core system. In this study we consider benzene as a simple test system. To treat the large number of possible molecules and to identify the best performing ones we make use of genetic/evolutionary algorithms. The optical properties are evaluated via a performance function that can be HOMO-LUMO gap, absorption or the spatial distribution of HOMO and LUMO, etc.

We show that our approach can be applied to organic molecules. We have developed a straightforward scheme for delivering the structural information of our systems via an input file to the source code. This contains information about the organic backbone, its substituent sites, the functional groups, and the symmetry of the core. The organic molecules are build up automatically and afterwards their structures are optimized locally. Subsequently, their optical properties are calculated and only the best ones are kept. These form the new generation within our genetic algorithm. It can be demonstrated that this approach is able to identify a larger number of good candidate structures in a short period of time. Although there are cases where not the best structures are identified during a calculation but "only" the 2nd or 3rd best, we are convinced that we can provide important information for experimentalists. Our approach provides a foundation for the treatment of large classes of larger organic molecules (e.g. porphyrines, BODIPY) for dye-sensitized solar cells. Not only materials with optimal optical properties can be identified, but our approach can also provide a starting point for other systems and/or properties (e.g. catalysis on crystalline surfaces).

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Benchmarking of Semi-Empirical QM/MM Methods for Proton Transfers between Biomacromolecules and Aqueous Solvent

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We are currently developing novel magnetic resonance imaging (MRI) methodologies for the characterisation of cartilage and other musculoskeletal tissues, based on the dispersion of the longitudinal relaxation in the rotating frame ($T_{1\rho}$). One of the mechanisms most likely contributing to the dispersion of $T_{1\rho}$ dispersion in cartilaginous tissues is the chemical exchange of protons between chondroitin sulfate and water. Our model system for chondroitin sulfate consists of a single disaccharide unit that is repeated in chondroitin-4-sulfate (β-GlcA-(1→3)-β-GalNAc4S), which is capped with methyl groups on both ends (cf. Fig. 1). For the simulation of the dynamics of the several simultaneously possible proton transfer reactions between this compound and the aqueous solvent we are planning to perform semi-empirical QM/MM molecular dynamics simulations. To determine the suitability of a number of different semi-empirical methods for modelling proton transfer reactions between this model compound and water, we have undertaken a series of benchmark calculations. On one hand we probe the methods concerning the accuracy of the model compound's proton binding by calculations of the gas-phase proton affinities of the different groups (cf. Fig. 2), and reaction coordinates for proton transfer reaction to isolated water molecules/hydroxide ions, both in comparison to ωB97XD/6-311++g(d,p) calculations. On the other hand, we test the suitability of the methods for the dynamics of protons in water by calculations of the 2-D PES of the Zundel ion, and the dynamics of proton transfers in isolated water clusters containing one excess proton, both commensurate to the simulations performed by Wu et al. in their model reparametrisation study.[1]

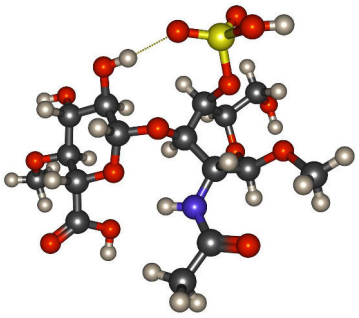

Figure 1: Model compound.

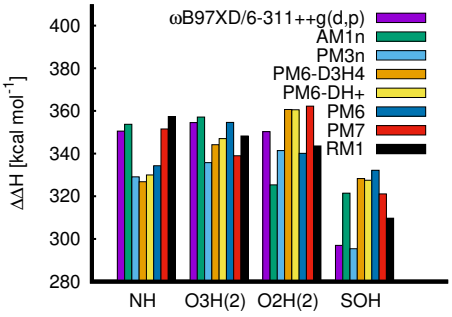

Figure 2: Comparison of gas-phase proton affinities.

We thank the Academy of Finland (project 297033) for funding, and CSC-IT Center for Science in Espoo, Finland, for computing time.

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Fast estimation of the dynamic electron correlation energy using localized molecular orbitals

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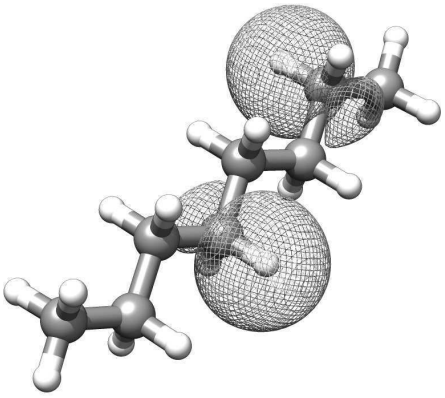
The largest source of error in quantum-chemical calculations is the insufficient description of electron correlation. Especially in cases of small energy differences (e.g. isomerization energies, which have a high importance in many industrial research projects) the accurate calculation of electron correlation energies is essential for obtaining predictions with chemical accuracy (± 5 kJ/mol). In the last decades, several wavefunction based *ab initio* methods have been developed, which are capable of providing highly accurate results. However, these methods are limited by their high computational costs, which make it very time-consuming or even impossible to carry out calculations for larger systems. At present, for large chemical systems mostly density functional theory (DFT) is the method of choice. As DFT does not allow for improvements in a systematic way and its results are often not sufficiently accurate, large systems can still not be treated satisfyingly.
We propose a novel approach for a fast estimation of electron correlation energies. For this purpose, the total correlation energy of a molecule is decomposed into pair correlation energies of localized molecular orbitals (LMOs). Based on calculations with accurate *ab initio* methods, these pair correlation energies are fitted with respect to the bond length as well as to the spatial extent and the distance between the centers of charge of the LMOs using physically meaningful functions. The total correlation energy of a large system can then be estimated as a sum of the parametrized pair correlation energies of all its LMOs.
Using our approach the total correlation energies for a test set of hydrocarbons could be reproduced within about 1 ‰. This opens up the possibility to estimate isomerization energies of large hydrocarbons with chemical accuracy.



Linear response formalism for internally contracted multireference coupled cluster theory to evaluate second order properties

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Internally contracted multireference coupled cluster (ic-MRCC) methods [1] have been developed and used successfully to calculate the energy of molecular states with pronounced multireference character. One of the variants of ic-MRCC has been extended to study excitation energies [2]. We have also attempted recently to evaluate one-electron first order properties using ic-MRCC which includes both the spin-independent (dipole moments, electric field gradients) and the spin-dependent properties (hyperfine coupling constants).
In this work we proceed towards calculation of second order properties, such as static and dynamic polarizabilities, by developing a linear response formalism for the ic-MRCC theory. The response formalism, developed earlier by Jørgensen *et al.*[3] for the single reference coupled cluster and pertubative methods, has been followed here. We have found that the appearance of unphysical second order poles in the response function is inherent to the ic-MRCC method. Approximations to the original equations to solve the first order parameters and to the expression for the response function have been made to avoid these artifacts. Some of the pilot applications to calculate the polarizabilities have been presented which suggest that the ic-MRCC provides better accuracy for second order properties than other multireference methods.

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Quantitative determinations of photochemistry from first principles: Photoluminescence efficiencies of phosphors for OLEDs

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Ir(III) complexes are often used as phosphors in phosphorescent organic light-emitting diodes (PhOLEDs). Optimizing their photoluminescence quantum yields (PLQY) at room temperature is key to attain highly performant PhOLEDs.[1] This work demonstrates for the first time that quantitative predictions of their photoluminescence efficiencies can be derived exclusively from electronic structure calculations and the use of kinetic models. More in details, our static approach consists of computing all the competing photodeactivation rates from first principles and then deriving the kinetic master equation. Most of the rates have been herein computed within the framework of the thermal vibration correlation function (TVCF) rate theory[2] in combination with time-dependent density functional theory (TD-DFT) calculations. The thermal processes are modeled with canonical variational transition state theory (CVT). Our preliminary approaches have been proven successful for green-to-blue phosphors.[3] Currently we are developing a general approach valid for all possible Ir(III) complexes, i.e., from red to deep-blue emitters.[4] These approaches are extremely beneficial for the *in silico* prescreening of promising PhOLED emissive materials.

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Daniel Escudero thanks funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 700961.

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Statistical calibration of parametric property models

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One of the major challenges in computational science is to determine the uncertainty of a virtual measurement, that is the prediction of an observable based on calculations. As highly accurate first-principles calculations are in general unfeasible for most physical systems, one usually resorts to parameteric property models of observables, which require calibration by incorporating reference data. The resulting predictions and their uncertainties are sensitive to systematic errors such as inconsistent reference data, parametric model assumptions, or inadequate computational methods [1]. Here, we discuss the calibration of property models in the light of bootstrapping, a sampling method which we apply to assess a linear property model linking the ^{57}Fe Mössbauer isomer shift to the contact electron density at the iron nucleus [2]. The contact electron density is calculated for a diverse set of molecular iron compounds with twelve density functionals across Jacob's ladder. We provide systematic-error diagnostics (e.g., outlier detection) and reliable, locally resolved uncertainties for isomer-shift predictions. Moreover, we show that both model parameters and prediction uncertainty depend significantly on the composition and number of reference data points. This study presents the first statistically rigorous calibration analysis for theoretical Mössbauer spectroscopy, which is of general applicability and not restricted to isomer-shift predictions.

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Reactivity of copper carbenoid toward insertion in O-H bonds. A Density Functional Theory Study

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One of the major challenges in organic chemistry is the formation of carbon-heteroatom bonds [1], especially in the synthesis of products of industrial interest. A novel solution to this problem is the use of metal carbenoid insertion reactions on O-H bonds. These reactions have attracted considerable interest because they provide a direct and efficient way for the formation of carbon-heteroatom bonds. The use of metal carbenoid is an attractive method, since the O-H activation induced by the metal does not interact directly with it, but rather with the electrophilic carbenoid carbon [2]; additionally the metal complex, initiating the reaction is easily regenerated, so the whole process is recognized as a catalytic reaction.

The main goal of this theoretical study is to propose and evaluate alternative routes (see Figure 1(c)) for the obtention of the mentioned products through a computational analysis. This study is based on the DFT description of the reaction mechanism of the carbenoid insertion reaction, in this particular case, the activation and insertion in O-H bonds effectively, using descriptors such as the reaction force [3] and the reaction electronic flux [4]. In addition, we investigated electronic distribution and the reactivity of carbenoid systems; through global and local reactivity descriptors (see Figure 1 (a)).

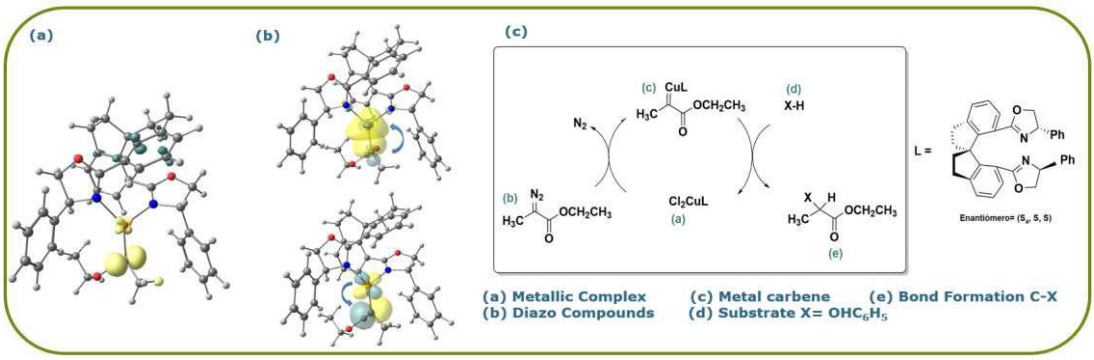

Figure 1: (a) Dual descriptor for copper carbenoid (b) natural bond orbitals (NBOs) associated with the donor–acceptor interactions Cu-Carbene (c) general reaction mechanism of insertion metal carbenoid in bonds.

Acknowledgments: This work was supported by FONDECYT, grant. No. 1170837.

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Hidden Electrostatic basis of Dynamic Allostery in a PDZ Domain

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Allostery is a phenomenon in which ligand binding at a site is linked to the structural or dynamical changes at a distant site. Although, numerous models have been proposed to understand the molecular mechanism of allostery, a quantitative description of signal propagation still remains elusive. With the newly evolved theories based on thermodynamics and conformational entropy which focuses on slow dynamics and population shifts as crucial determinants of the structural features in information transmission, it will be interesting to gain new insights into allostery, "the second secret of life" at the molecular level.

PDZ domains have been widely used as a model system to understand allosteric transition without structural changes where distal side chain dynamics is modulated upon ligand binding and the origin has been attributed to entropic effects.[1] In this work, we have speculated and explored the energetic basis of the observed "dynamic allostery" in a PDZ3 domain protein using molecular dynamics simulations. Our results suggest that ligand binding information propagates in the form of change in inter-residue interaction energies, especially towards the N-terminal residues and α1-β4 region. Interestingly, we find shift in the inter-residue contacts and accompanied side chain orientations as a reason for the large change in interaction energies at a distant region of proteins. Our analyses clearly demonstrate a "population shift" in the hydrogen bonded network and salt bridges upon ligand binding. Interestingly, the internal redistribution and re-wiring of side chain interactions lead to large cancellations resulting in a small change in the overall enthalpy of the protein, thus making it difficult to detect experimentally. This could be the reason for the prevailing focus on "dynamic" or "entropic" effects, whereas the energetics seems to be the more fundamental factor that drives allosteric effects in PDZ3 domain protein.[2]

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Computer-aided molecular design and modeling of catalysts capable of convert N_2 into ammonia.

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Ammonia (NH_3) is increasingly being considered as a real substitute for petroleum as a transportation fuel. The heavy energy-consumption and the considerable, complex plant infrastructure that the classical Haber–Bosch process requires, make the electrochemical synthesis of NH_3 an alternative for a cheap and clean technology of paramount importance from both the industrial and environmental points-of-view.[1] Our efforts are mainly focusing on the use of well-resolved DFT calculations with the aim to study the mechanistic aspects of the electrochemical conversion of dinitrogen (N_2) into NH_3 when occurring on a catalytic surface, not only for the unraveling of the physicochemical events taking place during the reaction mechanism, but also advancing catalytic behaviors on promising materials for the N_2 reduction at mild conditions: N_2 reduction challenges are mainly due to the searching of active materials enabling a spontaneous N_2 fixation[2] and decreasing the thermodynamics impediment[3] for the limiting step, usually the first proton–electron transfer. We also deal with the estimation of activation barriers (kinetics) that emerge in the form of over-potentials.[4,5] In this sense, accurate calculation of over-potentials is a current challenge for DFT, but is also critical for experimentalists to make full use of the calculated results.

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Theoretical study on the redox reaction mechanism of quinone compounds in industrial processes

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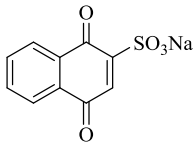
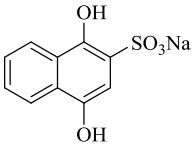
Coke oven gas (COG) that is exhausted from coke oven furnace in steelworks contains useful components as fuel.[1] However, since COG also contains undesirable elements such as ammonia and hydrogen sulfide (H_2S) that cause environmental problems when burned, they should be removed from COG before it could be utilized as fuel. To remove H_2S from COG, so-called Takahax process is widely used in Japan. In this process, the following fundamental reactions are known to occur.[2]

$$H_2S + Na_2CO_3 \rightarrow NaSH + NaHCO_3 \quad (1)$$



$$+ NaSH + NaHCO_3 \rightarrow$$



$$+ S + Na_2CO_3 \quad (2)$$

(NQS-Na) (NQSH$_2$-Na)

$$NQSH_2\text{-}Na + 1/2\ O_2 \rightarrow NQS\text{-}Na + H_2O \quad (3)$$

As indicated by eq. (1), H_2S contained in COG is dissolved into an alkaline aqueous solution in the form of hydrogen sulfide ion (SH^-). In the next step shown by eq. (2), the aqueous SH^- is oxidized to S (solid sulfur) by 1,4-naphthoquinone-2-sulfonic acid (NQS) that itself is reduced to 1,4-dihydroxynaphthalene-2-sulfonic acid ($NQSH_2$). Because NQS is regenerated via the reaction of eq. (3) with the oxygen blown into the process, NQS can be regarded as catalyst in the Takahax process.

The purpose of the present study is to reveal the underlying mechanisms for redox reactions constituting the Takahax process. The elementary reactions in eqs. (2-3) were investigated by DFT calculations combined with PCM solvation model. On the basis of our calculations, we demonstrate that the rate-determining steps in eqs. (2-3) can be characterized as the proton coupled electron transfer (PCET)[3] reactions that are preferable to sequential electron and proton transfers. In addition to the fundamental reactions, we specify the reaction pathways for the degradation of NQS under alkaline conditions.

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Au Charge and its Role in WGS Reaction on Reduced Gold-Substituted $Ce_{1-x}O_2$(111) Surfaces

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We investigate the surface structures and the charge on Au for a gold atom adsorbed on the cerium vacancy of the (111) surface of CeO_2 in the presence of oxygen vacancies via density functional theory calculations. The charge of Au can be significantly altered by creating oxygen vacancies on the surface. Detailed analyses show the variation in the Au charge can be attributed to the distribution of the leftover electrons after the oxygen vacancies were created, which, in turn, depends on the vacancy number and locations of the vacancies. Furthermore, we find that hat the Au^{3+} and Au^{-} are not catalytically active for the water-gas-shift (WGS) reaction because of a high energy barrier of +1.54 eV required to dissociate water and that of +1.40 eV to produce H_2 and CO_2, respectively. However, Au^{+} is concluded to play a significant role in the WGS reaction at low temperatures (T < ~550 K), because the overall reaction barrier for the WGS reaction via the carboxyl mechanism is reduced to be 0.79 eV ~ 0.98 eV in the case of the Au being in a modest oxidation state of +1.

The Fluctuating Charge Model for improving Force Field electrostatics

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Many different force fields exist which differ in the functional form of energy contributions, the number of cross terms included or the reference data used for fitting the parameters. The majority of commonly used force fields model the electrostatic contribution by fixed atomic charges centered on atoms.
One way of modelling geometry dependent charges is the Fluctuating Charge (FQ) model[1] where the main idea is to expand the electrostatic energy with respect to atomic charges up to second order, with the keys quantities being atomic electronegativities and hardness. Such a model has been used in reactive force fields where bond breaking/forming is described since it allows charge transfer[2], however, current FQ models are incapable of correctly describing covalent bond dissociations[3][4][5].
The geometry dependence of charges is usually introduced in the out-of-diagonal elements of the hardness matrix, often represented by Coulomb terms. This is reasonable for large interatomic distances but atomic wavefunctions have a significant overlap at short distances and a purely Coulombic behavior here seems inappropriate. The correct functional form of out-of-diagonal elements for the hardness matrix represents an open question as well as a consistent geometry dependence of atomic charges.
The out-of-plane dipole moment derivatives (APTs) for planar system allow a unique set of atomic charges that are able to reproduce both molecular charge and dipole moment[6] and these quantities can be calculated for different molecular geometries.
We present analyses of atomic polar tensors and FQ models aimed at reproducing ab initio calculated APTs.

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Insight into molecular reactivity and reaction mechanisms from reactive molecular dynamics simulations

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Following reactions over time is of key importance for analysing and understanding the mechanisms that govern chemical processes. Utilising the reactive molecular dynamics implementation MS-ARMD (Multi-Surface Adiabatic Reactive Molecular Dynamics[1]) allows to study adiabatic reactions related to, i.e. atmospheric chemistry, organic synthesis, and biochemistry. MS-ARMD allows to simulate statistically significant number of trajectories which allows for extensive studies on a system. Furthermore it can be used to calculating converged reaction rates. Example systems that show the versatility and efficiency of MS-ARMD are OH-stretching overtone induced photodissociation of HSO_3F[2] and the Claisen rearrangement reaction of allyl-vinyl-ether (AVE) and chorismate in gas and condensed phase[3].

Extensive simulation of OH-stretching overtone induced photodissociation of HSO_3X (X = F, Cl[4]) in the ns-time scale reveals dynamical effect on the dissociation reaction that differ for the two systems. HSO_3F shows a lack of dissociation in comparison to the previously studied system HSO_3Cl. Detailed analysis implies that coupling of the OH-local mode to bending and torsional degrees of freedom is of importance for the elimination reaction.

Claisen rearrangement is an important [3,3]-sigmatropic rearrangement. In aqueous solution and in the enzyme chorismate mutase (CM) Claisen rearrangement is catalysed by the stabilisation of the cyclic transition state (TS). Utilizing a well parametrised force field of AVE the experimental barrier height[6] of chorismate in CM was reproduced. Analysing the TS conformation shows difference between AVE, AVE-dicarboxylate and chorismate.

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Polypyridyl iron(II) complexes as promising photoredox catalysts. Theoretical calculation of excited state redox potentials

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Photoredox catalysis has emerged as a very powerful tool in synthetic organic chemistry, giving access to a unique reactivity impossible to achieve in the ground state. As a matter of fact, Ir and Ru complexes have proved their worth as photoredox catalysts by activating otherwise inert substrates like aryl halides and N-protected amino acids **[1]**.

However, their toxicity has triggered the search of alternative "green catalysts", capable of performing such transformations while being eco-friendly. In this context, Fe and Ni complexes have been succesfully tested as Pd replacements for cross-coupling reactions; moreover, Ni has been recently applied as a photoredox catalyst **[2]**.

In this work, we assess the potential use of Fe(II) polypyridyl complexes as substitutes for Ir / Ru derivatives in photoredox catalysis by considering the calculated excited state redox potentials for several of these Fe(II) complexes, following the methodology described in ref. **[3]** in the framework of DFT and TD-DFT. Functional screening shows that a modified version of B3LYP **[4]** provides the best fit for both vertical excitations and oxidation potentials compared to experimental data. The combination of these results with the calculated reduction potential of several synthetically relevant organic substrates represents encouraging results for the plausible activation of these latter by Fe(II) complexes.

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Fast and Accurate Geometry Optimization of Lanthanoid Complexes with an extended Tight Binding Method

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The computational handling of large lanthanoid complex structures is fundamental for theoretical and mechanistic studies in various fields of applied science like lanthanoid-based metal-organic frameworks or homogenous catalysis to only name a few. The recently developed GFN-xTB[1] (G: geometries; F: frequencies; N: non-covalent interactions) tight binding based electronic structure approach was applied for geometry optimization of 78 lanthanoid complexes (La (Z = 57) – Lu (Z = 71)). The results were evaluated with reference to high quality X-ray molecular structures obtained from the Cambridge Structural Database (CSD) and DFT-D3 calculated reference structures for Pm (Z = 61). The structural heavy atom root-mean-square deviation (RMSD) and the mean coordination number change of the lanthanoid atoms for GFN-xTB, Sparkle/PM6[2] and HF-3c[3] are compared. It is shown that GFN-xTB yields reasonable structures and performs well in terms of overall computational speed compared to other low cost state of the art methods. The high quality reproduction of large lanthanoid complex structures corroborates the wide applicability of the GFN-xTB approach and its high value as very effective low cost method.

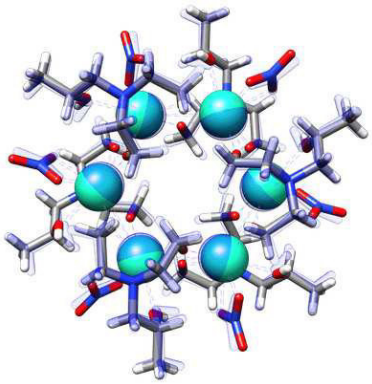

Figure 1: Overlay of GFN-xTB optimized and experimental (X-ray) structure for a prototypical lanthanoid complex

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Automated Exploration of Complex Chemical Reaction Networks

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To be able to accurately predict the product distribution of chemical reactions, a complete reaction network consisting of all relevant intermediates and elementary reactions is necessary. The complexity of such a network may grow rapidly, in particular, if reactive species are involved that might cause a myriad of side reactions. Therefore, only the expected, dominant reaction paths of a chemical reaction network (e.g., a catalytic cycle) are usually explored in practice. In addition, conformational diversity, which is essential for the understanding of catalytic processes, is rarely taken into account. Without a robust protocol, automation, and appropriate data handling, a truly predictive theoretical investigation is tedious and possibly unfeasible.
We present a computational protocol and its implementation that constructs such networks in an automated manner [1, 2]. For each intermediate, conformers are generated and selected based on structural similarity and energy criteria. Pairs of conformers are placed in a *virtual flask* and reactive complexes are formed between them by applying heuristic rules derived from conceptual electronic-structure theory. With a constrained geometry optimization employing quantum-chemical methods, activation barriers are overcome and new intermediates are formed. This procedure is followed by a transition state search.
We demonstrate not only the infrastructure necessary for handling such large amounts of data but also a graphical user-interface for visualization and manipulation of the reaction network. With this framework, a comprehensive picture of the chemical process can be obtained and further studies (e.g., kinetic analyses) can be performed [3]. We demonstrate our approach at the example of the formose reaction [4], an autocatalytic oligomerization reaction of formaldehyde.

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H_2 dissociation and surface oxygen vacancy formation on (111)-CeO_2 surface: a periodic DFT approach

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Most of the applications of ceria are linked to its redox properties associated to the easy formation of oxygen vacancies and so the simple change in oxidation states of cerium: $Ce^{IV} \leftrightarrow Ce^{III}$. Moreover, ceria is important in heterogeneous catalysis, especially in the alkyne semi-hydrogenation where it has been shown to be able to split H_2 in the absence of noble metal [1]. Interestingly, the hydrogenation of ceria is found to take place through a hydride specie that plays a key role [1,2,3].
In the present study, we investigate the detailed mechanism for the formation of surface oxygen vacancy via H_2 dissociation following by H_2O desorption on (111)-CeO_2 using PBE+U method and periodic approach as implemented in VASP software.

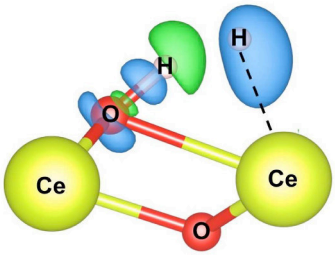

Figure 1. Charge density difference illustrating the ion pair $H^{\delta+} – H^{\delta-}$ formation: blue and green isosurfaces display an electronic density gain and depletion, respectively.

It was found that molecular hydrogen adsorbs very weakly to the surface. Then, the strong ionic nature between cerium and oxygen in ceria induces the polarization of the H – H bond and favor an heterolytic dissociation of H_2 with the formation of an ion pair $H^{\delta+} – H^{\delta-}$ [2]. However, the product of the heterolytic dissociation being metastable [2,3], the hydride can easily move on to a hydroxyl group to form water molecule. Finally, water desorption leads to the formation of one surface oxygen vacancy along with the reduction of two cerium. Several hydrogen species – like hydride, radical hydrogen and proton – are involved during the different steps of the reaction.

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Reaction rate constants from system-specific, black-box force fields parametrized by quantum chemical data

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In this work we present a method for automated construction of system-specific force fields used to describe given elementary reaction steps [1]. Based on the quantum-mechanically derived force field (QMDFF) [2] and its empirical valence bond extension EVB-QMDFF [3], the optimized force fields are able to represent a reliable potential energy surface for any given reaction step in an essentially black-box manner. To generate and parametrize such a force field just a limited and pre-defined set of reference data near the reaction path is needed. Depending on the chosen reaction, different EVB coupling terms might be used to optimize the force fields performance. Built on this data, the new force field establishes an accurate approximation of the reference potential energy surface, on and off the reaction path. This intermediate representation can be used to generate reaction rate data using ring polymer molecular dynamics (RPMD) [4], with far better accuracy and reliability than with traditional approaches based on transition state theory (TST) or its variational extensions (VTST), even if those include sophisticated tunneling corrections. However, the additional expense at the reference level remains very modest. We demonstrate the ability of our approach for three arbitrarily chosen example reactions.

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$\pi-$Conjugated Macrocycles with High Radical Character

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Nowadays, there are many examples of molecules with an open-shell singlet diradicaloid ground state but organic molecules with higher polyradical character (e.g.,tetraradical, hexaradical,...) are quite rare, to say the least. Recently, two organic stable macrocycles with large polyradical characters were synthesized and characterized, exhibiting singlet ground states that can be regarded as a tetraradicaloid and an hexaradicaloid, respectively [1].

In this work, we present the computational study of the ground state electronic structure of two new polycyclic molecules (8MC and 10MC) holding very large polyradical nature synthesized by Prof. Wu's group. The study includes the relative stability of structural conformers, the quantification of their polyradicaloid character by means of natural orbital occupancies, the vertical energy gaps between low-lying states of different spin-multiplicities and rationalization of global aromaticities. The computational strategy employed combines density functional theory (DFT), constrain DFT (C-DFT) and restricted active space spin-flip (RAS-SF) [2] calculations. Our results suggest 8MC and 10MC as octaradicaloid and decaradicaloid species, respectively.

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Ligand–Field States of Aqua Complexes Revisited with Multireference Calculations: Importance of Solvation Effects

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Although aqua complexes $[M(H_2O)_6]^{n+}$ (where M^{n+} is a transition metal ion) are among the simplest and experimentally best characterized coordination compounds, it is not trivial at all to reproduce their d–d excitation energies by means of quantum chemical calculations. Recently, there were significant controversies regarding the lowest electronic excitation $^6A_{1g} \rightarrow {}^4T_{1g}$ for $[Fe^{III}(H_2O)_6]^{3+}$ [1, 2]: Whereas the DFT:B3LYP method seems to reproduce the experimental excitation energy quite well, advanced wave function theory (WFT) methods, such as CASPT2 and CCSD(T), appeared to overestimate it by more than 10 kcal/mol! Similar problems may also be noticed for aqua complexes of other 3d-electron metals. However, our recent paper demonstrated that the discrepancies for $[Fe^{III}(H_2O)_6]^{3+}$ may be plausibly resolved by accounting for hydrogen–bonding interactions with water molecules present in the second solvation sphere, leading to systematic stabilization of the lower-spin state [3]. This approach is now extended to aqua complexes of all 3d-electron metal ions with electronic configurations from d^0 (Ti^{III}) to d^9 (Cu^{II}). Multireference methods CASPT2 and NEVPT2 are applied to treat their various ligand-field states for which excitation energies are experimentally available. Reliable models with second solvation sphere and extensive active spaces (accounting for covalency of metal–ligand σ-bonds) are employed. It is demonstrated that once an adequate multireference methodology and a realistic solvation model are used, the computed excitation energies are systematically in a very good agreement with the experimental band positions. Since the experimental data of aqua complexes contain a number of d–d transitions between states of different multiplicities (*i.e.*, spin-forbidden transitions), the results obtained also contribute to calibration of computational methods for the problem of spin-state energetics. The latter is generally recognized as a grand challenge for theory in the field of (bio)inorganic chemistry [4]. In this regard, the present work suggests that accounting for solvation/medium effects in the second coordination sphere may be quite important for a balanced description of relative spin-state energetics.

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Benzene probes in molecular dynamics simulations reveal novel binding sites for ligand design

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Proteins are intrinsically flexible and frequently undergo conformational changes on ligand binding. This poses a major challenge in the identification and characterisation of ligand binding sites. Several computational pocket detection methods that utilize small-molecule probes in molecular dynamics (MD) simulations have been developed to address this issue. In these simulations, the probes interact dynamically with the protein surface, allowing for ligand-induced conformational changes and revealing the locations of binding sites. The use of hydrophobic probes is of particular interest because it reduces solvent polarity, thus facilitating the opening and enlargement of cryptic hydrophobic pockets that may otherwise remain undetected in simulations of the protein in pure water. Ligand-mapping MD (LMMD) [1-3] is one of two current probe-based MD simulation methods [4] that employ hydrophobic probes for pocket detection. Here, we report the use of benzenes as probe molecules in LMMD simulations to predict the existence of two novel binding sites on the surface of the oncoprotein MDM2. Through biophysical assays and X-ray crystallography, we serendipitously validated one of them as a functional binding site by using peptidic ligands that were specifically designed to target the other putative site. These results highlight the predictive power of LMMD, and suggest that predictions derived from LMMD simulations can serve as a reliable basis for the identification of novel ligand binding sites in structure-based drug design.

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Molecular Quantum-Dot Cellular Automata Based on Diboryl Radical Anions

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As a promising alternative to field-effect transistors (FETs), molecular quantum-dot cellular automata (MQCA)[1] has attracted considerable research interests for building the next-generation microelectronic elements. In MQCA, binary information is represented by the charge configuration of a cell with four dots (Fig. 1a). The signal transmission is achieved via Coulomb interaction between neighboring cells with no current flow and extremely low power dissipation[2]. Although a variety of MQCA candidates have been reported, including mixed-valence organometallic complexes, metal cluster carboxylates, zwitterionic boron−allyl complexes, and double-cage fluorinated fullerene anions, it is still a challenge to put them into practical applications due to difficulties in synthesis or surface attachment. Herein we proposed a new candidate system − diboryl radical anion, with the boron radical center as the charge container (Fig. 1b). Such compound has already been isolated and characterized experimentally, demonstrating elegant synthesis and versatile modification in the end groups. Based on this framework, a series of analogous candidates with different substituents and spacers have been investigated and the ones with best performance have been suggested.

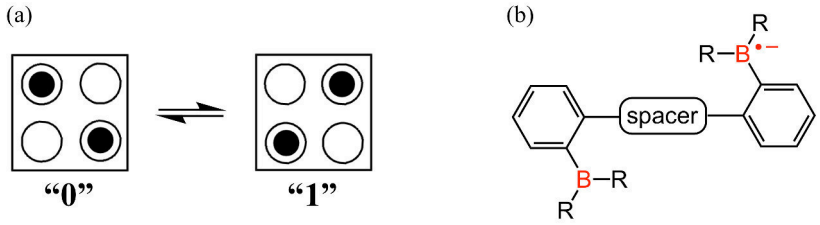

Fig. 1 (a) Schematic illustration of MQCA cells. (b) Molecular skeleton of diboryl radical anion based MQCA candidate.

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Computational Insights into the Gas Phase Heterogeneous CO_2 Reduction via Surface Frustrated Lewis Pairs

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Abstract: The significant challenge faced by our global society, from issues of climate change to question of energy security could be solved if we can find a champion catalyst that can convert atmospheric CO_2 to carbon based fuels. However, designing catalytic nanostructures that can thermochemically or photochemically convert gaseous CO_2 into fuels is a significant challenge which requires a keen understanding of the physical and chemical properties of complex materials and the processes happening on them at atomic and electronic level. In this context, this work will present our recent findings [1-3] that showed that the Frustrated Lewis Pairs (FLPs) created by sterically hindered Lewis acid and Lewis base have the capacity of capturing and reacting with a variety of small molecules, including H_2 and CO_2, which extends a new strategy for CO_2 reduction. Specifically, I will highlight the insights provided by density functional theory (DFT), time-dependent DFT and metadynamics calculations into the surface chemistry of CO_2 reduction reaction on $In_2O_{3-x}(OH)_y$ nanoparticles, in the presence and the absence of light and temperature. This work not only resulted in the discovery of a new class of FLP heterogeneous photocatalysts but also provided a path to effectively maximize the activity of surface FLPs in nanocrystalline $In_2O_{3-x}OH_y$ through isomorphous substitution of In(III) with more electronegative Bi(III) [3], which will also be discussed in this presentation.

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A scalable explicitly correlated local coupled-cluster method with pair natural orbitals: PNO-LCCSD-F12

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An efficient explicitly correlated local coupled-cluster method PNO-LCCSD-F12 is presented. The method is a part of a new generation of parallel local correlation methods developed in our group [1, 2] using pair natural orbitals (PNOs) to span the virtual space. The PNOs are constructed from projected atomic orbitals (PAOs) and orbital specific virtuals (OSVs). A hierarchy of strong, close, weak, and distant pairs are selected using approximated LMP2 pair energies, and different levels of theory are applied to these pair classes to reduce the computational cost without significant loss of accuracy. The explicit correlation theory is adapted from the cost-effective CCSD-F12x($x = a, b$) theory [3, 4]. The cost of the explicitly correlated terms scales linearly with the molecule size asymptotically.

Extensive benchmark results are presented, which demonstrate that the PNO-LCCSD-F12 method yields relative energies within $\sim$ 1 kJ mol^{-1} of the canonical values for a variety of chemical systems. The F12 terms are shown to improve the basis set convergence, and to reduce the domain errors that originate from the truncation of PAOs and PNOs. On a small computer cluster with 100–200 of CPU cores, PNO-LCCSD-F12 calculations of three-dimensional molecules with $\sim$100 atoms using the augmented triple-ζ basis sets can be performed in 1–3 hours of elapsed time. In particular, despite drastic improvements of the accuracy, the explicitly correlated terms typically add only 20–30% of the computational time to a corresponding PNO-LCCSD calculation. The exclusive use of the explicitly correlated variant is therefore strongly recommended.

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Phosphinidene Chalcogenides: DFT modeling of monomer trapping, ring expansion and mixed ring systems

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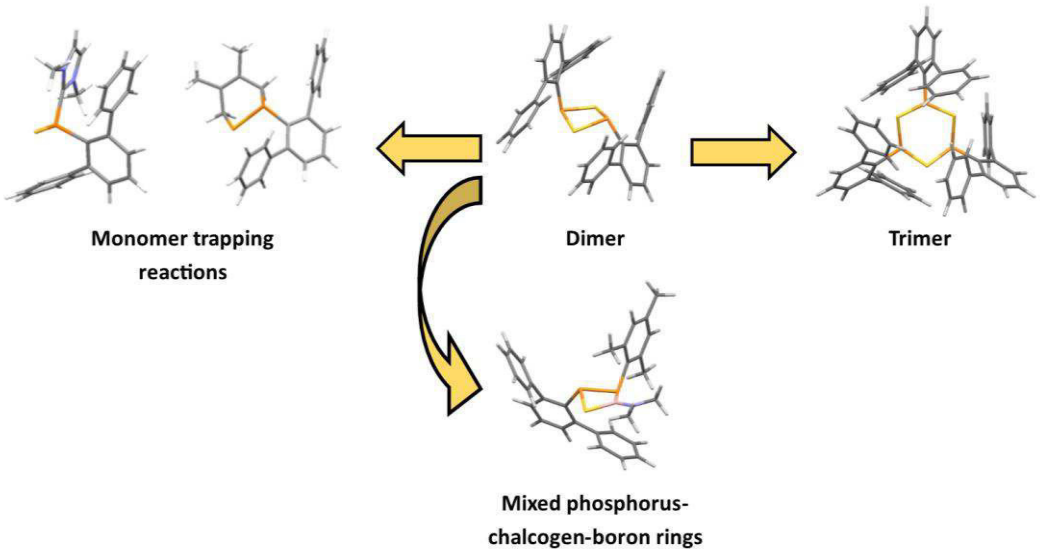
The reaction mechanisms of four-membered phosphinidene chalcogenide rings have been solved using density functional theory calculations. These molecules with P_2Ch_2 cores (Ch=S,Se) represent the first four-membered organophosphorus-chalcogen rings with phosphorus in the +3 oxidation state. The rings can be broken down using Lewis bases to yield monomeric R–P=Ch, which can be stabilized by the base or trapped with a diene [1]. The liberation of monomeric R–P=Ch units enables a base-assisted ring expansion reaction from the four-membered rings into the more stable six-membered $(RPCh)_3$ rings [2]. The formation of mixed four-membered phosphorus-chalcogen-boron rings with phosphinidene boranes is also modeled.



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QM/MM modeling of PoXeR:

A light-driven inward proton pump with unidirectional rotary motion

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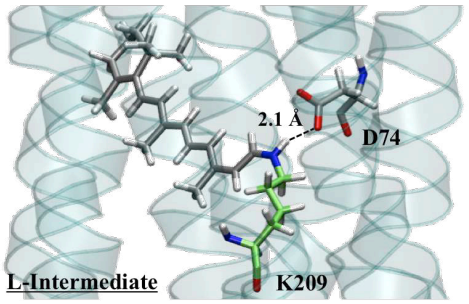
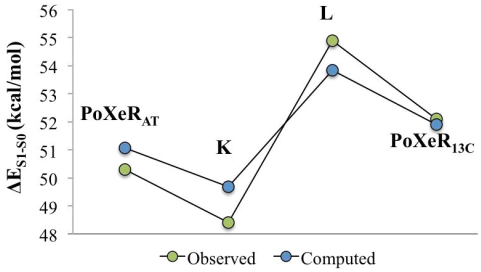
There are two types of membrane-embedded ion transport machineries in Nature: inward and outward. Two of the rhodopsins contained in the deep-ocean bacterium, *Parvularcula Oceani*, have a light-driven inward (from the outer to the inner side of the cell membrane) ion pump function. The *P. Oceani* inward H^+ pump rhodopsin PoXeR has, surprisingly, similar (51%) amino acid sequence to Anabaena Sensory Rhodopsin (ASR): a sensory rhodopsin which can be transformed into an inward H^+ pump via a single amino acid replacement.





In a previous computational study we have provided evidence that ASR works as a four-stages molecular rotor powered by two photons. Here, we present a parallel study on PoXeR. The results indicate that the same rotary motion is possible in PoXeR, even if powered by a single photon. The same results are also employed to understand how this rotary motion could couple to the inward H^+ transport. After looking at the computed structure of the L intermediate, we propose that a key event in the transport mechanism is the reorientation of the NH bond of the Schiff base towards the counterion (D74) thus facilitating the counterion protonation.

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Reaction Mechanisms of Polycyclic Aromatic Hydrocarbons with Oxygen: Site and Size Effects

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Coal-fired power plants produce about 40% of global electricity. Oxy-fuel combustion technology applied to conventional coal-fired power plants can reduce CO_2 and NOx emissions by operating under oxygen rich environments rather than those of normal atmospheric air. (To find details of the SFB/TRR 129 Oxyflame project visit the webpage: `http://www.oxyflame.com/`) Even though there is an intensive body of research on this technology, the governing reaction mechanisms are poorly understood and are mostly limited to simplified reaction models.

As an initial attempt to build a detailed reaction model, we aim to understand the reactions during the combustion of char. As a starting point to understand this process, we investigate the reaction mechanisms of polycyclic aromatic hydrocarbons (PAHs) with oxygen atoms. We use density functional theory calculations (DFT), TPSSh hybrid meta-GGA functional and the TZVP basis set. We particularly try to understand the effect of different molecular regions (Figure 1) and sizes of PAHs. Here, we report initial results for the reactions of triplet oxygen ($O(^3P)$) with different sites of PAHs.

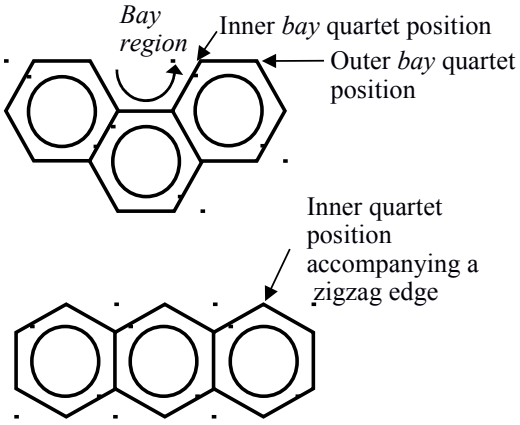

Figure 1: Phenantrene and anthracene as an example to different molecular regions of PAHs.

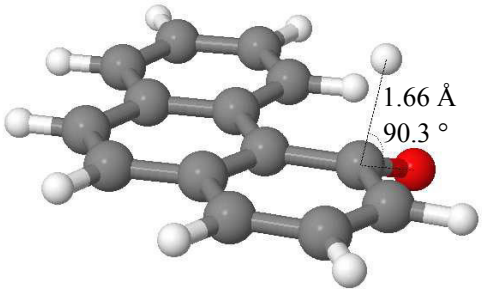

Figure 2: The transition state structure of phenanthrene for the *second step* of the oxygen addition reaction, $C_{14}H_{10}+O(^3P) \rightarrow \cdot C_{14}H_{10}O\cdot \rightarrow \cdot C_{14}H_9O+H\cdot$, to the inner bay quartet position.

Studying the redox properties of DNA with hybrid quantum/classical molecular dynamics simulations

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While the structure and function of enzymes involved in the recognition and repair of damaged bases in DNA is known, the mechanism through which they coordinate their action to interrogate the entire genome in a physiologically relevant time scale remains elusive. Recently, a scheme based on charge transfer has been proposed [1],[2], according to which DNA lesions are detected based on differences in redox properties compared to natural DNA bases. To investigate whether such a mechanism is possible, native and damaged DNA fragments in physiological conditions are simulated at the mixed quantum/classical level of theory, and their redox properties are computed using a theoretical method that associates them with the distributions of the vertical energy gaps between the two oxidation states [3-5]. Replacement of a guanine (G) by an 8-oxoguanine (8OG) defect leads to an increase of the DNA's oxidation potential by 0.93 V. This difference between G and 8OG is significantly higher than the corresponding value at the single nucleoside level (0.55 V [6]). The same methodology is currently applied to an isoguanine defect, while more lesions are also under consideration.

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Towards Branching Ratio Control in Hot Photoassociation of Mg_2 – Theory, Numerics and Experiment

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Recently, coherent control of bond making has been successfully demonstrated under thermal conditions [1]. Specifically, in a strong-field multiphoton experiment using femtosecond laser pulses, it was found that the yield of detected magnesium dimer molecules was enhanced for positive chirps pulses and suppressed for negative chirps. Using an *ab initio* model it was demonstrated that control is achieved by purification combined with chirp-dependent Raman transitions. We will discuss the theoretical and numerical aspects that went into our modeling of the experiment and present new results which shed light onto the chirp-dependent dynamics invoked by the laser field. In particular we find that the optimal chirping rate depends on the considered UV emission wavelength, which provides a signature of the photoassociated dimers. This feature points towards the possibility to achieve branching ratio control in photoassociation experiments at room temperature.

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Missing states and irregularities in excited states manifold of 2,2'-bithiophene – basis set dependence study

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At the example of the 2,2'-bithiophene it is shown that the excitation energy spectra computed using sequences of cc-pV*n*Z and aug-cc-pV*n*Z basis sets reveal surprisingly strong dependence of the excited states manifold on the quality of the basis set. The observed computational artefacts include: numerous missing states, wrong order of states, and considerable shifts in the energy spectrum [1]. The presented results suggest that the cc-pV*n*Z basis sets are completely unsuitable for modelling optical spectra of organic molecules and that the aug-cc-pV*n*Z basis sets are capable of predicting only the lowest portion of the energy spectrum. A simple and inexpensive remedy for the observed problems is suggested: an additional, molecule-centered, Rydberg basis should be rudimentarily used in quantum chemical calculations aiming at modeling optical spectra of molecules. The main conclusions seem to be general and independent of the chemical identity of the studied system (as demonstrated also for other organic chromophores) and of details of the employed computational methodology.

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Computational study of the reaction mechanism of the selective catalytic reduction of NO_x using the copper(II) zeolite catalyst SSZ-13

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The development and improvement of cheap and efficient ways to remove NO_x from the exhaust gas of Diesel engines remains a major challenge for research in catalysis.

The selective catalytic reduction (SCR) of NO_x by ammonia over copper-based catalysts is presently the predominant way to remove hazardous NO_x from exhaust gases. In particular, the chabazite-based catalyst Cu-SSZ-13 has recently attracted strong interest due to its outstanding performance and hydrothermal stability. Although Cu-SSZ-13 has already been commercialized, the reaction mechanism and the structure of the active sites are strongly debated. A prerequisite for improving this known catalytic system is to understand the SCR mechanism over Cu-SSZ-13 [1,2].

Here, we present energetic studies for the SCR reaction based on density-functional theory (DFT) calculations. We choose the simplest possible model of the zeolite catalyst, which is used to explore different possible reaction paths for the reduction half-cycle. At every step of the proposed mechanism, different reaction steps are explored in order to identify or exclude possible intermediates. We also consider different possible charge states of the catalytic center [3].

We find that the SCR reaction on Cu catalysts proceeds via absorption of NH_3, followed by building a NH_2NO species which decomposes to nitrogen (N_2) and water (H_2O). The proposed mechanism is consistent with spectroscopic data [3].

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Fast QM/MM Electronic Coupling Calculations for Charge Transfers in Proteins

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Long-range biological electron transfer (ET) reactions play an essential role in biological processes such as respiration, photosynthesis and enzymatic reactions. Complex and inhomogeneous ET requires computationally cheap approaches, in order to address the complexity of the medium and thermal fluctuations through many conformations.[1] Driving force and reorganization energies associated with ETs can be determined from QM/MM free energy calculations assuming a sufficient conformational sampling. However, the rate constant is also proportional to the square of the electronic coupling, while this latter decrease exponentially with distance. Biological complex environment helps to maintain a good electronic coupling value using intermediate redox states or tunneling the charge through protein backbone, aromatic residues or solvent.

Determination of the electronic coupling between the electronic states remain however more controversial at the theoretical level allowed by the size of the protein systems (DFT or semi-empirical/MM). To assess the necessary approximations associated with cheaper calculations, benchmarking analyses provide a base from which to investigate and compare the accuracy of the different methods and their respective sources of error.[2–4]

After a description of these benchmark studies, we focus on electronic coupling calculations for different ETs in protein using the FO/DFTB approach developed in our group [5,6]: tunneling in Azurin, comparison between direct and bridged transfer in a photolyase, long range charge transfer in ribonucleotide reductase through backbone, polar and aromatic residues.

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Solvent Accessibility and Ligand Binding in Copper Nitrite Reductases

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Microbial copper-containing nitrite reductases (CuNiRs) are enzymes that catalyze the reduction of NO_2^- to NO, a key denitrification step in the global nitrogen cycle. This process involves a proton-coupled electron transfer reaction involving the two copper sites, the electron donating T1Cu site and the catalytic T2Cu site. We are investigating the pathways of proton and electron transfer and the reductive mechanism at the T2Cu site using multiscale computer modelling.

Initial classical MD simulations starting from crystal structures of two-and three-domain CuNiRs in their native state give an insight into how the flexible active site residue Asp_{CAT} facilitates water and proton accessibility to the active site of NO_2^- reduction (T2Cu). The protonation state of Asp_{CAT} enhances the mobility of either itself or other active site residues and this movement strongly influences solvent accessibility. With standalone QM and hybrid QM/MM studies on both native and ligand (NO_2^- and NO) bound states we identify the conformations of the ligand binding at the T2Cu site. We further establish a correlation between the copper oxidation state and the conformational orientation of ligands bound at the T2Cu site. Our results corroborate closely to our serial crystallography observations of two different binding modes of NO_2^- at the T2Cu site to its oxidation state and loss of one water in native state on reduction of Cu at T2Cu site [1,2]. These results lay the foundation for combined QM/MM simulations to understand the underlying mechanistic reasons for the observed behaviors.

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MetScore: Site of Metabolism Prediction beyond CYP P450 enzymes

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The complexity and diversity of chemical transformations involved in drug metabolism impose a hurdle on computational models for Site of Metabolism (SoM) prediction [1]. Ligand-based machine learning models are general and potentially useful tools for SoM prediction. Contrary to typical QSAR problems where one can use molecular descriptors, reactivity is atom-centered and needs atom descriptors that capture the reactivity-determining features, especially the anisotropy of the electron distribution.
Earlier, we developed multiple novel atom reactivity descriptors that characterize the steric and electronic environment, approximated by the mass or partial charge distribution in the atom's proximity. The charge distribution is based on charge schemes (NPA, CM5 DFTB+ charges) that have (a) a low method- and basis dependence and (b) a low dependence on conformation and therefore allow for a one-conformer approach [2].
High effort was put into the extraction, verification and cleaning of the training data, reducing the raw amount of more than 120,000 metabolic transformations from three different sources of published data to about 12,000 transformations for phase I and 6,000 transformations for phase II metabolism.
Random Forest machine learning with DFTB+ charge-based and steric atom descriptors as well as selected molecular descriptors yield two classification models for phase I [3] and phase II, respectively, with Matthews correlation coefficients of 0.63 and 0.75.
Even more important from the perspective of a medicinal chemist in need to stabilize his compound versus metabolism, the precision, *i.e.* the ratio of experimentally verified predicted SoMs, increased from 0.3 for our predecessor model CypScore to 0.6 for MetScore for a Bayer-internal benchmark data set as well as for a literature data set not included in training.

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DFT investigation for a new Route of the Prins-Reaction

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1,3-Dioxanes are important building blocks in organic synthesis, being found in natural products and bioactive compounds[1]. Motivated by a green protocol using no catalyst in aqueous medium[2], we investigated the mechanism for the unexpected formation of 2-amino-1,3-dioxanes from phenyl- (Ph) or methyl- (Me) amine and acetaldehyde, in a Prins-like mechanism as the main step. Structures were optimized with the ωB97X-D/6-311++G(d,p) combination of functional and basis set. Implicit and explicit solvation effects (water) were included using the IEFPCM solvation method or the supermolecule model. Figure 1 gives relative Gibbs free-energies (kcal mol^{-1}) for the three first steps.

STEP 1

$RNH_2 + CH_3CHO \rightarrow$ (1) $\rightarrow$ (2) $\rightarrow$ Imine, (3)

	R	Initial Complex	(1)	(2)	Imine, (3)
G_{rel} /kcal.mol^{-1}	Me	0.00	-2.00	-5.08	-9.27
	Ph	0.00	9.66	-0.28	-4.51

STEP 2

Imine, (3) $\rightleftharpoons$ Enamine, (4)

	R	Imine, (3)	Enamine, (4)
G_{rel} /kcal.mol^{-1}	Me	0.00	5.95
	Ph	0.00	3.19

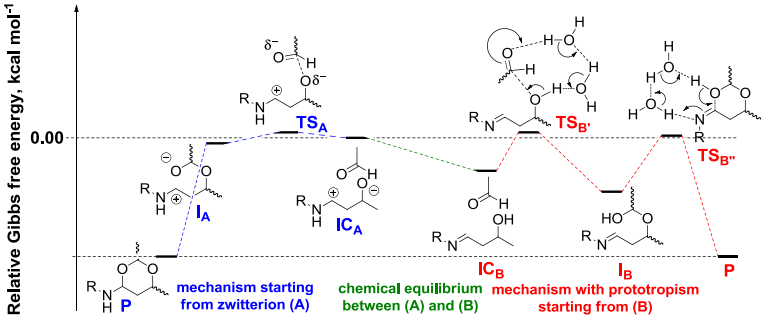
STEP 3

Initial Complex, (5) $\rightleftharpoons$ (A) $\rightleftharpoons$ (B)

R	Initial Complex, (5)	(A)	(B)
Me	0.00	-1.75	-13.70
Ph	0.00	8.50	-7.88

Figure 1. Relative Gibbs Free Energies (kcal mol^{-1}) for the initial steps.

The reaction steps represented above, which precede the Prins-like cyclization, occur with low relative energies for both amines. In the first step, explicit microsolvation is required to allow formation of the imine in aqueous medium [3]. In **step 3**, two isomers can be obtained: a zwitterion (**A**) and a molecule with no charge separation (**B**). Thus, two possibilities arise. In both of them stepwise pathways were found. Explicit water molecules are necessary to stabilize charges in the intermediates. Starting from **A**, the relevant transition state is $\mathbf{TS_A}$. Cyclization occurs with low activation energy, since it connects atoms with opposite charges. Starting from **B**, the mechanism involves prototropisms with transition state $\mathbf{TS_{B'}}$ forming intermediate $\mathbf{I_B}$ which can cyclize through $\mathbf{TS_{B''}}$ leading to the product **P**. Although IC_B is more stable then IC_A, the transition states connecting the products have essentially same energy, therefore both pathways can be followed. Microsolvation is required in the mechanism involving prototropism. The final computed stereochemistry is consistent with experimental observation.



	Structure	G_{rel} (R=Me)	G_{rel} (R=Ph)
Mecha-nism starting from (A)	IC_A	0.00	0.00
	TS_A	3.37	4.46
	I_A	-0.09	1.75
	P	-21.74	-27.69
Mecha-nism starting from (B)	IC_B	-16.04	-16.96
	$TS_{B'}$	6.82	4.08
	I_B	-18.27	-20.65
	$TS_{B''}$	-1.90	-0.95
	P	-21.74	-27.69

Figure 2. Mechanistic possibilities of the Prins-like step to afford 1,3-dioxane.

Acknowledgements: UFF, PPGQ-UFF, IQ-UFF, IFRJ.

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Developing Inhibitors of the Enzyme "TRMT2A" for the Treatment of PolyQ Diseases

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Polyglutamine (PolyQ) diseases are a heterogenic group of neurodegenerative disorders including Huntington's disease (HD), for which no cure is available at this time. [1] Their common feature is an expanded CAG repeat in the coding region of the gene, which results in an extended Q tract in the protein, which leads to the formation of toxic aggregates.

Recently, experimental evidence produced by Dr. Voigt, in Prof. Schulz's group, showed that inhibiting tRNA methyltransferase 2 homolog A (TRMT2A) function might cause an error-prone translation, leading to an increased number of non-Q insertions in the otherwise uninterrupted polyQ stretch. These interruptions decrease the probability of polyQ stretches to form toxic aggregates. Upon silencing the TRMT2A gene, decreased PolyQ aggregation was observed in yeast, flies and HEK293T cells.

TRMT2A features a catalytic domain (CD) and an RNA recognition motif (RRM). Successful inhibition of one of the two is thought to hamper TRMT2A function. We built a ligand-based pharmacophore model across known tRNA methyltransferase inhibitors against the CD. This was combined with structural models of the domain to allow educated guesses about spatial requirements of the binding pocket and protein-ligand interaction hotspots. The resulting molecules of this first ligand-based *in silico* screening successfully inhibit polyQ aggregation in HEK293 cells. In parallel, we are analysing the structural and dynamic properties of the RRM (crystalized by Dr. Niessing's lab) by molecular dynamics simulations and bioinformatics tools. Possible druggable binding pockets have been identified, and structure-based virtual screening has been performed. Ligands are currently under test in Dr. Voigt's lab. *Ex vivo* and *in vivo* magnetic resonance imaging on healthy and HD mouse brains will be performed in Prof. Shah's lab.

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Mechanistic insights into trifluoromethylation of a planar aryl-Ni^{II} complex involving Ni^{III}/CF_3• and Ni^{IV}-CF_3 intermediate species

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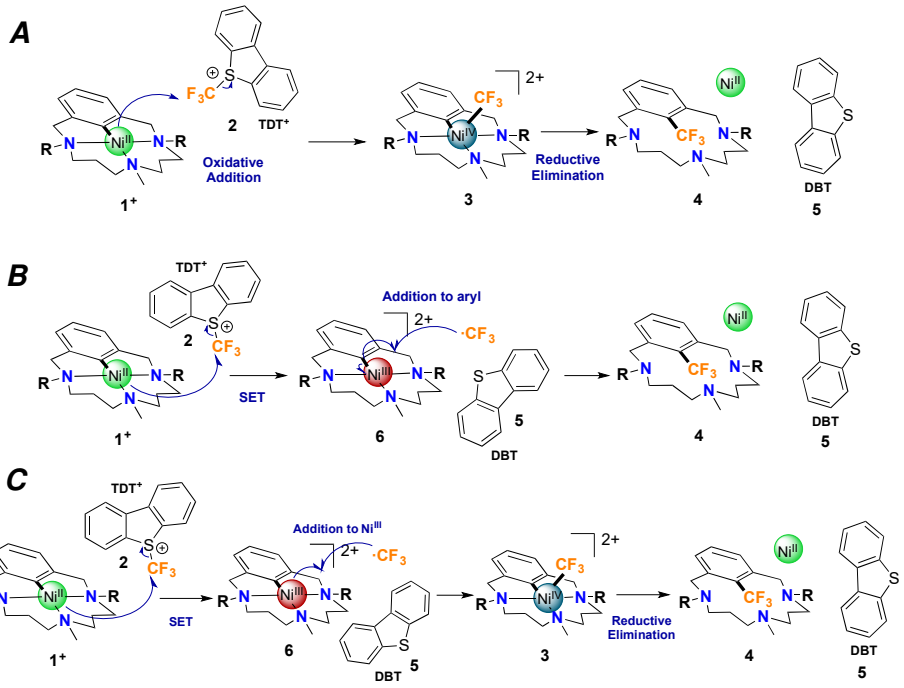
The mechanism of the Nickel mediated trifluoromethylation of a model macrocyclic ligand (L_1) has been studied by means of DFT. The reaction of [L_1-Ni^{II}](OTf) with CF_3^+ sources afforded L_n-CF_3 products in quantitative yield. A combined experimental and theoretical mechanistic study provides new insights into the operative mechanism for this transformation. Three proposed mechanism A, B and C (see figure) were proposed. Computational analysis indicate the occurrence of an initial Single Electron Transfer (SET) to 5-(trifluoromethyl)dibenzothio-phenium triflate (TDTT) furnishing a transient L_1-Ni^{III}/CF_3• adduct, which rapidly recombines to form a [L_1-Ni^{IV}-CF_3]$(X)_2$ intermediate species. A final facile reductive elimination affords L_1-CF_3. To the best of our knowledge, this is the first example of well-defined square-planar model platforms allowing stepwise information all the way through the redox chemistry of nickel, from Ni^0 to Ni^{IV}, thus gaining insight into the geometry-dependent reactivity of multiple oxidation states and facilitating the development of new Ni-based trifluoromethylation methodologies.



New aspects of the reactivity of rhenium tricarbonyl complexes towards activated alkynes through DFT calculations

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The reactivity of rhenium(I) complexes of type [ReX$(CO)_3$(bipy)] (X = OMe (methoxo), OH (hydroxo), NH*p*Tol (*para*-tolylamido), PPh_2 (diphenylphosphanido); bipy = 2,2'-bipyiridine) towards activated alkynes has been studied experimentally [1] and, in some cases, theoretically. [2] All reactions start with an initial attack of the nucleophilic ligand X to one of the acetylenic carbon atoms. In the alkoxo complex a vinyl carbanion forms and inserts into the Re-OMe bond, whereas in the hydroxo and amido complexes the just added alkyne bonds to a CO ligand in *cis* disposition forming a metallacycle that becomes highly stabilized by the transposition of a proton from the nucleophilic ligand to the attacked CO. Phosphanido complexes open the way to a new kind of product coming from the addition of the vinyl carbanion to the bidentate ligand, in spite of the inertness attributed to this kind of ligands. Neither experimental nor theoretical works have been reported for the reaction of [Re(NRR')$(CO)_3$(bipy)] complexes with activated alkynes such as methyl propiolate (HMAD, HC≡CCO_2Me), so in this poster we present a theoretical study of the mechanism of this reaction and predict the expected product. On top of this, interesting issues come from the comparison of this information with that obtained for the analogous reaction with [Re$(PPh_2)(CO)_3$(bipy)].

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In silico design of zero thermal expansion materials

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Materials showing no expansion with changing temperature have numerous applications ranging from commonplace ceramic hobs to astronomy. Among these materials are glass ceramics containing crystal phases with negative thermal expansion in one crystallographic direction, *e.g.*, the high temperature (HT) phase of $Ba_{1-x}Sr_xZn_{2-y}M_ySi_{2-z}Ge_zO_7$ (*M*=Mg, Mn, Cu, Ni, etc.) solid solutions [1, 2]. Such a wide range of possible chemical compositions allows the targeted design of the structure and materials properties (*cf.* Figure), but makes the experimental characterization to a very demanding task. This work employs simulations at the DFT level for determination of the atomic structure, phase stability, mechanical properties and thermal expansion of $Ba_{1-x}Sr_xZn_{2-y}Mg_ySi_2O_7$ solid solutions. Structure optimizations yield not only a good agreement between calculated and experimentally observed cell parameters, but also a correlation of relative energies of the HT phase and the measured phase transition temperatures allowing a rapid, qualitative prediction of the phase stability with varying chemical composition. Furthermore, *ab initio* molecular dynamics simulations at constant pressure were used for calculation of the thermal expansion showing a remarkable agreement with experiments. Together with the predicted elastic constants, this provides vital information for optimization of the microstructure and fabrication of these zero thermal expansion glass ceramics.

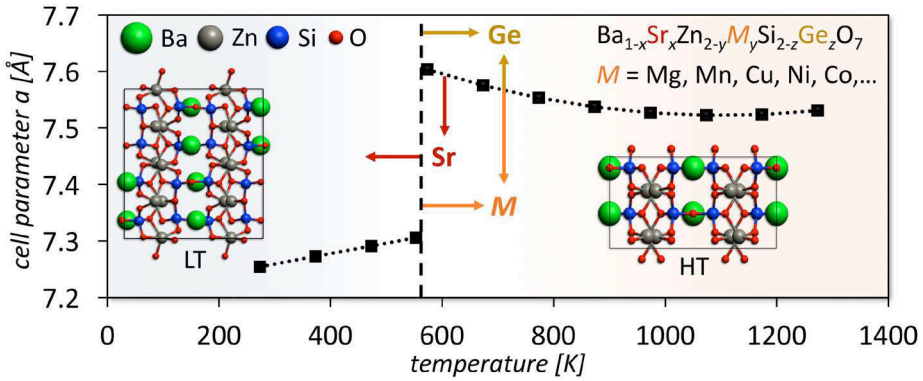

Figure Change of structure and phase stability of the low (LT) and high temperature (HT) phase of $BaZn_2Si_2O_7$ (black curve) caused by variation of the chemical composition.

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Structure Over Energy: An Alternative Approach for Low-Cost Methods in Crystal Structure Prediction

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In silico prediction of crystal structures (CSP) strictly from a molecular diagram is a challenging task. The difficulties, in part, lie in developing electronic structure methods that are accurate enough to capture small energy differences, while remaining computationally inexpensive. While the various low-cost approximate methods proposed in the literature [1, 2] provide a framework to tackle the issue, the levels of accuracy achieved for computed energy differences between structures are unsatisfactory; it can be argued that their accuracy is insufficient to rank polymorphs or candidate crystal structures in the context of CSP. We propose an alternative approach: using low-cost methods as a means of yielding geometries that are transferred to single-point energy calculations with higher-level methods. Provided the low-cost method gives reliable geometries, this removes the need to correct for any errors due to, e.g., localized basis sets. The same accuracies for lattice energies as if one had used the high-level method alone are then obtained. Applications to organic molecular solids [3] and to preferential crystallization of chiral molecules [4] will be presented.

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A Kinetic Model for Singlet Oxygen Photosensitization

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Thio-modified nucleobase derivatives have been often investigated as potential phototherapeutic agents, in which the generated singlet oxygen is the reactive oxygen species.[1,2] Using multireference quantum chemical methods, we have explained the unique phenomena during their photoexcitation and intersystem crossing process to T_1 state.[3] On the basis of the double ππ* minimum topography of T_1, a two-step mechanistic model is proposed to explain the triplet intrinsic decay dynamics to S_0 in thionucleobases, which is accompanying and competitive process with the singlet oxygen production.[4]
Based on these works, we focus on the last step of singlet oxygen generation, the photosensitization of PS-O_2 complex, where the photosensitizer PS is a thionucleobase:

$$^1\left[^3PS + \left(^3\Sigma_g\right)O_2\right] \longrightarrow {}^1\left[^1PS + \left(^1\Sigma_g/{}^1\Delta_g\right)O_2\right].$$

To investigate this weakly-coupled intermolecular energy-transfer process directly from quantum chemical calculations, we have built a kinetic model for computation of the reaction rates. Based on a divide-to-conquer principle, the model splits the system into sets of orthogonal coordinates, to compute diabatic couplings, activation energies, and reorganization energies at minimum computation costs. It offers an effective way to evaluate the reaction probability along different incidence/orientation directions between the monomers of the PS-O_2 complex, thus, connecting reaction kinetics and quantum chemical calculations.

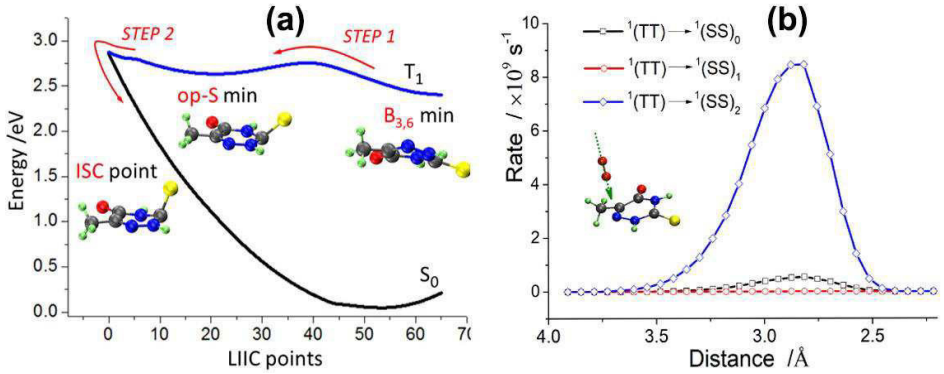

Figure 1. (a) Two-step model for triplet decay dynamics of thionucleobase; (b) The singlet oxygen photosensitization rates along one direction from the kinetic model.

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The role of acceptor-donor capacity in amide and imide dimerization. A theoretical–experimental study

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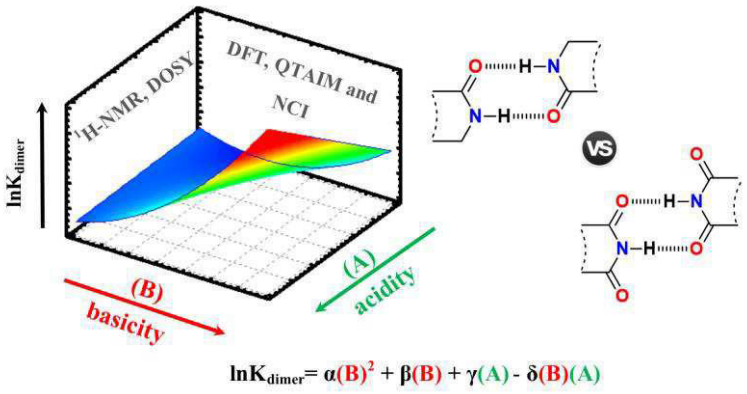
Amides dimerize more strongly than imides in spite of the larger acidity of the latter functional group. This unexpected result had been explained regarding repulsions involving the spectator carbonyls in imides [1]. However, we did not find any indication of this repulsion by electron density topology analysis. Intrigued by this result, we studied the self-association of amides and imides through NMR experiments and theoretical calculations to give a rationale of this phenomenon based on electronic effects. We found that there is a good relationship among self-association constant, acidity of the N-H and the basicity of the carbonyl group, which conforms to a second-order polynomial model. This model describes an appropriate balance between the acceptor and donor capacity, which in turn explains the experimental results. The findings not only explain the studied phenomenon but also provide a predictive model which can be used to examine more complicated hydrogen bonded systems involving these functional groups in areas such as molecular recognition, synthesis of supramolecular materials, crystal engineering, organocatalysis and sensor design.



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Molecular Dynamics Study of Lignin Degradation under High Pressure and Temperature

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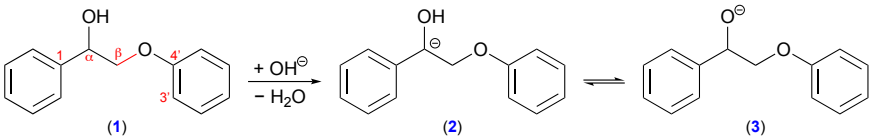
The base catalysed depolymerisation (BCD) of lignin [1] into small molecules as an alternative feedstock becomes increasingly important in the search for sustainable chemical feedstocks. A recent computational study [2] of the hydrolysis of 2-phenoxy-1-phenylethanol (1) as model for the βO4' linkage in lignin showed that the cleavage of the βO4' link can either arise from the carbanion (2) or the alkoxide (3).



(1) (2) (3)

Both anions yield the desired products, but the reaction path starting from the alkoxide (3) passes through intermediate oxiranes which can partake in the formation of undesired byproducts. While the different pathways are clearly separated from each other at low temperatures, QM/MM molecular dynamics simulations of (2) and (3) in aqueous solution indicate that this difference vanishes at high temperatures and low solvent densities mimicking the reactors used for the BCD experiments in the laboratory. Hence, any attempt to increase the selectivity of the lignin hydrolysis has to include a reduction of the reaction temperature.

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Excited state gradients in polarizable QM/MM models: an induced dipole formulation

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Charge and structural properties of electronically excited states in embedded systems are strongly affected by the environment. Multiscale approaches where different levels of theory are combined in a single calculation, have shown to properly describe such effects combining accuracy with computational efficiency.
Here we present an extension of a fully polarizable QM/MM scheme to analytic excited state gradients following a Lagrangian approach [1, 2]. Time-dependent density functional theory is used as the QM method of choice, whereas the classical environment is treated in terms of a polarizable force-field, where the polarization is included through induced dipoles [3]. The method is applied to study of formation and relaxation of the bright excited state of an organic dye (DAPI) intercalated in a DNA pocket. The results indicate the non negligible effect of polarization between the DAPI and DNA pocket, in determining the fluorescence properties of the embedded dye [4].

Acknowledgments: MM gratefully acknowledges financial support from the European Union's Horizon 2020 research and innovation program under the Marie Curie Skłodowska-Curie grant agreement No.642294.

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Computational insights into induction period of ethylene polymerization by the CrO_x/SiO_2 (Phillips) catalyst

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The (CrO_x/SiO_2) Phillips catalyst is one of the most commonly used chemical system to perform ethylene polymerization that currently accounts for about 40-50% of world's annual total production of high-density polyethylene [1]. However, a chemical nature of this catalyst is not well known. In particular, one of the biggest questions concerns the so-called induction period, i.e., the initial stage of the reaction when its rate is very low. We still do not know how do the initial oxidized Cr(VI) species transform into Cr(II) and Cr(III) and what is the reason for the observed induction period. Here, based on DFT investigations, we aim to solve these issues.

The cluster models of the system studied were developed employing two different amorphous silica structures: (i) derived from β-cristobalite framework [2] and (ii) from previous periodic simulations [3-5]. Geometry optimization were performed using the PBE0 functional combined with the def2-SVP basis sets. Dispersion interactions were included in the single point energy calculations at the PBE0-D3/def2-TZVPP level of theory. In some of the reaction pathways studied, spin-crossing occurs and we calculated minimum energy crossing points (MECPs) between two potential energy surfaces, following the methodology developed by Harvey and co-workers.

We have found that the most kinetically favored reduction pathway involves the reaction between ethylene and both oxo ligands of the major dioxo Cr(VI) surface species. Consequently, the Cr(II) site should be formed together with two formaldehyde molecules. The calculated energy barrier for reduction is comparable with that for initiation [6]. We also propose that surface defects might be involved into one-electron Cr(II) to Cr(III) transformation [6].

Acknowledgments: This work was supported by the National Science Centre, Poland, Project No. 2015/19/N/ST4/00007, and by the PL-Grid Infrastructure.

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Theoretical studies on the cobalt(III)-based catalysts for CO_2/epoxide copolymerization

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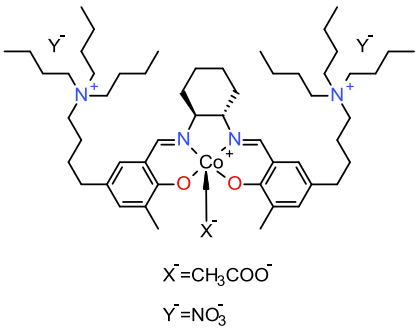

Over the last few years several highly active and selective catalytic systems towards transformation of CO_2 into biodegradable polycarbonates have been reported [1]. One of the most promising catalyst generation is based on cobalt(III)-salen-type scaffolds and includes so-called binary and bifunctional catalytic systems [2]. The former consist of electrophilic part (electroneutral organometallic octahedral Co(III) complex with tetradentate salen-type ligand) and nucleophilic part (quaternary ammonium salt) acting as a co-catalyst; both playing a significant role during formation and growth of a polymer chain [2]. In the latter (see the figure), electrophilic and nucleophilic parts are combined into a single chemical entity, resulting in much higher catalytic activity of bifunctional vs. binary systems. Based on experimental premises from studies on simple Co(III)-salen complexes, the ability to adopt distinctive geometrical isomers is listed among factors that affect the catalytic activity of these compounds [3,4]. However, there is still no information which of possible isomer is preferred in a case of bifunctional catalysts and whether such preference is affected by structure and arrangement of cationic chains.

The main goal of presented theoretical studies is to provide insight into stability of geometrical isomers for bifunctional catalytic systems. To ensure a proper sampling of the conformational space of such complexes the computational protocol employing extensive conformational search at the level of semiempirical method for preliminary selection of conformers followed by DFT optimizations and energy refinement was proposed. Preliminary analysis of possible intermediates in the catalytic CO_2/epoxide copolymerization cycle for simplified catalyst models will also be presented.

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An Algorithm to Locate Optimal Bond Breaking Points on Potential Energy Surfaces for Mechanochemical Reactions

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Mechanochemistry is an emerging research field that focuses on the promotion of chemical reactions by means of mechanical forces.[1] It is well established that the force-induced structural changes of minima and saddle points can be described by a Newton Trajectory (NT) on the original or stress-free potential energy surface (PES).[2] Given a reactive molecular system and a well-fitting pulling direction, there is a sufficiently large value of the force for which the minimum configuration of the reactant and the saddle point configuration of a transition state collapse at one point on the corresponding NT. This point is called barrier breakdown point or bond breaking point (BBP).[3] The Hessian matrix at the BBP has a zero eigenvalue and the corresponding gradient indicates which force (both in magnitude and direction) should be applied to the system to mechanically induce the reaction in a barrierless process. Within the manifold of BBPs, there exist optimal BBPs [3] which indicate what is the optimal pulling direction and what is the minimal magnitude of the force to be applied for a given mechanochemical transformation. At the optimal BBPs, the gradient coincides with the eigenvector of the Hessian matrix with null eigenvalue. Since these special points are very important in the context of mechanochemistry and catalysis, it is crucial to develop efficient algorithms for their location. Here, we shall present a Gauss-Newton algorithm that is based on the minimization of a positively defined function (the so called σ-function). The behavior and efficiency of the new algorithm will be shown for 2D test functions and for a real chemical example.

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A Stochastic approach to thermal density functional theory

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Warm dense matter (WDM) is a phase characterized by temperatures of the order of 10,000 K and high nuclei densities. WDM is of high interest in many fields of physics, chemistry, planetary sciences and even industry: from giant gas planets, the earth's core, laser-heated solids and surfaces, and up to ignition of inertial confinement fusion capsules. Nowadays, using intense lasers, WDM properties can be investigated in the laboratory, thus requiring attention to theoretical research for interpretation and understanding of the results. In terms of tools for theoretical description it is considered a complex regime, being the intermediate between condensed matter physics (i.e., quantum description) and plasma physics (classic thermodynamics). WDM is often described theoretically using finite-temperature Kohn-Sham (KS) density functional theory (DFT) calculations with reasonably good agreement to experiments. These calculations in finite (non-zero) temperatures are, however, extremely expensive due to the large number of fractionally occupied KS orbitals involved in them. In fact, the computational cost exhibits exponential scaling with temperature. Orbital-free DFT is often considered a solution to this problem as it uses non-interacting kinetic energy approximations that depends directly on the electronic density, thus avoiding the use of KS orbitals. This approximation, however, has been known to be less accurate than the KS single particle wave function approach.
Stochastic methods, developed recently [1] appear to be a fitting approach to this scaling problem, since it is somewhat of an orbital free KS method. It uses the states occupation operator to calculate the energy, but skips the step of finding the orbitals and finds the electronic density by taking the trace of it using random orbitals. We introduce stochastic calculations of the canonical free energy. We further demonstrate our ability to calculate the zero pressure lattice constant (first order derivative) and the bulk modulus (second order derivative) of bulk silicon in different temperatures, despite the noise associated with the calculations. I will discuss the calculations' convergence as a function of temperature and system size as well as the computational effort that is required for it.

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Comparing non-empirical DFT tuning procedures as a starting point for G_0W_0

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The ability to accurately predict the ionization potential (IP) of organic molecules and polymers is imperative for progress in theoretical calculations of organic electronic materials. Many body perturbation theory within the GW approximation is a method widely used for the calculation of IPs, both self-consistently (known as $ScGW$) and as a single step correction on top of a DFT calculation (known as G_0W_0). It has been shown that, in combination with the right DFT starting point, G_0W_0 calculations can give extremely accurate IPs for a wide range of systems at a fraction of the cost of $ScGW$. The choice of the functional used in the underlaying DFT calculation is, however, non-trivial, as a strong starting point dependence of G_0W_0 can be observed.

To obtain a reliable IP from G_0W_0, using an exchange-correlation functional as a starting point that already describes the IP relatively well is imperative. Such an accurate description of a systems IP by DFT can be achieved by non-empirical tuning procedures, which vary the amount of exact exchange in a hybrid functional, resulting in a system specific functional. While in general non-empirical tuning methods have been shown to give improved results for a range of problems over standard DFT functionals, they can suffer from a lack of size consistency. Unfortunately, size consistency is a crucial characteristic for the investigation of organic polymers following the oligomer approach, where polymer properties are extrapolated from the property trends of increasingly long oligomer chains.[1]

We have investigated three unique tuning procedures, both with and without size consistency, as a starting point for G_0W_0 to predict the IPs of a series of polyacetylene oligomers. The DFT ΔSCF IPs showed a strong dependence on the fraction of exact exchange present in the functional and hence on the size consistency of the tuning procedure, with the most reliable results given by the most size consistent method. In contrast, the HOMO eigenvalue IPs obtained after the G_0W_0 correction seemed not to depend on size consistency, as the G_0W_0 correction step was able to counteract the trends with increasing oligomer length. It was shown that although IP tuning lacks size consistency, making it problematic for many calculations on π-conjugated polymers, it is a good starting point for G_0W_0 calculations of IPs and provides results in excellent agreement with CCSD(T) reference data.[2]

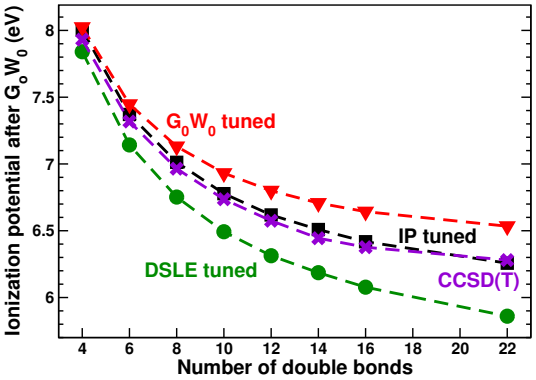

Figure 1: Evolution of ionization potential with polyacetylene chainlength for different G_0W_0 starting points.

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Comparing anharmonic *ab initio* methods: Determining IR spectra of N_2O_5 + X^- (X^-=Cl^-, Br^-, I^-)

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N_2O_5 participates in many complex and essential reactions in the regulation of atmospheric ozone, formation of secondary organic aerosols, and deposition of acid precipitation on the Earth's surface. Specifically, multiphase reactions of atmospheric N_2O_5 at the ocean surface have gained much scientific interest due to the high density of accessible reaction pathways at ambient temperatures. While many mechanisms for these heterogeneous reactions have been proposed, laboratory experiments and theoretical analysis are necessary to confirm these hypotheses. Our work analyzes the IR spectra of the model system N_2O_5 + X^- (X^-=Cl^-, Br^-, I^-) reacting in water. Due to the weakly-bound character of these systems, harmonic analysis alone cannot be expected to accurately predict experimental frequencies and intensities. In this work we present the IR spectra of N_2O_5 + X^- computed using two anharmonic methods: vibrational self-consistent field theory (VSCF) and spectra determined from classical Born-Oppenheimer molecular dynamics (BOMD). We find that at the ωB97X-D/aug-cc-pVDZ level, anharmonic frequency shifts are much smaller than the differences between calculated harmonic and experimental frequencies, indicating the system's strong dependence on chosen potential. Significant anharmonic blue shifts in the asymmetric NO_2 and NO_3 stretches are found in these calculations, which point to the potential "hardening" effect of the halide. Intensities calculated by each method are compared and discussed showing that VSCF-computed relative intensities compare significantly more favorably to experimental results than those calculated from BOMD trajectories, indicating significant quantum effects (i.e. interference) not well-described by classical BOMD. Despite the two theories' starkly different theoretical underpinnings, we find that for these systems, anharmonic frequency shifts calculated from VSCF and BOMD trajectories are qualitatively similar, though VSCF remains far superior in generating relative intensities due to its quantum foundation.

Accurate Embedding based on Potential Reconstruction: Top-Down *vs.* Bottom-Up

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Approximate QM/QM embedding methods based on Frozen-Density Embedding theory suffer from rather poor approximations to the non-additive kinetic energy and the corresponding potential in applications to strongly interacting systems [1]. Several accurate embedding approaches related to Frozen-Density Embedding using potential reconstruction techniques have been proposed in the literature [2, 3, 4, 5]. It could be shown that this allows to generate potentials that accurately reproduce Kohn–Sham DFT densities [3, 4]. Within our quantum chemistry code Serenity, we implemented a variety of reconstruction techniques. We distinguish between the "top-down" reconstruction approach [4], requiring an initial supersystem calculation, and the "bottom-up" reconstruction approach [3, 6], which iteratively generates supersystem densities as a sum of subsystem densities. Both are available in this implementation. Here, we compare the advantages and disadvantages of these approaches as well as their dependence on initial guesses/fragmentations and explore possible simplifications suitable for larger systems.

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The Global Reaction Route Map DB and QM-based Conformational Search

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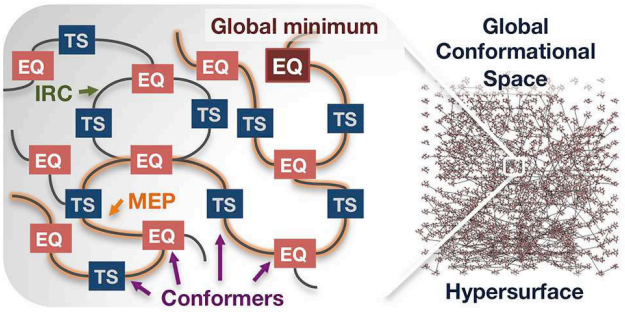
Our QM-based data centric chemistry project is based on *Global Reaction Route Mappings* (GRRM) for molecular and reaction discovery.[1] The approach globally explores potential energy surfaces (PES) of various chemical formulae in different QM levels to obtain reaction route maps (r-maps). We have developed a tool to collect data about r-maps (r-map DB) and an interactive analytical software system for the r-map DB, called RMapViewer (https://github.com/ReactionMap/RMapViewer). Each of the r-map is composed of equilibrium (EQ) and dissociation channel (DC) structures connected by IRC reaction routes via transition state (TS) structures obtained by the PES-search using the *Scaled Hypersphere Search of the Anharmonic Downward Distortion Following* method (SHS-ADDF)[2]. In the QM-based data centric chemistry project, we have applied the SHS-ADDF and RMapViewer to automatic deduction of conformational transition networks.[3] This search uses large ADDF, which makes it possible to trace only low TS barriers while restraining bond lengths and structures with high free energy. We have obtained conformational landscapes of D-glucose conformers with this method. We present the overview of our project, the development of the r-map DB and RMapViewer, and the application to the QM-based conformational search.



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Large-Scale First-Principles GW+Bethe-Salpeter Simulations Targeting 200 Atom Systems

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First-principles GW+Bethe-Salepter method is a well-established method, based on many-body perturbation theory that goes beyond the framework of density functional theory (DFT). This method is capable of simulating the optical properties of not only isolated systems such as molecules and clusters but also extended systems such as crystals. The applications of this method have increased over the recent years. However, greater computational expense compared with conventional DFT, strongly restricted the tractable system size. We addressed this problem in the past several years by employing large-scale parallel computations. Our original program employs an all-electron mixed basis approach, in which a one-particle wave function was expressed as a linear combination of numerical atomic orbitals (AOs) and plane waves (PWs), is now capable of handling thousands of CPU cores without significantly reducing the parallel efficiency. Moreover, we can complete the GW+Bethe-Salpeter calculations for the molecules composed of up to N=200 atoms without necessitating any reduction in the computational accuracy.

In this demonstrative study, we applied our method to some carbon-based molecules such as a defective warped nanographene (= 110 atoms) [1], cycloparaphenylene (= 30-160 atoms) [2], and carbon nanocages (= 108-198 atoms) [3]. The theoretical accuracy of our method was evaluated and agree quite well with the available experimental UV-vis absorption spectra. In addition, we propose the exciton wave function-based analysis method [4] to quantify each type of exciton. We discuss a novel perspective arising from our method, which elucidates the detailed optical properties of the above molecules in terms of overlap strength between electron and hole wave function, exciton size, electron-hole separation distance, electron (hole) delocalization, exciton binding energy, and exciton maps.

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Implementation of divide-and-conquer density-functional tight-binding method for large-scale quantum mechanical molecular dynamics simulations

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We have recently reported an implementation of divide-and-conquer density-functional tight-binding molecular dynamics (DC-DFTB-MD) method for achieving quantum mechanical simulations of large systems [1]. The advantage of the present approach is three-fold in terms of computational efficiency: (a) linear-scaling computational cost with respect to system size by fragmentation of the entire system, (b) small computational pre-factor due to parameterized electronic structure calculation, and (c) development of massively parallelized program which makes it possible to perform energy and gradient calculations of millions of atoms on a supercomputer consisting of numerous nodes with multiple cores. The ubiquitously occurring chemical bond formation and cleavage can be treated in an automatic manner by dividing the system into several grid boxes at each time step. The multipole- and interpolation-based evaluation of charge-charge interaction enables an acceleration of periodic calculations with arbitrary accuracy. Sampling free energy profile is easily accessible in combination with metadynamics technique [2]. As we have demonstrated for proton transfer in aqueous solution models containing thousands of atoms [3–5], the DC-DFTB-MD simulation can track mechanisms involving chemical reactions and evaluate dynamical properties in reasonable agreement with experiment. In this presentation, theoretical aspects and numerical results on performance of DC-DFTB calculations will be discussed.

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Electronic Structure Properties of [*n*]Cyclacenes Investigated by Semi-Empirical and Wave Function Methods

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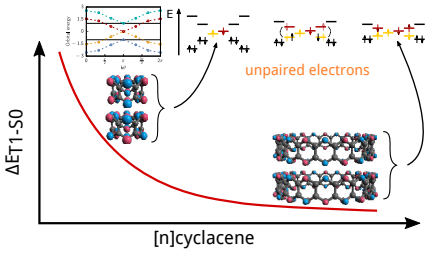

The first *ab-initio* calcultions on [*n*]cyclcacenes appeared almost 20 years ago[1, 2] and these systems are still under active investigation today because of their complicated electronic structure and their potential applications[3, 4]. Similarly to their linear counterparts, the polyacenes, theoretical investigations have been proven difficult from a methodological perspective, which resulted in contradicting results. In this contribution, different properties such as the total position spread tensor, the singlet-triplet energy gap and the radical character of the ground state are presented as a function of the system size at different levels of theory. An active space selection method suggested by the semi-empirical results is presented and used for the subsequent high-level multireference wave function calculations. Dynamic electron correlation effects are taken into account by perturbation theory.
The results obtained show a decreasing singlet-triplet gap and an increasing radical character with increasing size of the system in agreement with the most recent study based on TAO-DFT[3]. This work complements and enlarges the knowledge on this type of systems and confirms by wave function theory the behavior of the studied properties when the size of the cyclacenes is increased.

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Nonadiabatic simulations of carbon monoxide photodissociation in H64Q neuroglobin

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Carbon monoxide (CO) is a leading cause of poisoning deaths worldwide, with no available antidotal therapy. Building upon a new potential treatment paradigm for CO poisoning based on longtime binding of CO by an engineered (H64Q) neuroglobin (Ngb) [1], we study temporal, structural and energetic determinants of the photodissociation and geminate recombination of CO in Ngb by means of molecular dynamics simulations. A model for the ground and the excited diabatic states is constructed based on available experimental data. The hopping between the diabatic surfaces is treated using the Landau-Zener theory [2]. In our computational scheme, the relaxation of the photon energy into the protein matrix is also considered in a simulation that match a complete experimental setup. Simulations are conducted for the native form of Ngb and for the mutant, H64Q. We collected 1-microsecond of aggregate simulation time, allowing us to observe many photodissociation and geminate recombination events. Our investigation suggests that the mutation of the distal histidine to glutamine in Ngb has an impact on the concurrent binding to the heme. Moreover, our results show that cavities of the native form and the Ngb mutant are differently populated by the photodissociated CO. This study may bring the structural, temporal and energetic basis for the mechanisms of the near-irreversible binding of CO to the engineered Ngb, providing a better understanding to the new treatment for CO poisoning. The proposed methodology is general and thus may serve as a starting point for development of new methods suitable for simulating ligand diffusion in proteins beyond the Born–Oppenheimer approximation.

JR acknowledges funding (grant 2015/19/N/ST3/02171) from National Science Centre, Poland. The results used in this study were obtained using Interdisciplinary Centre for Modern Technologies computational facilities, NCU.

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Difference of electron chirality between enantiomers as a possible solution to homochirality in Nature

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The electron is known to have its chirality determined by the directions of spin and momentum. It has been found that total electron chirality in chiral molecules is different between enantiomers. Here the total electron chirality is defined as the integration of electron chirality over a molecule. In this work, we propose that this difference of the total electron chirality may explain the origin of the (biological) homochirality, which means that amino acids produced biologically are dominantly L-chiral, while those produced in laboratories are racemic.

It is widely believed that the generation of the homochirality is deeply related to the weak interaction of the standard model of particle physics, which violates the parity symmetry. The weak interaction works only for left-handed electrons, while right-handed electrons do not have any gauge charge for the weak interaction. Hence, if the numbers of the left-handed electron in molecules are different, reaction rates of molecules for weak interaction are different. In general, the left-handed electron has usually the same number as the right-handed one due to the electron mass, which is known as the interaction with Higgs field in the vacuum. Thus, for most molecules, the reaction rate for the weak interaction is the same for molecules of the same structure.

In our work, we report that in chiral molecules have different total chirality between enantiomers, that is, the number of the left-handed electron is different between enantiomers of the same molecule. This difference has been known for only H_2Te_2 [1]. We report that this difference is general property for chiral molecules. Therefore, we suggest that this difference of the total electron chirality may be the origin of the (biological) homochirality. Different total chirality means different reaction rate for the weak interaction. The different reaction rate probably induces different numbers between D- and L-chiral amino acids in the early universe.

In this work, we report that chiral molecules have different total chirality of electron for such as H_2X_2 (X=O, S, Se, Te) and alanine. H_2X_2 is one of the simplest structure chiral molecule. Hence this molecule is suitable for the study of the relation between molecular parity violation and the electron chirality.

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Heme vs. Siroheme Models of the Sulfite Reductase Active Site

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A test set of models that describe bioinorganic centers was employed to benchmark the performance of several density functional methods for the accurate description of overall spin states of these centers. The set comprises four models derived from biological active sites that possess different ground state multiplicities (high-spin, low-spin and intermediate-spin state), as depicted in Figure 1.

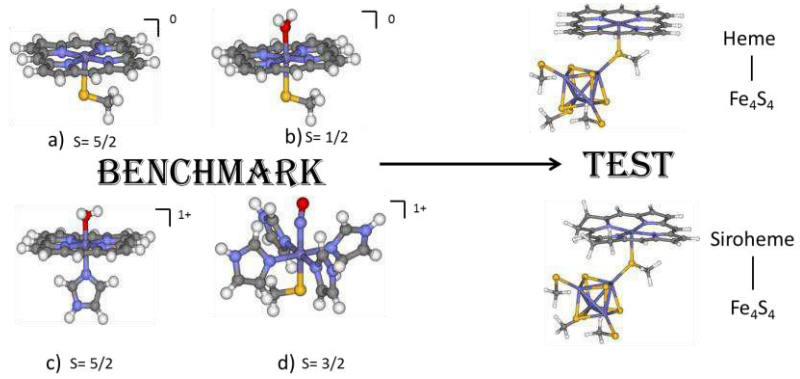

Fig.1. Left: Bioinorganic models derived from the active sites of the following proteins: ferric cytochrome P450 with a vacant distal position (a) and aqua-bound (b), ferric haemoglobin (c) and ferrous-nitrosyl superoxide reductase (d). Right: heme-[Fe_4S_4] and siroheme-[Fe_4S_4] systems

In general, when conducting quantum chemical calculation on open-shell systems using the framework of density functional theory, it is observed that hybrid functionals tend to overestimate the stability of high-spin states, while pure functionals over stabilizes low-spin states. Thus, finding a functional that performs acceptable in all spin state situations encountered in bioinorganic molecules is not a trivial task. In this study, we engage in such a quest, by choosing a set of functionals that use a different amount of exact Hartree–Fock exchange in their evaluation of the exchange integrals.

Further theoretical investigations are carried out with the best performing functionals on bioinorganic models derived from the active site of sulfite reductase in which differences in terms of energetics, bonding, spin coupling are emphasized between the biologically occurring siroheme-[Fe_4S_4] system and the fictive heme-[Fe_4S_4] system in order to get more insights on nature's preferences for the former system.

Improved GBSA force field with modified CMAP and non-bonded interactions

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Abstract

Compared with conventional force fields with explicit water molecules, implicit solvent models can significantly accelerate the computational efficiency by reducing the total degrees of freedom in simulation. However, current GBSA-based force fields are usually less accurate than the explicit solvent counterparts and still require improvement. In this work, we improved the GB-Neck2 combined with ff14SBonlysc force field, which is one of the most accurate implicit solvent models in literature. We implemented a CMAP potential energy term to adjust the secondary structure propensity for each type of residues. Moreover, non-bonded parameters regarding side chains containing aromatic rings were modified to better mimic the pi-pi interaction. The simulation results show improvement on secondary structure propensity as well as tertiary structure accuracy.

A test set of 19 small peptides with known native PDB structures and with diversified secondary structures was constructed to test the accuracy of our force field. For 84.2% (16 in 19) cases, the experimental native structures were correctly produced from extended starting structures by replica-exchange simulations, using a RMSD criterion of 0.45 nm. This result is significantly superior to that using the original force field with the success ratio 47.3 % (9 in 19 cases). Additionally, some small proteins were selected to investigate the force field's performance on larger systems, and better results from our modified parameters were also observed for those cases. Furthermore, the free energy surfaces from the protein simulations illustrate that our force field produces global free energy minima in the vicinities of native structures, while a broad range of conformations can still be sufficiently sampled in the simulations. In conclusion, we developed a new GBSA-based atomistic force field with improved secondary and tertiary structure results. Our force field can efficiently sample the conformational space of peptides and small to median sized proteins.

Photochemistry of Acrylic Acid: Semiempirical and Ab Initio Molecular Dynamics vs. Experiment

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The photochemistry of acrylic acid is of considerable atmospheric importance. However, the mechanisms and the timescales of the reactions involved are unknown. In this work, the photochemistry of acrylic acid is investigated theoretically by molecular dynamics simulations on the second excited state $\pi\pi^*$ using the semiempirical OM2/MRCI method and the ADC(2) method. Over a hundred trajectories were computed for both methods. Results are compared to experimental finding of Okumura [1]. The objectives of this research are twofold: 1) The simulations enable the interpretation of the experiments in terms of molecular mechanisms, yields and timescales of the processes involved. 2) Comparison between the ADC(2) method and the semiempirical OM2/MRCI gves insight into the performance of both methods.

A rich variety of reaction channels are predicted for the single potential energy surface employed using the OM2/MRCI method. Products predicted by the calculations are in accord with experiments. Insights are obtained into the mechanisms of the various channels. Timescales and yields are provided for some of the channels.

ADC(2) simulations predict fewer pathways than the semiempirical OM2/MRCI method. Insights are gained from comparing both methods. The differences in the reaction pathways is attributed to different heights of barriers in the two methods.

The results encourage further simulations of this kind as a tool for interpreting photochemical dynamics of carboxylic acids.

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Combined Quantum Chemical Calculations and QSPR on Olefin Polymerization using *ansa*-Zirconocene for Designing New Catalysts

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ABSTRACT

The Density Functional Theory (DFT) study on homopolymerization of ethene (ET), propene (PP), 1-butene (BT), 1-hexene (HX), and styrene (ST) by a *Rac* [Zr{1-Me_2Si(3-Pr-(η^5-C_9H_5))(3-H-(η^5-C_9H_5))}$ClCH_3^+$] *ansa*-zirconocene catalyst were investigated. The study unveils the following: (i) PP, BT, HX, PS monomers prefer 1,2-insertion over 2,1-insertion and the 1,2-*si* is the most probable insertion path, (ii) *ansa*-zirconocene is regio- and stereoselective catalyst for PP, BT, HX, PS polymerization, (iii) with *ansa*-zirconocene calculated %isotactic for PP, BT, HX, and ST monomers are 94.9, 92.2, 96.4, and 89.50, respectively. In addition, new *ansa*-zirconocene catalysts for ethylene polymerization have been suggested by QSPR model. The model suggests that potent *ansa*-zirconocene catalysts should have more number of propyl groups on indenyl ligands and less positive charge on Zr atom. This information will provide guides for the development of zirconocene catalysts for ethylene polymerization.

Keywords: *ansa*-zirconocene, polyolefin, metallocene, QSPR, homopolymerization

Theoretical Analysis on Ion Conduction in Superconcentrated Electrolyte Solution for Na-ion Battery

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Na-ion batteries (SIBs) attract growing attentions as the alternative to Li-ion batteries (LIBs) with shrinking resources of lithium. Electrolyte solutions, one of the main components of secondary battery, have a crucial impact on the performances of batteries. Among the electrolyte solutions, the superconcentrated solutions receive intense interests as a novel class of electrolyte for the specific favorable characteristics, such as high electrochemical (oxidative/reductive) stabilities, low volatilities, and so forth [1].

Since superconcentrated solutions generally show high viscosities, the carrier ion conductivity is a crucial problem. The ion diffusion mechanism is one of the remaining fundamental issues for superconcentrated electrolyte solutions with small number of free solvents, in which conventional vehicular-type diffusion mechanism cannot take place.

The present study analyzed the diffusion properties of electrolytes for SIB by using the divide-and-conquer density-functional tight-binding molecular dynamics (DC-DFTB-MD) simulations. Dimethoxy ethane (DME) and Na-FSA (FSA; bis-fluorosulfonyl amide anion $(NSO_2F)_2^-$) were employed as solvent and salt, respectively. Simulation boxes were setup for dilute and superconcentrated systems with 5% (3454 atoms), 10% (3388 atoms) and 40% (2924 atoms) of salt concentrations, under the three-dimensional periodic boundary condition. Production runs were performed for 20 ps under NVE ensemble following 10 ps of equilibration runs under NVT ensemble (T = 298.15 K).

Averaged coordination number of Na ion was ca. six for all systems. The numbers of free DME decreased from 77 – 83% to 11% with increasing concentration. Diffusion coefficient of DME decreased to ca. 1/4 in superconcentrated system (6.8×10^{-10} m^2/sec) compared to dilute system ($24.9 – 25.8 \times 10^{-10}$ m^2/sec), while that for Na ion decreased by about a half (5%/10%/40% = 8.4/7.2/3.2 (10^{-10} m^2/sec)). Ligand exchange reactions were newly found as an alternative conduction path of Na ion. The time-correlation analyses of ligand-exchange reactions showed ca. 1.5 – 2.0 times frequent reaction rates in the superconcentrated solution than the dilute solutions.

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Decomposition of intermolecular interaction energies in the DLPNO-CCSD(T) framework. Theory and applications in homogenous catalysis.

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The domain-based local pair natural orbital CCSD(T) (DLPNO-CCSD(T)) method [1] allows for single point coupled cluster energy calculations to be performed on systems with hundreds of atoms. In order to facilitate the interpretation of DLPNO-CCSD(T) results, we recently proposed a Local Energy Decomposition (LED) scheme for the interaction energy between two fragments. [2, 3] This approach exploits the locality of the occupied and virtual orbitals in the DLPNO-CCSD(T) framework for decomposing both the HF and the correlation energy into physical meaningful contributions (see Figure 1).

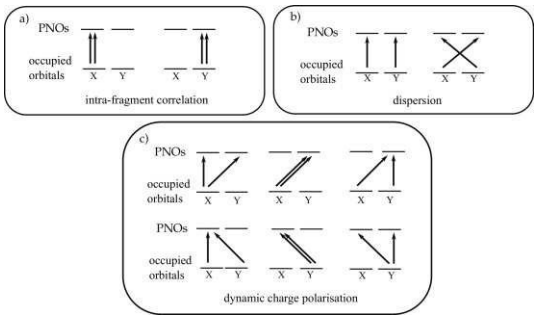

Figure 1: Double excitations constituting the: a) intra-fragment, b) dispersion, and c) charge transfer components of the correlation energy (X and Y are molecular fragments).

In this work, this approach is used for characterizing a wide range of covalent and non-covalent interactions of importance in various fields of homogenous catalysis, including: (i) the interaction of Lewis acids and bases in classical Lewis adducts and Frustrated Lewis pairs for the activation of molecular hydrogen in solution; [3] (ii) the interactions contributing to the stability of the lowest energy diastereomeric transition state of the chirality-determining step of organocatalytic asymmetric transformations.

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Interpreting the hydrolysis/transglycosylation partition in a β-glucosidase using constant pH molecular dynamics

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β-glucosidases play an important role in cellulose degradation by relieving endoglucanase and cellobiohydrolase product inhibition through hydrolysis of cellobiose to glucose. Among those used in commercial enzyme cocktails is Cel3A from *Hypocrea jecorina* (*Hj*Cel3A), which was found to enhance the conversion of various cellulosic substrates by nearly 10% [1]. However, the catalytic activity of *Hj*Cel3A and other β-glucosidases is significantly reduced at high cellobiose or glucose concentration due to transglycosylation, a competing pathway to hydrolysis, wherein another sugar, instead of water, is transferred to the glycosyl-enzyme intermediate. Previous studies, such as that by Turunen et al. [2], suggest that the partition between the two reactions depends on the pK_a of the acid/base residue and/or nucleophile. The impact of the pK_a of ionizable residues on the pH-activity profile and hydrolysis/transglycosylation partition of *Hj*Cel3A is investigated using constant pH molecular dynamics. In this method, ionizable residues are switched between the protonated and deprotonated states through the introduction of a titration coordinate, λ, which continuously changes between 0 (protonated) and 1 (deprotonated) [3]. pK_a changes during the catalytic reaction are monitored and factors that modulate this property, including hydrogen bonding, charge coupling with other residues, and solvent accessibility, are identified. The findings of this study could serve as guide to protein engineering of β-glucosidase variants with improved hydrolytic activity.

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Calculation by QM of UV spectra of short-lived intermediates of $OsCl_6^{2-}$ in aqueous solutions.

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Ultrafast dynamics of transition metal complexes is an active area of research in chemical physics [1]. Plyusnin's scientific group have reviewed the efforts in studying the primary photophysical and photochemical processes in hexahalide complexes of tetravalent ions of platinum group metals [2].

We have recently performed experiments on ultrafast spectroscopy of $Os^{IV}Cl_6^{2-}$ in aqueous solutions [3]. The main result of [4] was the registration of the intermediate (further – key intermediate, KI) with the maximum in the region of 450-470 nm and plateau in the region of 550-650 nm. The characteristic lifetime of the KI is about 20 ps.

In accordance with the method of identification of KI in [3], two possible preliminary mechanisms of the reaction of photoaquation of $Os^{IV}Cl_6^{2-}$ were proposed. According to the first mechanism KI is the lowest electronic excited state of $Os^{IV}Cl_6^{2-}$. According to the second mechanism KI is the ionic pair $^3Os^{IV}Cl_5^-...Cl^-$.

To determine which mechanism [3] is preferable, quantum-chemical calculations of the geometric and electronic structure of $Os^{IV}Cl_6^{2-}$ were performed. The calculation was carried out using a program package FireFly 8.1 [4], electronic spectra were computed at the framework of XMCQDPT [4] the electronic excitation energies were computed with 8 active orbitals and 10 active electrons. Effect of solvent (water) was taken into account at the framework of the PCM. The report presents the results of calculations of the geometric and electronic structure and also UV spectra of $^3Os^{IV}Cl_6^{2-}$ and $^3Os^{IV}Cl_5^-$.

The calculated spectra for $Os^{IV}Cl_6^{2-}$ and $Os^{IV}Cl_5^-$ in the triplet and quintet states are in good agreement with the experimentally observed spectra [3]. While for singlet states the calculated spectral bands start in the far short-wavelength region, that differs significantly from the observed band maxima in the experiment [3]. The results indicate the possibility of the reaction of photoaquation of $Os^{IV}Cl_6^{2-}$ through a sequence of stages: $^3Os^{IV}Cl_6^{2-}$ (LMCT) → $^5Os^{IV}Cl_6^{2-}$ → $^5Os^{IV}Cl_5$→ $^3Os^{IV}Cl_5^-$ (KI) → $^3Os^{IV}Cl_5(H_2O)^-$. This sequence of stages is similar to second mechanism proposed in [3]. Thus, $Os^{IV}Cl_5^-$ in the triplet state is a key intermediate of the reaction of photoaquation of $Os^{IV}Cl_6^{2-}$.

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Activation Strain Model to understand oxidative addition of Carbon-Carbon Bonds to Gold(I) complexes

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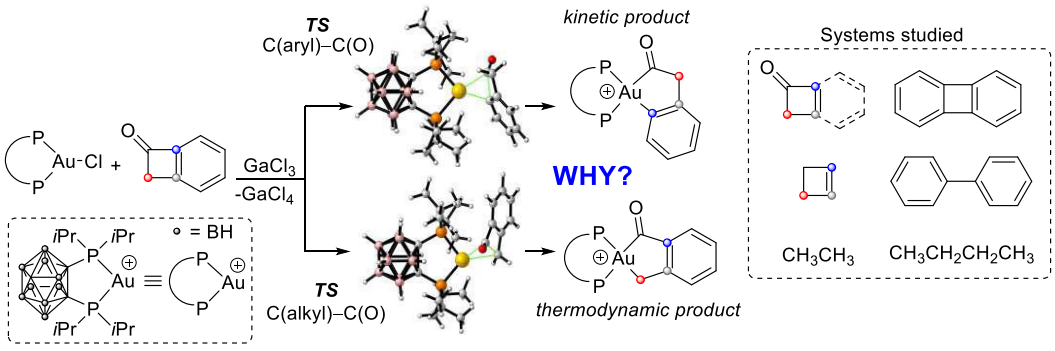
The C–C bond cleavage by transition metal complexes is one of the most challenging reactions in organometallic chemistry.[1] Only few efficient complexes, based on late transition metals of group 9 and 10 (Rh and Pt) have been described to date. Recently, A. Amgoune, D. Bourissou and co-workers characterized cationic organogold(III) complexes resulting from oxidative addition of strained C-C bonds to diphosphino-carborane gold(I) complexes (DPCbAu$^+$). Especially, these bent gold complexes insert into four-membered rings of benzocyclobutenone (see Figure) and cleave selectively either the C(aryl)–C(O) or the C(alkyl)–C(O) as a result of kinetic/ thermodynamic control.[2]

This poster will report the use of the recently introduced activation strain model (ASM) [3] to understand the activation of these non-polar σ-bonds at gold center gold. This approach recently allowed us to understand other process like β-elimination reactions at Ni, Pd and Pt centers.[4] Here, a deeper understanding of the oxidative addition of different C–C bond to Au(I) will be presented. The energy profiles have been calculated at the DFT level of theory. The physical factors that control the energy barriers of this process and the origin of this unusual selectivity will be explained in detail thanks to ASM approach.



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Sigma-Hole Carbon-Bonding Interactions in Carbon-Carbon Double Bonds: An Unnoticed Contact.

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Apart from the hydrogen bond there are also other types of noncovalent interactions in which the H bridging atom is replaced by a member of group IV, V, VI, VII or VIII, usually denoted as tetrel,[1] pnicogen, chalcogen, halogen and aerogen bonds, respectively. These interactions share an important feature: an electron-rich region of a system interacts with an electron deficient region of another system, corresponding to a region of surface electrostatic potential. These electrostatic potential regions can be regarded as σ- and π-holes and are due to the anisotropy of the atom's charge distribution resulting from the formation of covalent bonds.[2] The σ- and π-holes are regions of lower electron density which are along the extension of a covalent bond to an atom for the former, and perpendicular to a portion of a molecular framework for the latter. Particularly σ-hole complexes with group IV atoms mostly focus on the heavier tetrel atoms,[1] leaving carbon-bonding (CB) much less studied. Also π-hole CB has only been studied for several systems, namely, $X_2C{=}O$ (X=H, F, Cl),[2] $F_2C{=}X$ (X=S, Se, Te) and XCN (X= F, Cl, Br, I).[3] Despite having a σ-bond, the C=C group remains unexplored in terms of its potential for establishing σ-hole CB interactions. Due to the abundance of methylene groups in both organic chemistry and biochemistry, here we study the feasibility of noncovalent CB for a series of alkenes as donors and both neutral and anionic systems as acceptors (Chart 1). This is the first time that σ-hole interactions are reported between an sp^2-hybridized carbon atom of a Lewis acid and a Lewis base.[4]

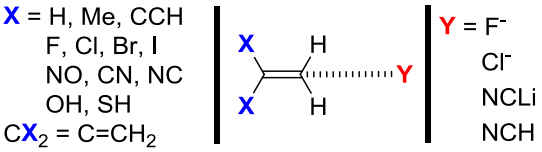

Chart 1. Complexes under study.

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§ Atom Types Introduction and RMSD-based Selection for Drug Metabolites Collision Cross Section Calculation Using MOBCAL

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Ion Mobility Mass Spectrometry (IM/MS) is a technique that allows separation of isomeric species based on differences in their collision cross sections (CCSs) in the gas-phase, thus providing specific information on the potential structure of a compound [1]. In combination with Molecular Modelling, it is considered as a potential tool for small molecule identification by measuring their gas-phase CCSs and comparing them to theoretically derived CCS databases. A protocol for theoretical determination of CCS has been introduced in [2] and its improvement is at the core of this project.

In the initial stage of the project we have developed a script – an extensive automation of the protocol, which allows all the routine and necessary steps of the algorithm to be performed automatically. It minimises human intervention and saves valuable time. Further research aims to investigate deeper possible sources responsible for the differences between the theoretical and experimental CCS values.

In the present work, new atomic parameters employed in the CCS determination software (MOBCAL [3]) have been introduced: the protocol has been modified to be able to distinguish between different atom types and to assign appropriate parameters. Another modification includes an additional step in the protocol that calculates RMSDs of the found conformations and performs filtering based on the level of similarity among structures. Extensive tests of the protocol with the introduced changes are to be made in order to assess the performance of the new script. Additionally, the calculation of the partial charges used by MOBCAL to calculate the ion-induced part of the potential is to be included in the protocol. Further research includes the study of the possible effect of the dipole moment on the CCS of a metabolite and the assessment of the possible use of QSAR in the protocol.

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Uncommon molecular insertion complexes: Non-dipoles and dipoles inside of dipoles

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Highly polar molecular systems are in demand as means of enabling many important practical applications based on light-matter interactions. Novel insertion complexes of non- and polar molecules noncovalently trapped between alkali-halide (MX) counter-ions are studied and compared [1,2], revealing useful insights. For specific selected compositions, the M-molecule-X systems are predicted to exhibit from a metastability (being higher in energy) to a stability relative to molecule + MX by up to 1 eV. Moreover, the polar-molecule insertion complexes can be even more bound than their common dipole-dipole MX-molecule isomers, thus being thermodynamically stable highly polar species, with dipoles of around 20 D. The features of interest include the nonobvious contributions of the molecule polarity to the system stability and dipole moment, the cooperative non-additivity of pair interactions, molecule reshaping and linking by framing ion-pairs.

In addition, due to the neutralization of the M-X charge-transfer in the excited triplet state, these complexes represent unique spin-controlled dipole-switch molecular systems with a large dipole reversibly turned off or even inverted by the spin state, hence potentially allowing various spintronic and optoelectronic applications. The IR spectra are predicted to sensitively indicate the formation of both the M-molecule-X and MX-molecule isomers, with intensities increasing by up to an order of magnitude in the complexes, thus facilitating their reliable detection and differentiation in experiments. In particular, the above indicates possible ways of adding polarity (via attached ion-pairs) to nonpolar molecules and thus of their efficient experimental detection and characterization. The increased attraction could also promote molecular self-assembly, chemical reactions.

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Tri-coordinated oxygen at the surface of graphene oxide (GO)

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Abstract

In recent years, graphene (Gr) has attracted significant attention due to its exceptional electronic, optical, mechanical and chemical properties, which have found potential applications in many fields. Different oxygen-containing functional groups (such as carboxyl, carbonyl, hydroxyl, epoxy, peroxy, lactols) are present in graphene oxide (GO) and reduced GO (RGO), formed during the oxidative preparation of graphitic oxide from graphite and reduction processes, respectively. Structures of GO and RGO are still not fully understood and continuation of studies may reveal fruitful new information to define all of the structural details of these fascinating materials. Understanding of such structures will be essential to control and tune properties in developing application-oriented products.

Determinations of the structures of atomic oxygen-doped graphene are guided by basic concepts of organic chemistry. So far, researchers thought of ether, epoxy and lactols arrangements for such GO/RGO structures. However, a completely new structural arrangement of oxygenated Gr structure is possible where an oxygen atom is linked to three carbons at the junctions of hexagons of the carbon network.

Such tri-coordinated oxygen is known in organic chemistry as open (OR_3^+, R = H, CH_3 etc) and cyclic oxonium ions. An oxonium ion is a species containing an oxygen atom that has an octet of valence electrons but bears a formal charge of +1. Stable alkyloxonium salts exist and play significant roles in chemistry, such as ion-neutral complexes, and play a role in medicinal chemistry. Thus, chemistry of GrO may have significant implications mediated by tri-coordinated oxygen.

Density functional theory (DFT) is employed to determine structure and properties of tri-coordinated oxygen at the surface of graphene sheet, where a single carbon atom is substituted by an oxygen atom. IR, NMR and XPS spectra obtained from DFT calculations are used for structural characterization and compared with experimental spectra.

Mechanistic Insight into Imidazopyrazinone Bioluminescence by TD-DFT Calculations.

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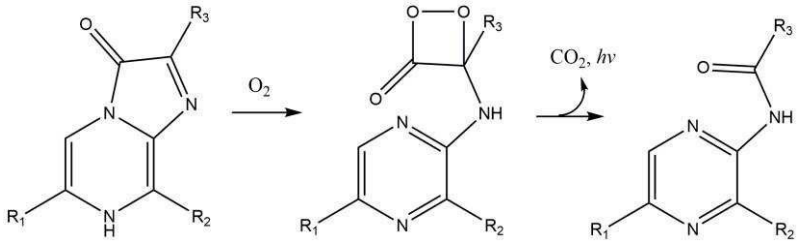
Bioluminescence (light emission from a biochemical reaction) has gained use in bioimaging, bioanalysis and biomedicine [1]. While bioluminescence can be found in 700 *genera*, most species use substrates containing an imidazopyrazinone scaffold [1,2]. These compounds undergo oxygenation to form a dioxetanone intermediate, which thermolysis allows for chemiexcitation (Scheme 1) [1]. While the thermolysis reaction of dioxetanone is a key step, its known instability has prevented its experimental characterization [1,3,4].
We studied the thermolysis of different imidazopyrazinone dioxetanones by performing TD-DFT calculations with the ωB97XD functional [3,4]. Both anionic and neutral dioxetanones decompose via a stepwise-biradical mechanism. However, the biradical is formed either by electron transfer (anionic species) or by homolytic bond cleavage (neutral species). Efficient chemiexcitation is explained by a long PES region where the ground and excited states are degenerated, which can only be accessed by neutral dioxetanone.



Scheme 1 - Bioluminescent reaction of imidazopyrazinone.

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Perturbative Monte Carlo Simulations - a Hybrid QM/MM Approach

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Processes in condensed phase are strongly influenced by environmental effects. Simulations with Molecular Mechanics (MM) are well established but for many effects a description of the electronic structure trough Quantum Mechanics (QM) is necessary. One is faced with the questions of how to consider environment effects in the QM calculation.
Hybrid QM/MM approaches are routinely used in the recent years. However, several challenges restrict the scope of this approach for simulations. Molecular Dynamics (MD) coupled with QM/MM requires expensive electronic structure calculations to compute the energy and gradient at every step. Hundreds of picoseconds simulations are required to exhaustively sample the phase space. Although by far most of the degrees of freedom are in the environment many QM calculations have to be carried out. This limits the simulated time scales as well as the size of the QM part or the accuracy of the QM method.
We propose to use perturbation theory to decouple the dependency of the QM and MM part based on work of Truong and Stefanovich[1]. It allows us to independently sample the configurational space of QM and MM part with Metropolis Monte Carlo (MC) simulations. Compared to MD, no gradient evaluations are necessary and the larger number of energy evaluations is more than outweighted by the negligible computational costs of perturbative steps. Only a limited number of full QM calculations has to be carried out during a simulation to ensure the accuracy of the perturbation approach. Furthermore, we brought forward a hybrid implementation utilizing GPUs which cuts down the computational costs by an order of magnitude[2].
The influence of the approximations and technical parameters on the results have been thoroughly investigated. Benchmark studies have been carried out by looking at the solvent structure, the description of thermodynamics and reactivity in solution and properties as well as electronic spectra of the solute.

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Structures and Properties of Silicon-Doped Boron Clusters B_nSi, with n = 15–24, and Their Anions

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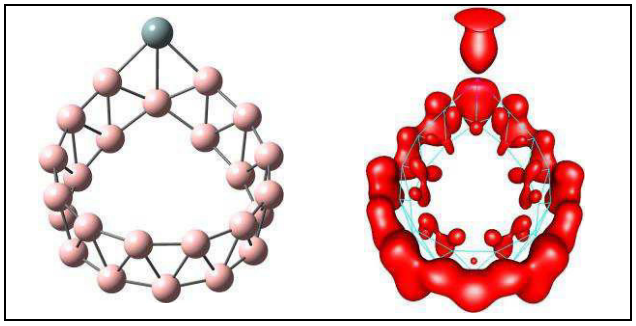
An investigation on silicon-doped boron clusters B_nSi (n = 15–24) in both neutral and anionic states has been explored systematically using quantum chemical calculations. Thermochemical properties of the lowest-lying isomers of $B_nSi^{0/-}$ clusters such as average binding energies, detachment energies, dissociation energies, etc. were predicted by using CCSD(T) method. The growth behavior for $B_nSi^{0/-}$ with n = 15−24 can be established as follows: i) $B_nSi^{0/-}$ clusters tend to be form by substituting B-atom by Si-atom or adding one Si-impurity into the parent B_n neutral or anionic clusters, and ii) Si prefers an external position of the B_n framework. Our calculated results reveal that similar to pure boron clusters, the tubular drum-shape appears at size n = 20 and 24 of impurity B_nSi clusters. Especially, the double ring $B_{24}Si$ exhibits the enhanced stability due to possessing high average binding energy and π aromatic character based on the MOs and ELF analysis.



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Spectroscopic Properties of the Redox Active Tyrosine-D in Photosystem II

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Photosystem II contains two redox-active tyrosine residues, D1-Tyr161 (Y_Z) and D2-Tyr160 (Y_D). These tyrosines plays vital roles [1] when there is a light-driven charge separation in the reaction center, which triggers the redox chemistry. The Y_Z is involved in direct electron transfer to reduce the reaction center, and the Y_Z radical subsequently oxidizes the oxygen evolving complex (OEC), which in return oxidizes water to produce dioxygen. The other tyrosine, Y_D, being spatially far from OEC (~20 Å) plays two important roles, i.e. *redox* and *electrostatic*. In its redox role, it reduces the reaction center; in addition, it participates in redox control of the OEC, where the S_2 state is reduced by Y_D-OH to S_1 in the dark to form Y_D-O$^\bullet$ and electron transfer from S_0 to Y_D-O$^\bullet$, which results in the dark-stable S_1 state. The formation of the tyrosyl radical is coupled with proton transfer, facilitated by a robust hydrogen bonding network [2]. The crystallographic structure [3] depicts only one water molecule occupying two positions, proximal and distal, near Y_D-OH. The proximal water molecule (~2.7 Å from phenolic oxygen atom) is hydrogen bonded to hydroxyl group of Y_D-OH, whereas the distal one forms a proton transfer pathway starting from Arg180. In this work, we present the correlation between the proposed positions of the water molecule and the spectroscopic properties of the tyrosine radical. The electronic structure of the Y_D-O$^\bullet$ radical is deciphered in terms of its EPR parameters and comparisons are made with the available experimental data in order to understand how the local hydrogen bonding network and the positioning of the mobile water molecule regulate the redox properties of Tyr160.

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Evaluation of Heats of Formation of Giant Fullerenes using Density Functional Tight Binding with Isodesmic Reactions

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Carbon-based nanomaterials (fullerenes, nanotubes, graphene, etc) have attracted particular interest due to their unique electronic, optical, thermal, mechanical and chemical properties. In 1985 the first of these carbon nanostructures to be discovered was buckminsterfullerene, (I_h)C_{60} [1]. Despite the wealth of investigation into this remarkable molecule, the $\Delta_f H$ for C_{60} (2560 kJ mol^{-1} according to NIST) remained uncertain, with experimental values spanning ±100 kJ mol^{-1} [2]. Recently, double hybrid density functional theory and W1h theory [3] have been employed to obtain an accurate $\Delta_f H$ for C_{60} (2520.0 ± 20.7 kJ mol^{-1}) [4] and some higher fullerenes [5] via isodesmic reaction schemes. However, such high-level approaches are impractical for comprehensively studying giant fullerenes, due to their size and the huge number of cage isomers. Here we demonstrate the utility of dispersion-corrected 3rd-order density functional tight binding (DFTB3-D/3ob) method for predicting $\Delta_f H$ in larger fullerenes using isodesmic reactions. Errors in $\Delta_f H$ are minimised through judicial choice of reaction schemes, which conserve the fullerene curvature, minimize the total number of species involved, and utilize complementary species with adequate uncertainties. The DFTB3-D/3ob theoretical heat of formation for C_{60} ($\Delta_f H$ = 2539.4 kJ mol^{-1}) is shown to be within an acceptable range of the DSD-PBE-PBE/cc-pVQZ value ($\Delta_f H$ = 2520.0 ± 20.7 kJ mol^{-1}) [5]. We also show that DFTB3-D/3ob performs very well in predicting trends in $\Delta_f H$ for larger fullerenes (Figure 1).

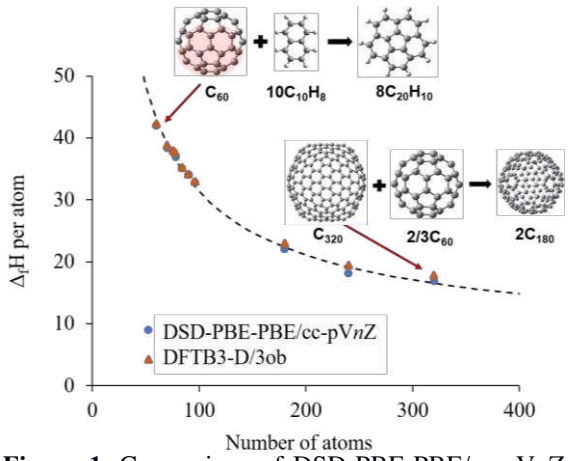

Figure 1. Comparison of DSD-PBE-PBE/cc-pV*n*Z and DFTB3-D/3ob $\Delta_f H$ (kJ mol^{-1}) values for giant fullerenes.

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Theoretical study on the optical properties of *fac*-Ir(ppy)$_3$ and its derivatives

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Recently, organic electroluminescence (EL) devices are often used as next-generation flat panel displays and illuminations. Ir(III) complexes have attracted much attention as important materials for such organic EL devices due to their high quantum yields and their phosphorescence emission. It is known that *fac*-Ir(ppy)$_3$ complex, where ppy denotes 2-phenylpyridine, shows a luminescence property[1][2]. This compound exhibits high quantum yields, but little is known about their optical properties when the coordination species are changed to others. There have also been no specific design guidelines especially for the substituent effect on optical properties. In this study, therefore, a difference in the optical properties among substituted *fac*-Ir(ppy)$_3$ complexes is examined in detail by DFT and TD-DFT calculations. In addition, the structure, absorption spectrum and maximum emission wavelength of several unreported complexes are also predicted. Finally, we summarize the effect of electron-withdrawing and electron-donating functional groups of substituents on the optical properties of the complexes.

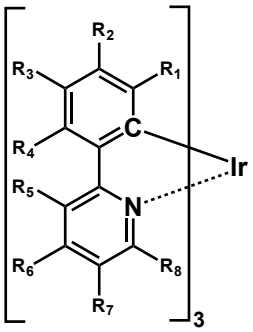

Fig.1 Framework of *fac*-Ir(ppy)$_3$.

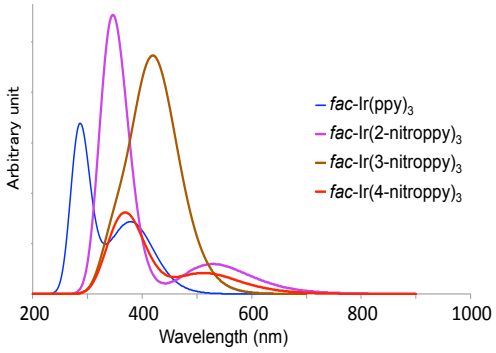

Fig.2 Calculated UV-Vis absorption spectra of *fac*-Ir(*x*-nitroppy)$_3$. (*x* = 2, 3, 4)

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Investigating the Interactions of Novel Anti-Cancer Therapeutics with DNA using Computational Modelling and Spectroscopic Techniques

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Platinum-based drugs, such as cisplatin, carboplatin, oxaliplatin and nedaplatin, are among the most commonly used drugs to combat cancer.[1]

Infrared (IR) spectroscopy is a non-disruptive analytical method that can provide structural information of a sample. With the development of new techniques, it is now possible to study samples in the far IR (FIR) region (<600 cm^{-1}). This would provide information on the platinum-based drugs as the vibrational modes between Pt-ligand would fall in the FIR region. This is important as the activity of metal-based drugs is directly related to the changes in metal coordination to its ligand, making it necessary to assign the vibrational bands to the respective vibrational modes.[2]

Another area of interest is the Donor-Acceptor bonds of these platinum-based between the Pt and its ligands, differing them to typical covalent bonds, thus requiring the use of more accurate quantum chemical methods. The Donor-Acceptor bonds are usually observed in the FIR region. It has been noted that stretching vibrations that reflect the strength of the bond are more likely to be affected by the accuracy of the selected level of theory, making it vital to select the appropriate level of theory to study such complexes.

In this work, we incorporate the use of computational chemistry methods to predict FIR spectra of four platinum anti-cancer drugs (cisplatin, carboplatin, oxaliplatin and nedaplatin). A series of factors such as functionals (PBE, PBE0, M06-L and M06-2X), basis sets (cc-pVDZ, cc-pVTZ, aug-cc-pVDZ and aug-cc-pVTZ) and solvation models (PCM, CPCM and SMD) were utilised to predict vibrational frequencies in the far IR region with the view of identifying the importance of each factor. With statistical analysis to compare data between experimental and theoretical spectra, the best combination of DFT functional, basis set and solvent model was identified to predict vibrational frequencies of the platinum complexes in the far IR region.

In addition, the identity of the activated form of cisplatin was investigated by comparing the calculated vibrational frequencies of both the mono- and di-hydrated forms to experimental data, with cisplatin being measured in either serum or saline solutions.

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Electron fate and mutational robustness in the mechanism of (6-4) photolyase-mediated DNA repair

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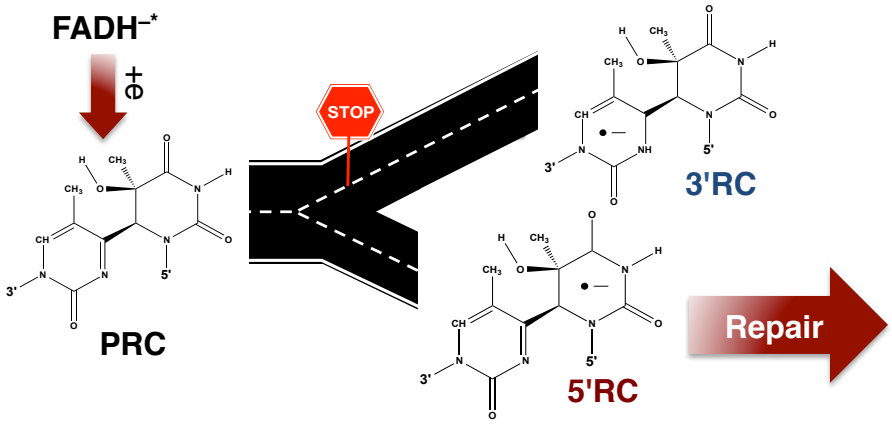

(6-4) photolyase ((6-4) PHR) are evolutionally ancient enzymes that are essential in maintaining genetic integrity by repairing UV induced cytotoxic DNA lesions, pyrimidine(6-4)pyrimidone photoproduct ((6-4) PP)[1-3]. It harvests sunlight to repair the DNA covalently linked pyrimidine bases via structurally and chemically challenging reaction[1]. Due to biological importance of the (6-4) PP repair, extensive experimental and computational studies have been performed, however, the mechanism is still elusive and debated, because of its challenging assignment and reaction complexity[1-3] . Here we synergistically use molecular dynamics simulations, quantum mechanical/molecular mechanical (QM/MM) calculations, Large-QM/MM which includes 982 atoms in the QM layer, Marcus theory and Fourier transform infrared (FTIR) spectroscopic measurement, to first investigate the electronic nature of reactive complex (RC) after forward electron transfer (FET) and subsequently to investigate in detail the photorepair cycle.

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Computational Study of MEA Adsorption on Hydroxylated Cr_2O_3 Surfaces

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Aqueous alkanolamine – and more specifically monoethanolamine (MEA) – solution are frequently used for the removal of CO_2 from flue gas and natural gas. However, corrosion represents one of the major operational issues in these processes. It is therefore essential to evaluate the stability of the protective Cr_2O_3 layer of stainless steels, when it is in contact with different species found in CO_2 capture processes, e.g. water, MEA CO_2, and the reaction products like bicarbonate and the carbarmate of MEA.
The adsorption of MEA on the hydroxylated (0001)-Cr_2O_3 surface was investigated by periodic density functional theory, using both static and dynamics calculations [1]. Two different adsorption modes were investigated: by direct adsorption of MEA onto the surface and by the substitution of a surface water molecule by MEA. Several MEA coverages were studied (from 0.25 to 1 monolayer), as well as temperature and solvation effects. The calculations show that MEA adsorption onto the surface with a density up to 2.37 MEA per nm^2 (0.5 ML) is exergonic at 298 K in an aqueous environment, while the substitution process was found to be endergonic at all coverages at temperatures of 298 K and above.
In an analogous way to MEA, we also studied the adsorption of carbonic and carbamic acid [2].
We are currently fine-tuning the parameters of the ReaxFF reactive force field, allowing us to model larger systems, including the most abundant species in the aqueous phase and to explore larger time scales [3].

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Empirical Force Fields for Simulating Proton Transfers: Molecular Dynamics and Spectroscopy

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Abstract:
The empirical force field method of Molecular Mechanics with Proton Transfer (MMPT) follows concepts from a QM/MM scheme which treats the proton transfer (PT) process in its full dimensionality while improving on three important aspects of the problem: speed, accuracy, and versatility. In a recent generalization, MMPT was extended to treat proton transfer in the condensed phase. This was possible by combining MMPT with multi-surface adiabatic reactive molecular dynamics (MS-ARMD). In this approach, a global potential energy for proton transport is built by mixing multiple potential energy surfaces, each of which corresponds to a localized PT reaction. That enables, for instance, all hydrogen atoms in a bulk phase with excess protons to equally participate into the transfer reactions in a force field regime. The integrated MMPT-MS-ARMD method was applied to performing MD simulations for $[H_2O]_nH^+$ clusters at the gas phase and results were compared with quantum mechanical (QM) and semi-empirical QM MD simulations.
Complementary to this, recent applications focused on the computation of infrared signatures for the shared proton between a donor and an acceptor site. This was complemented and - in part - motivated by recent experiments. Both, conventional molecular dynamics and more advanced ring polymer MD simulations were carried out to charaterize the energetics, dynamics and spectroscopy of transferring protons in topical systems including FAD, AcAc, protonated oxalate. The simulations were found reproducing absorption spectra in good agreement with experimental results.

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Quantum chemical modelling of magnetic anisotropy and exchange interactions in lanthanide systems with $4f^n5d^m$ configurations

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Lanthanide ions in molecular complexes are most often encountered in their trivalent oxidation states. The anisotropic magnetic properties of such systems can be efficiently modeled by *ab initio* multireference methodology developed over the past decade.[1] Much less computational studies have been performed on low-valent systems where the lanthanide ions possess $4f^n5d^m$ configurations as opposed to the more common $4f^n$ case encountered in the trivalent ions. The spatial extent of the 5d orbitals is much greater than that of the strongly contracted 4f shell leading to both strong covalent interactions with the ion surroundings and to much stronger exchange coupling. This introduces considerable challenges in the quantum chemical description of the $4f^n5d^m$ systems as first-order spin-orbit coupling and static electron correlation effects outside the 4f shell both play an important role. In the present contribution we will discuss the quantum chemical modelling of the electronic structures and magnetic properties in low-valent monometallic $4f^n5d^m$ lanthanide complexes and endohedral metallofullerenes encapsulating mixed valence lanthanide dimers. The calculations utilize methods based on multireference wave function theory, DFT, and *ab initio* model Hamiltonians. The results provide insight into the magnetic anisotropy of the monometallic complexes and to the complicated energy spectrum of the lanthanide dimers resulting from interplay of spin-dependent delocalization and strong spin-orbit coupling.

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Potential energy surface interpolation with neural networks for instanton rate calculations

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For the calculation of reaction rate constants with instanton theory an accurate description of the sector of the potential energy surface (PES) containing the transition state and the reactant state of the reaction of interest is needed. However, obtaining information on the PES on the fly during the rate constant calculation is computationally very demanding. Therefore, we interpolate the PES with artifical neural networks (NNs) and calculate the reaction rate constants with the instanton method using this NNPES. In instanton theory it is assumed that the energy, but also the gradient and the Hessian of the energy with respect to the input coordinates are continuous functions of the input coordinates. Therefore we incorporate not only information on the energy, but include also information on the gradient and Hessian in the NN-fit to ensure their continuity and accuracy.

To demonstrate the capabilities of this approach we calculated reaction rate constants with the instanton method for the reaction $CH_3OH + H \rightarrow CH_2OH + H_2$ on an average NNPES fitted to CCSD(T)-F12/VTZ-F12 data. We demonstrate that these rate constants are in excellent agreement with rate constants that were calculated on the same level of theory performing energy, gradient and Hessian calculations on the fly, while the computational effort of the rate calculation is significantly lower if a NNPES is used instead of on the fly calculations.

Electronic Properties and Reorganization Energies of the Metal-Metal-to-Ligand Charge Transfer Transition in Pt(II) Complexes

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Abstract: The phosphorescence emission from the metal-metal-to-ligand charge transfer (^{3}MMLCT) state of dinuclear transition metal complexes can be used for high-performance near-infrared (NIR) organic light-emitting diodes (OLEDs).[1] However, the molecular factors controlling the quantum yields of these NIR dyes remain elusive. In particular, the effects of electron-vibration coupling have not been clearly elucidated previously. In this study, we employ density functional theory calculations to investigate the electronic properties and reorganization energies of a series of Pt(II) complexes in both the monomer and dimer cases. We reveal that the lowest excited state of the monomers are delocalized on the ligands and consequently the intramolecular reorganization energies of the excited state (λ_{in}) are dominated by the ligand stretching vibration modes. On the other hand, the bond length alternations on the ligands are significantly reduced in the dimers, because the lowest excited state are predominantly located on the two Pt atoms. Therefore, the values of λ_{in} can be significantly reduced in the Pt complex dimers with emission from the ^{3}MMLCT state. The reduced λ_{in} indicates that NIR emitters with weak electron-vibration coupling could suppress the non-radiative emission to achieve high quantum yield according to the energy gap law.[2] In summary, on the basis of the magnitude of the λ_{in}, we provide a ligand design perspective for effective formation excimers and importance rules to improve NIR OLED materials.

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Calculation of reaction rate constants via instanton theory in the microcanonical ensemble

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The phenomenon of quantum tunneling is crucial in order to make accurate predictions for chemical reaction rates, particularly for those involving the transfer of light atoms such as hydrogen. This is especially true for reactions that take place in extremely cold environments as for instance in gas clouds in interstellar space.

A widely used method to describe tunneling effects in large systems is the use of instanton theory in the canonical ensemble which allows the calculation of reactions rates at well defined temperatures. However, canonical instanton theory is fundamentally restricted to temperatures below the crossover temperature T_c. Additionally it can be challenging to obtain instanton solutions at very low temperatures as well.

An alternative approach to obtain thermal rates is provided by a microcanonical formulation of instanton theory which in principle is able to provide thermal rates at all temperatures. The objective is therefore to obtain microcanonical rates first in order to calculate thermal rates later while circumventing the existing limitations of using canonical instanton theory directly.

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DFT+D calculations of non-binding interactions of oligopyrrole aggregates doped with heptafluorotantalate (V) ions in presence of different solvents

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Polypyrrole is a long known conducting material. It has interesting properties, like mechanical flexibility, good charge storage capacity and is quite easy to synthesize[1,2.] However, not much is known about its structure and, in particular, about the structural changes accompanying insertion of metallic ion dopants, such as heptafluorotantalate, TaF_7^{2-}, which enhance the material's conducting properties. Furthermore, the joint system (polypyrrole and the heptafluorotantalate) must be affected in an environment of solvent molecules. In order to shed some light on the interactions between TaF_7^{2-} ions and polypyrrole, dispersion corrected density functional theory[3] (DFT+D) calculations were carried out, investigating aggregates between two to four pentapyrrole molecules and two TaF_7^{2-} ions. These were submitted to environments of randomnly distributed solvent molecules in controlled numbers. The solvent species chosen for this work were water and acetonitrile. Water, because of its facility to interact with both, ions and oligomers through hydrogen bridges and its capacity to form hydrogen bond networks. The results are contrasted to those obtained with acetonitrile solvent molecules, the latter being the aprotic solvent which was used by the experimentalists[4] to synthesize the material.

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The Influence of Chemical Change on Protein Dynamics: A Case Study with Pyruvate Formate-lyase

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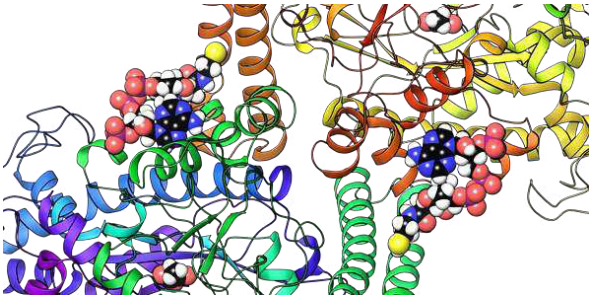
Pyruvate formate-lyase (PFL) is a glycyl radical enzyme requiring activation by a member of the radical SAM enzyme superfamily.[1] Such radical enzymes are receiving increased interest because of their possible applications in biotechnology.[2] PFL catalyzes the break down of pyruvate into formate and the acetyl group upon the addition of a thiyl radical located at Cys418.[3] The radical is initially stored at Gly734 is shuttled to Cys418 via Cys419. The addition of radical Cys418-S· to pyruvate leads to C-C bond dissociation, resulting with formation of formyl radical and acetyl-Cys418. The latter species acts as a temporary acetyl carrier and a reactant in the subsequent half-reaction with the second substrate CoA to produce acetyl-CoA. Formation of AcCoA, the final product, closes the catalytic cycle of PFL.[4]



The investigated aspect of this mechanism concerns the process that allows CoA to enter the active site, which is a prerequisite for the second half-reaction. The problem with this step is that the binding site of CoA is located at the protein surface, while the active site is buried in the protein interior.[5] In search for possible solutions to this problem, the PFL system was subjected to long unrestrained molecular dynamics simulations. The models representing the PFL system before and after the first half-reaction with pyruvate were used to examine the possible effect that acetylation of the enzyme has on the necessary conformational changes.

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Energies of Molecular Crystals from Many Body Expansion combined with Frozen Density Embedding

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Molecular crystals are relevant in different research fields such as pharmaceuticals or organic based semiconductor technologies. Of particular interests are the energy difference between different polymorphic structures of molecular crystals. Predicting these small energy differences with quantum chemical methods is an incredibly difficult task [1].

Wave-function based electronic structure methods are a powerful tool for describing intermolecular interactions, but are in general not available for periodic crystal structures. Instead, (dispersion-corrected) DFT is routinely available for periodic crystal structres, but often does not provide the required accuracy. The many-body expansion provides an appealing approach for calculating the lattice energies of molecule crystals by decomposing it into contributions of subsystems such as dimers, trimers, etc. The decomposition into smaller subsystems allows for the use of wave-function based methods to calculate the interaction energies with sufficiently high accuracy [2].

However, the convergence with respect to the subsystem order in the many-body expansion remains a bottleneck, because the contributions of trimers and tetramers can in general not be neglected. Here, we explore the use of quantum-chemical embedding methods to implicitly account for such high-order contributions. Specifically, we employ frozen-density embedding (DFT-in-DFT and WFT-in-DFT) for the monomer, dimer and trimer calculations. As test cases, we consider ice as well as two organic compounds (acetylsalicylic acid, oxalyldihydrazide) in different crystal structures [3].

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Assessment of density functionals for computing thermodynamic properties of lanthanide complexes

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Electron transfer using lanthanide complexes has found numerous applications in the last decades, e.g. for the reduction of small molecules such as CO_2 or the development of newly designed luminescent and magnetic compounds.
Recently, it was shown experimentally that the electron transfer from a divalent lanthanide complex to the phenanthroline ligand induces a coupling reaction with the formation of a new C-C [1, 2]. The evaluation of the thermodynamic properties of this coupling reaction is a real challenge for computational chemistry and we propose to assess a variety of density functionals in order to reproduce the available experimental data of this equilibrium between the radical phenanthroline complex $Cp^*_2Sm(phen)$ and the coupling product $(Cp^*_2Sm(phen))_2$. The role of the Hartree-Fock exchange in the functional is pointed out. Finally, the PBE0-D3 and M06-2X functionals lead to a good evaluation of the energies and enable a correct description of the ligand to metal charge transfer, both in the 4f and 5d metal orbitals [3]. Furthermore, topological analyses pointed out that the C- C bond created has a partial covalent character explaining why both the monomeric and the dimeric forms exist in equilibrium.

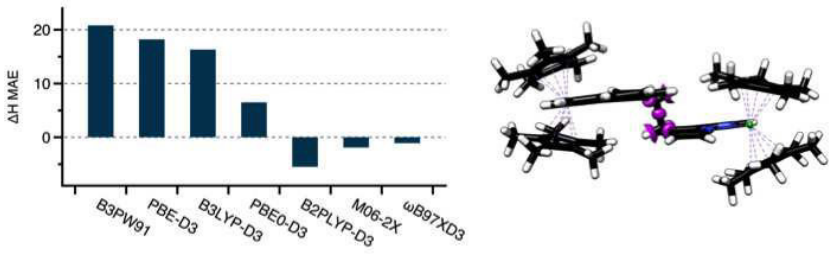

Figure 1: Mean Average Signed Deviation between the theoretical and experimental ΔH (kcal/mol) for samarium complexes using different density functionals (left) and ELF representation of the V(C,C) synaptic basin (right)

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Azobenzene photoisomerization in the strong coupling regime

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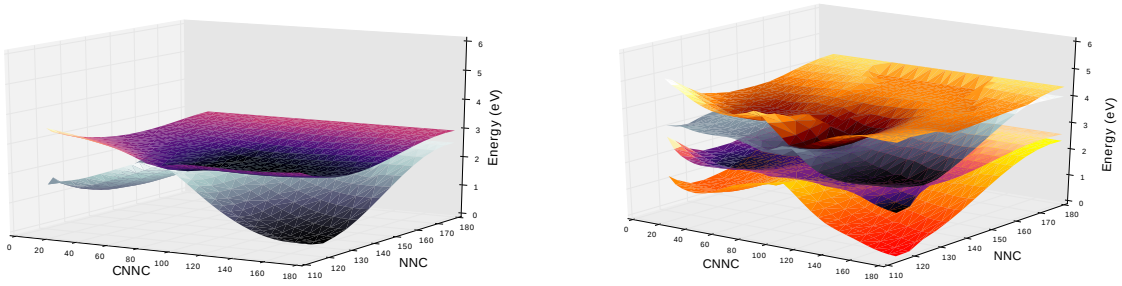
The experimental achievement of single-molecule strong coupling regime in nanocavities for organic molecules [1] has risen a deep interest in the theoretical comprehension of such phenomenon [2]. Such regime can be achieved as the resonant frequency of a cavity coupled to the excited states of a molecule. Under this condition, the Rabi oscillations of a single molecule inside the cavity are much faster than the dissipation effects. Therefore, the coupling allows stable hybrid light-matter states to be formed (polaritonic states). Various theoretical treatments on model molecules show the possibility to manipulate the dynamics of photochemical processes, such as photocatalysis and photoisomerizations [3]. However, no realistic molecules have been theoretically treated so far. Here, we present the formation of polaritonic states in a photopolarizable molecule at different resonant energies. As it was recently argued by Flick *et al.* [4], the correct description of the coupling term is still controversial. In order to clarify the problem, we compare such term within two different gauges: the dipolar hamiltonian and the minimal coupling hamiltonian. Finally, the influence of the strong coupling on the photoisomerization process in azobenzene is investigated through direct (on-the-fly) trajectory surface hopping (DTSH). The electronic problem is solved by exploiting the semiempirical wavefunction approach devised by Persico, Granucci and coworkers [5]. The photoisomerization is studied in vacuum for the time being, comparing the results to the state-of-the-art literature references for the photochemistry of azobenzene.



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Interpolation of Potential Energy Surfaces using Gaussian Process Regression

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One of the fundamental problems in theoretical chemistry is the steep scaling of electronic structure calculations with the system size. In many calculations one needs many evaluations of the potential energy surface and its derivatives (often up to second order).
It is well known that one can use interpolation schemes like Shepard interpolation to overcome this problem to a certain extend.
Over the last years the increasing usability of machine learning methods like neural networks and Gaussian process regression (GPR) lead to many scientific advancements in several fields. Many of these methods aim at interpolating high dimensional functions and therefore, they seem well suited for the purpose of interpolating a potential energy surface as well.

We already studied the usability of neural networks for the interpolation of potential energy surfaces in our group. In out work we are currently investigating Gaussian process regression as an alternative approach. In contrast to neural networks this method is more tractable, easier and faster to set up for a new system, and also, formulated in a Bayesian setting, has the capability of giving uncertainty measurements and the possibility of optimizing its parameters with e.g. the maximum likelihood method. In both methods we include derivative informations up to second order to train our model and improve the inference of derivative information.

We apply this method to interpolate several potential energy surfaces to be able to do geometry optimization and instanton calculations with fewer electronic structure calculations and therefore, faster than before.

π Electron Effects Control Diels-Alder Regioselectivity to Empty Fullerenes

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Diels-Alder (DA) cycloadditions are a powerful tool for the introduction of a six-membered ring to a fullerene cage. They have enabled the preparation of many functionalized derivatives of empty and endohedral fullerenes with applications in material and biological sciences.[1] Due to the existence of different types of bonds, regioselectivity is commonly exhibited. For instance, for C_{60} fullerene, the [6,6] cycloadduct is distinctly preferred over the [5,6] one.[2] In the case of larger and less symmetrical cages, many possible regioadducts may be formed. In that context, several descriptors based on different physical arguments such as bond lengths, pyramidalization angles and fullerene LUMO shapes have been used to predict the DA selectivity of fullerenes, but none of them seem to be universally applicable.[3]

In this contribution, we show that the regioselectivity of DA cycloadditions to empty fullerenes is governed by the stabilization of the global π system of adducts. Reaction energies obtained from DFT calculations can be well reproduced by a computationally almost costless Hückel-based simple model.[4, 5] An extensive and systematic study of a whole range of fullerenes from C_{60} to C_{180} reveals that DA cycloaddition occurs preferentially at a few simple bond patterns. These simple rules provide us a visual guide for rapid prediction of DA regioselectivity. Moreover, we have proposed two quantitative reactivity descriptors that have a direct chemical interpretation in terms of bond forming and breaking ability and in terms of local aromaticity.

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Application of the Bethe-Salpeter Equation to cationic dyes and *n*-π* chromogens

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Among the different approaches that exist for modelling electronically excited-states, the Bethe-Salpeter (BSE) formalism that relies on the *GW* eigenstates, is becoming increasingly popular due to its good compromise between accuracy and computational cost [1]. Indeed, it offers an alternative to the Time-Dependent Functional Theory (TD-DFT) as it benefits from the same scaling with system size while allowing a significantly more limited dependency on the starting exchange-correlation functional [ADC(2)] [2]. In this contribution, we present the performances of BSE/*GW* regarding two challenging cases: cationic dyes and *n*-π* chromogens. First, we investigated the excited-state properties of a series of structurally diverse arylcarbonium derivatives. We compared the 0-0 energies as well as auxochromic and acidochromic shifts obtained with the BSE/*GW*, TD-DFT and the second-order algebraic diagrammatic construction [3]. Second, we studied the lowest singlet transition in twelve *n*-π* compounds based on the nitroso, carbonyl, thiocarbonyl and diazo chromophores. We compared the BSE/*GW* and TD-DFT descriptions with wavefunction-based theoretical best estimates [4]. This contribution supports the use of BSE/*GW* for modelling transitions that are not well described with TD-DFT.

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Flexible water docking and virtual screening using PLANTS combined with tuned water selection criteria

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Role of explicit water molecules in docking and virtual screening remains debatable and contradictory. In this study, we have assessed the docking performance including flexible water molecules using the PLANTS docking package[1]. This could provide a potential resolution to the efficient virtual screening including flexible water molecules. To enable the efficient assessment, a set of automatised selection criteria for water molecules within both the *holo* and *apo* structures was applied. The water molecules were selected from both crystal resolved water position and 3D-RISM calculations. Good correlation was demonstrated between the two and an ideal amount of water molecules can be preserved. Moreover, the selection procedures are also applicable to apo binding site, which allows further feasibility. We have demonstrated improved docked poses after inclusion of flexible water assessed using three test sets, two of which derived from CCDC-Astex "clean" list [2] and DUD-E database [3], and an additional apo test set. The performance of virtual screening was also assessed using several testing systems.

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Theoretical investigation of Herzberg-Teller effects in resonance Raman spectra

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Vibrational resonance Raman (RR) spectroscopy is a useful tool to provide information on structures and properties of molecular excited states [1]. Therefore, an accurate simulation of absorption and RR spectra, by quantum chemistry methods, can help in the interpretation of experimental data as well as in the design of new compounds for specific applications e.g. in dye-sensitized solar cells or as photocatalysts [2,3]. Moreover, the calculation of RR intensities and their comparison with experimental data offers an opportunity to assess the ability of standard quantum chemistry methods to predict excited state properties [4,5].

In this contribution, simplified sum-over-state expressions are presented to calculate RR intensities [6], which allow inclusion of Franck-Condon (FC) and Herzberg-Teller (HT) effects. The molecular properties are calculated with density functional theory and the different methods are applied to the molecule of Rhodamine 6G [6]. Additionally, HT effects are considered for the molecule of Porphycene and for a Ruthenium-Palladium supramolecular photocatalyst [3] and are shown to have a significant impact on the RR intensities.

Acknowledgments

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Automated Analysis of Exchange Pathways in Spin-Coupled Systems

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Spin coupling between spin centers plays an important role in systems containing transition metals such as enzymes and molecular magnets, and in organic di- and polyradicals. A reliable and efficient computation of spin-state energy splittings and magnetic exchange coupling constants is therefore an important task of theoretical chemistry.
We rederived, inspired by Ozaki and coworkers [1], an approach from solid-state physics based on Green's functions [2] by employing local projection operators and successfully applied it to various transition-metal complexes [3]. This methodology has the advantage that the coupling constant can be obtained from the electronic structure of the high-spin state only and does not require the calculation of the low-spin state.
Additionally, the Green's-function approach allows for a decomposition of the total coupling constant into molecular orbital (MO) contributions [4]. We also developed a scheme which can be used to obtain atomic contributions to the total coupling constant. This scheme allows us to evaluate the contributions to spin coupling from different fragments of the system (as for example ligands or surfaces; see Figure 1). Both decomposition schemes were successfully applied to transition-metal complexes in order to establish an automated analysis of exchange pathways in such compounds [4].

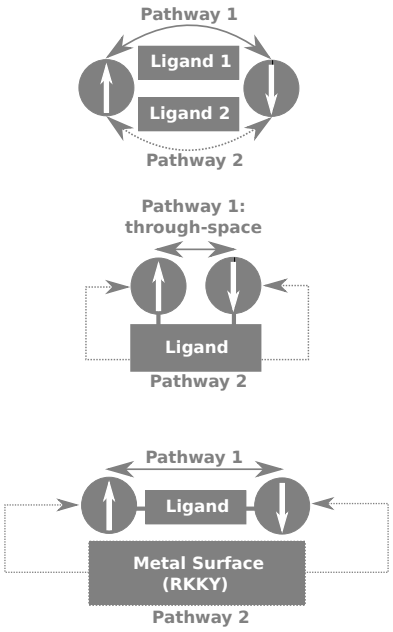

Figure 1: Three examples for systems with competing spin coupling pathways.

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New materials designed for absorption of non-steroidal antiinflammatory drugs

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Design of the efficient and selective non-steroidal antiinflammatory drugs (NSAIDs) sorbents is crucial for various branches of science and technology, starting from the pollution detection and removal from the environment and finishing in nanomedicine and designing of the drug delivery systems. NSAIDs are available over-the-counter and are applied widely in chronic diseases and popular ailments. Among their adverse effects the gastrointestinal problems, cardiovascular risk and erectile disfunction can be mentioned. NSAIDs themselves and their metabolites are discharged to the environment and can undergo the further photodegradation or other transformations that can possibly increase their hazardous action on living organisms. Despite their small amounts in environment (ppb) one does not know the precise influence of NSAIDs on the organisms assuming the long exposition times. Thus the current European Union regulations add diclofenac to the list of the most hazardous chemicals. Therefore, it is of particular importance to develop the methodology of NSAIDs detection and removal from the wastewaters and soils. Hence, the thorough knowledge of the mutual interaction of NSAIDs and their sorbents is essential. In the current project chitosan-based materials are proposed as the efficient sorbents. Computational study includes the characteristics of intramolecular interaction in chitosan chains, conformational study of chosen NSAIDs, their dimerization, and the influence of the chitosan modification on the mutual NSAID-biopolymer interaction.

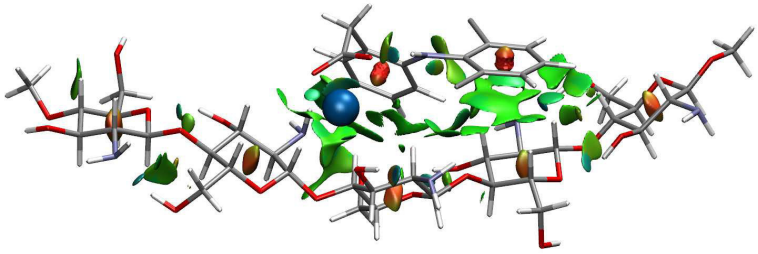

Figure 1: Diclofenac sodium-chitosan unit interaction

Acknowledgements
Support from National Science Centre, Poland grant No. UMO-2014/13/B/ST8/04342 is gratefully acknowledged. Calculations were performed in Wroclaw Centre for Networking and Supercomputing, Poznan Supercomputing and Networking Center and Academic Computer Centre Cyfronet AGH.

Two-component relativistic density functional theory based on infinite-order Douglas-Kroll-Hess method

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The infinite-order Douglas-Kroll-Hess (IODKH) method [1,2] is a promising technique to incorporate relativistic effects into quantum chemical calculations. We have established the accurate and efficient scheme based on the IODKH method within the framework of wavefunction theory. The key for efficiency in molecular systems is the local unitary transformation (LUT) method [3,4], which utilizes the local nature of relativistic effects. The divide-and-conquer (DC) method further accelerates the computation for large systems [5]. We also achieved quantitative agreement with spin-dependent four-component calculations at the post-Hartree-Fock level [6].
In this presentation, we focus on the extension of our scheme to density functional theory (DFT). In addition to the case of wavefunction theory, three points should be addressed: (1) picture change of the density operator [7,8], (2) noncollinear treatment of electronic spin, and (3) relativistic formulation of exchange-correlation functionals. We will present recent progress of theoretical development, together with the performance of DFT calculations.

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Phosphorescent mechanism of arylboronic esters at room temperature

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Recently, the phosphorescence of arylboronic esters has been experimentally[1] observed with a long lifetime in the solid state at room temperature (Fig. 1). Phosphorescence occurs via spin-forbidden transition, which is in general inefficient in the absence of heavy atoms. Thus, the phosphorescence of heavy-metal-free arylboronic esters is interesting. In this presentation, quantum chemistry calculations were performed to invesitgate the phosphorescent mechanism of arylboronic esters.

To achieve room-temperature phosphorescence, it is important to facilitate the intersystem crossing process and to suppress the non-radiative decay of triplet states. First, phosphorescent wavelengths and frontier orbitals of arylboronic esters were investigated by DFT calculations. The calculated wavelengths were in reasonable agreement with the experimental values. Next, the spin-orbit coupling constant was calculated to investigate the intersystem crossing process between singlet and triplet states for arylboronic esters. The structural deformation at T_1 state due to the boron functionality is responsible for the nonzero spin-orbit coupling. Finally, the minimum energy crossing point between S_0 and T_1 states was calculated to investigate the non-radiative decay process. The results will be shown in detail in the poster.

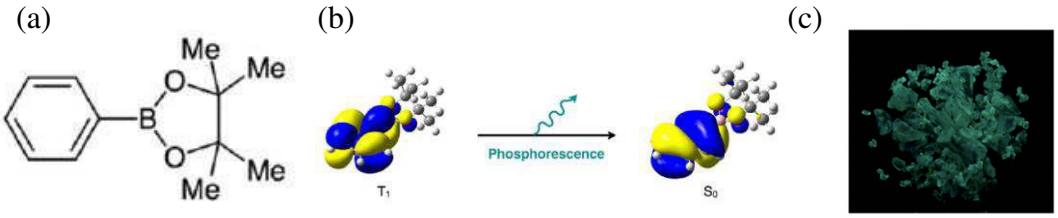

Fig. 1. (a) Molecular structures, (b) Kohn-Sham orbitals, and (c) phosphorescence emission of phenylboronic acid pinacol ester.

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A coupled state-averaged second-order MCSCF solver with fast convergence

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We present a new second-order MCSCF solver including the coupling between CI coefficients and orbitals and the capability of state-averaged calculations. The solver is based on the second-order energy expansion in the unitary transformation of the orbitals introduced by Werner and Meyer [1]. This energy expansion ensures fast convergence and a reduced number of the four index integral transformations. It is used in the solver of Werner and Knowles [2, 3], where the CI coefficients and orbitals are optimized in an alternating way (micro-iterations). In some cases, the indirect coupling through the alternating optimization yields convergency problems.
Our new solver considers the simultaneous and coupled optimization of CI coefficients and orbitals, based on the same energy expansion. Through the direct coupling of CI coefficients and orbitals, the convergence of the micro-iterations is improved. The CI coefficients and orbitals are calculated by a level-shifted second-order optimization and the coupling is realized by considering the mixed derivatives in the Hessian matrix similar to [4]. Also, we found a way to perform state-averaged calculations with a second-order optimization by using orthogonal projection operators. Hence, it is possible to perform coupled state-averaged calculations as well. To calculate the update in each optimization step, a system of linear equations with a level shifted Hessian has to be solved. To avoid the construction of the full Hessian matrix, we introduce an iterative subspace solver, where the equation is projected onto a suitable subspace. A good starting guess of the subspace yields fast convergence of the iterative subspace solver (mostly 4-6 iterations).
Through the coupling, our new solver needs half as many micro-iterations than the solver of Werner and Knowles [2, 3] and in some cases, the number of four index integrals transformations is significantly reduced. In all cases, the micro-iterations and subspace iterations converge to the demanded accuracy. This improves the robustness of the solver, such that new approximations will be possible. Also, the timing of calculations can be reduced by parallelization.

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Critical Analysis of Embedding Schemes for QM/MM Calculations in Condensed Phase

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The use of quantum mechanics/molecular mechanics (QM/MM) hybrid methods is still today the option of choice to describe chemical phenomena within an embedding environment. Its applications reach from reactions in the active sites of enzymes over explicit solvent simulations up to periodic structure calculations in solid states. The interaction between the quantum mechanical and molecular mechanical regions is a key element to the success of these QM/MM calculations[1] and can be included by different embedding schemes. While the interaction is simply calculated at the MM level in *mechanical embedding* schemes, the QM region is embedded in point charges for *electrostatic embedding* allowing for its polarization. The repolarization of the MM region, as taken into account in *polarized embedding* schemes, can have a significant impact in the properties under study.[2]
In this work, we critically address the different embedding schemes used in QM/MM approaches by comparing them to the results of an embedding with fragment Fock potentials.[3, 4] By separation of the Fock potentials into their components one gains insight into the resulting effect of Coulomb and exchange contributions to the description of the QM region. Mutual updates of the potentials in the presence of their environment allows for the analysis of the effect of repolarization. The benchmark systems involve periodic boundary crystal structure simulations and solutes in solution with explicit solvent treatment.

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Towards physical interpretation of the substituent effect.

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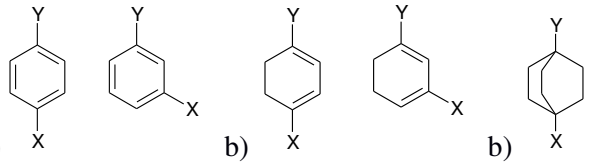
The general term "substituent effect" can be applied to different kinds of intramolecular interactions in X-R-Y systems. This concept is especially useful in elucidating: (i) the impact of substituent X on the properties of a fixed group Y, known as a **classical** understanding of the substituent effect, (ii) the effect of X on the properties of transmitting moiety R, (iii) interrelations between some properties of Y due to the influence of the distant substituent X, and (iv) influence of the fixed group Y or -R-Y on the properties of substituent X, named as the **reverse** substituent effect.

Scheme: 

Substituted derivatives of benzene (a), cyclohexa-1,3-diene (b) and bicyclo[2.2.2]octane (c).

B3LYP/6-311++G(d,p) method has been chosen to investigate the electron-donating properties of the Y group in a series of substituted systems (Scheme), where Y = NH_2, H, NO_2 and X = NMe_2, NH_2, OH, OMe, CH_3, H, F, Cl, CF_3, CN, CHO, COMe, $CONH_2$, COOH, NO_2, NO. The Hammett substituent σ, charge of the substituent active region (cSAR) and substituent effect stabilization energy (SESE) descriptors are applied as the substituent effect characteristics. The Y group is characterized by structural and cSAR parameters, whereas the transmitting moiety – by aromaticity index HOMA.
All used parameters are found to be mutually interrelated with much better correlations for the *para*- than the *meta*-derivatives. The reverse substituent effect is clearly documented by a comparison of the cSAR(X) characteristics for the studied series of derivatives [1-5].

Acknowledgements: The author gratefully acknowledges the Interdisciplinary Center for Mathematical and Computational Modeling (Warsaw, Poland) for providing computer time and facilities and the National Science Centre and Ministry of Science and Higher Education of Poland for supporting this work under the grant no. UMO-2013/11/B/ST4/00531.

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Quest for Pb^{II} Hydrides: When Theory Guides Experiment

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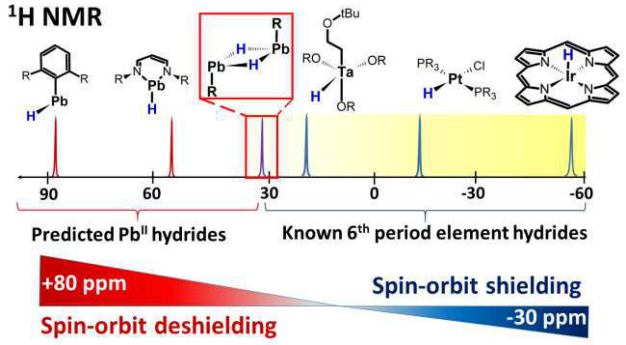
Although heavier low valent Group 14 hydrides are known to be versatile reagents in many chemical reactions, Pb^{II} hydride was never observed. Our fully-relativistic calculations of ^{1}H NMR chemical shifts of model Pb^{II} hydrides revealed possible reason. ^{1}H NMR chemical shifts of model Pb^{II} hydrides, including the most stable dimeric μ-H-bridged Pb^{II} hydride, were predicted in a region between 30 – 90 ppm, well beyond standard ^{1}H NMR experimental ranges. [1] High-frequency shifts of these ^{1}H signals originate from relativistic contributions of unprecedented size, up to 80 ppm, caused by spin-orbit coupling at heavy atom. Based on these findings, the preparation of dimeric Pb^{II} μ-H-bridged hydride was re-examined, and ^{1}H NMR chemical shift ranges broadened accordingly. [2] Indeed, the hydride ^{1}H NMR resonance was detected at 31.1 ppm in solid state and 35.6 ppm in solution respectively [3] (theoretical prediction 30.8 ppm *in vacuo*). The last unknown low-valent Group 14 hydride was thus experimentally confirmed.



Acknowledgement: This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic, Program NPU I (LO1504 to JV) and the Czech Science Foundation (grants 16-05961S to JV and 15-09381S to RM).

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Molecular Dynamics Study of the Thermoresponsive Polymer: poly(*N*-n-propylacrylamide) (PNnPAm).

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The breadth of technological applications of smart polymers relies on the possibility of tuning their molecular structure to respond to external stimuli. In this context, we present numerical simulation results on the phase transition of poly(*N*-n-propylacrylamide) (PNnPAm) oligomers. PNnPAm is a smart polymer that exhibits a coil-to-globule collapse transition in aqueous solutions when the temperature is increased above its lower critical solution temperature (LCST) (297 K). Compared with the better known *N*-substituted acrylamide-based polymer (poly(*N*-isopropylacrylamide)(PNIPAm), PNnPAm has a n-propyl group instead of the isopropyl group present on PNIPAm. Experiments show that the lower critical solution temperature of PNnPAm is lower than that of PNIPAM and that in PNnPAm solutions the collapsing transition steeper and stronger than in PNIPAm. We carried out all-atom molecular dynamics simulations to understand, from a microscopic point-of-view, the influence of chain size and concentration on the LCST of PnNPam. Our analysis not only shows that the oligomer chain length has a strong influence on the LCST but allow also to discriminate the role of the intra- and inter-chain non-bonded interactions in the collapsed transition.

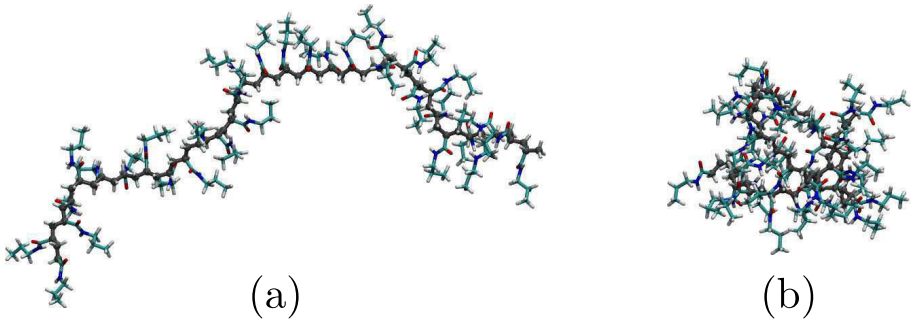

Figure 1: Snapshot of a PNnPAm chain for 32-mers at the end of 50 ns at two different temperatures: (a) below the LCST (280 K) and (b) above the LCST (340 K). The carbon backbone are shown in gray and water molecules have been omitted for clarity.

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The role of holes in borophenes, an *ab*-initio study of structural stability on Ag(111) surface.

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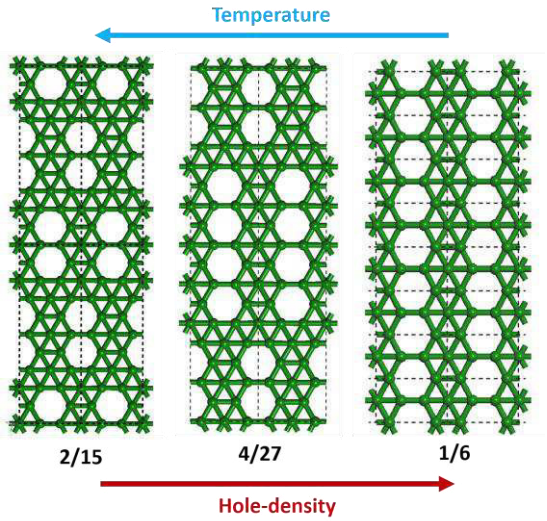
The discovery of 2D boron phases is one of the remarkable developments in the last few years.[1,2,3] The hexagonal hole density (HD) is explained by comparing to the electronic structure of MgB_2. The HD and distribution of holes determine the relative stability of the borophene phases on Ag (111) surface.[4] Several polymorphs of boron are energetically competitive on Ag surface. The conditions during the growth process control the nature of these phases. Sheets with higher HD are formed at lower temperatures. Upon increasing the temperature, the metal to sheet interaction decreases and the boron atoms rearrange to reduce the HD of the sheet. Detailed studies of first principles based simulations will be presented.



The temperature dependence of borophene phases

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Nonlinear Optical Properties in Helical Molecules with Pancake Bonding

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In our previous studies, we have revealed the correlation between the diradical character (y), which is defined by twice the weight of doubly excited configuration in ground states, and the second hyperpolarizability (γ), which is the molecular level property of third-order nonlinear optical (NLO) properties. On the basis of this "y–γ correlation", we have predicted large enhancement of γ values in a variety of open-shell singlet molecular systems with intermediate y values [1]. To realize such an electronic structure, several molecular structures have been investigated, like polyaromatic hydrocarbon, main group systems, metal-metal bonded systems, and open-shell aggregates. Among them, pancake bonded systems, which has the covalent-like bonding between the stacked π-radicals [2], are found to show the intermediate diradical systems and large γ value in the stacking direction [3]. Recently, we have theoretically investigated helical molecules with pancake bonding (Figure 1) [4], and have found that some of them have intermediate diradical character (Figure 2). Furthermore, azulene-lile molecules (Figure 2c) have been predicted to have assymmetric charge distribution, leading to further enhancement of the γ values [1]. Based on these studies, we expect that these helical pancake bonded systems are good candidates for highly-efficient NLO materials. In this study, therefore, we investigate those γ values using the LC-BLYP(μ = 0.33) method with 6-31+G(d) basis set. For example, the orientationally-averaged γ value of **7AZ** is found to be about 9 times larger than that of 7helicene, which is the closed shell reference to **7AZ**. This demonstrates that intermediate diradical character enhances the γ values in helical pancake bonded systems.

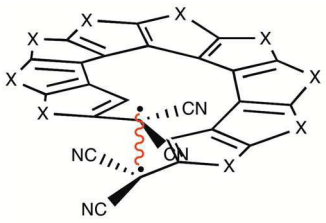

Figure 1. Helical pancake bond

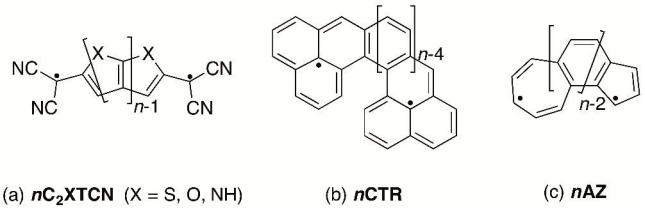

Figure 2. Model helical molecules with pancake bonds

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$ScSi_2^{-/0}$ AND $TiGe_2^{-/0}$: ELECTRONIC STRUCTURES AND INSIGHTS INTO ANION PHOTOELECTRON SPECTRA

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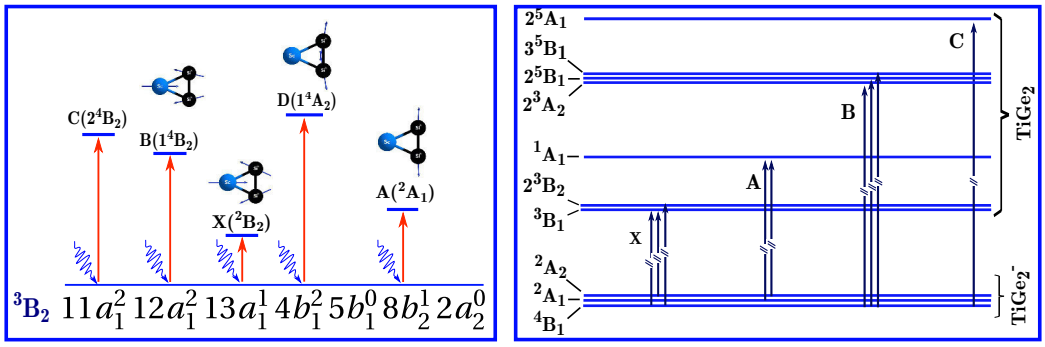
Theoretical studies on clusters containing transition metals are one of the interesting and challenging topics. The main reason is electronic structures of these systems need to be described with appropriate wave functions. Usually, single reference wave functions can describe electronic structures of many systems. For several systems especially those containing transition metals, single reference wave functions cannot be used efficiently with regard to correlation energy. In such situations, multireference wave functions are believed to be a positive alternative. Therefore, we utilize both single reference and multireference quantum wave function types (DFT, RCCSD(T), CASSCF, MRCI(Q), CASPT2 and NEVPT2) to synergistically investigate electronic structures of tiny clusters containing transition metals ($ScSi_2^{-/0}$ and $TiGe_2^{-/0}$). On the basis of their electronic structures, possible one-electron ionization processes, which are the removals of one electron from anionic clusters, are predicted. Ionization energies of these transitions, the so-called adiabatic and vertical detachment energy (ADE and VDE), are also calculated at several levels of theory mentioned above. These calculated ADEs and VDEs provide reliable evidences to understand nature of all experimental photoelectron bands in the spectra. In addition, multidimensional Franck-Condon factor simulations can be employed to confirm electronic transitions and/or to provide more details about experimental results.



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[2] L. N. Pham, M. T. Nguyen *J. Phys. Chem. A* **121**, (2017).

Stabilization of B-B triple bond in a metallaborocycle: Contrast between boron and carbon analogs

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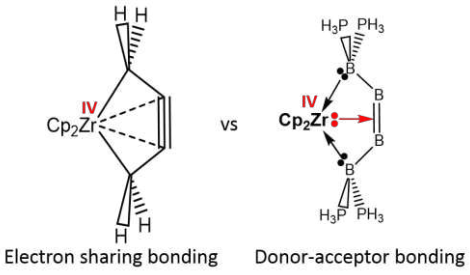
High strain energy resisted the synthesis of cyclic allenes, cumulenes, and alkynes. An effective way to stabilize these cyclic systems is the incorporation of metal fragments that induce stabilizing trans-annular interactions.[1] We present strategies to incorporate the B-B triple bond in a metallacycle and ways to stabilize it. Electronic structure of $(\eta^5\text{-}Cp)_2Zr(NH_2\text{-}BB\text{-}NH_2)$ suggests it to be a candidate for boron-boron triple bond in the cyclic system; however, computational study shows that it is a very high energy isomer on its potential energy surface. Replacement of amines with tricoordinate nucleophilic boron groups $(\eta^5\text{-}Cp)_2Zr[B(PH_3)_2\text{-}BB\text{-}B(PH_3)_2]$ reduces the relative energy dramatically. The B-B triple bond arises by the donation of two electrons from the metal fragment, $ZrCp_2$, to the in-plane π-bonding orbital of the central B-B unit. The stabilization of metal center (Zr) comes from the donation of electron pairs from terminal tricoordinate nucleophilic B-centers. The characteristic donor-acceptor bonding feature in metallacycloboryne contrasts with the electron-sharing bonding in metallacycloalkyne. Strong σ-donating and chelating bis-phosphine ligands ($L_2 = Me_2P(CH_2)_nPMe_2$), which stabilize donor-acceptor bonding interaction in gem-diborene $L_2B\text{-}BBr_2$, would be a good choice along the synthetic path towards, $(\eta^5\text{-}Cp)_2Zr[B_4(Me_2P(CH_2)_3PMe_2)_2]$. A comparison of the energetics of the reaction leading to cyclic boryne system, with the linear boryne isomer $[(B_2NHC^{Ph})_2]$ shows that the angle strain from cyclization is compensated by stabilization from the metal. [2, 3]



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Coupled electron-nuclear dynamics: A comparison of methods and dimensionality

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The purpose of this work is a first comparison of two methods describing a coupled electron-nuclear dynamics: the purely quantum mechanical ansatz NEMol and the Real-Time Time-Dependent Density Functional Theory (RT-TDDFT) based Ehrenfest dynamics. The NEMol ansatz was developed in our group to describe the coupled electron-nuclear dynamics of a photoexcited system. We introduce a novel form of the NEMol ansatz which is formulated for a single electronic state in a one-dimensional subspace. The comparison between this NEMol ansatz and the RT-TDDFT Ehrenfest dynamics is so far limited due to the difference in dimensionality. Therefore an approach for one-dimensional RT-TDDFT Ehrenfest dynamics is presented.

As an example the dynamics of (Z)-3-aminocarolein in the electronic ground state was analyzed. Using different quantum chemical methods the potential profile of the tautomerism was calculated and the critical points of the reaction were identified to set up the one-dimensional potential energy surface along the reaction coordinate. Using this surface we were able to compare the coupled electron-nuclear dynamics calculated purely quantum mechanical (snapshots are shown in Figure 1) with the semiclassical Ehrenfest dynamics and observed significant differences for the electron motion. In order to probe the influence of the reduced dimensionality the full-dimensional RT-TDDFT based Ehrenfest dynamics simulation was performed, too. In addition a short outlook is provided how to select and evaluate the choosen dimensions for a dynamic simulation using the principal component analysis (PCA).

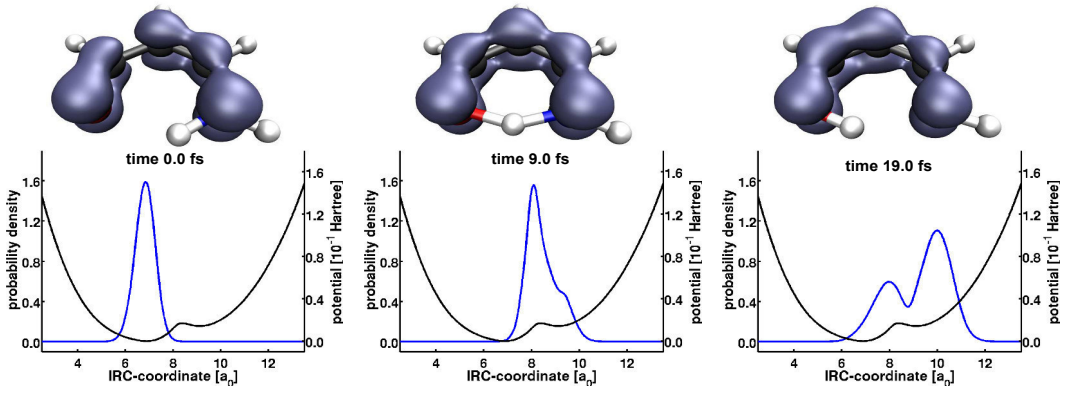

Figure 1: Snapshots of the coupled electron-nuclear dynamics of (Z)-3-aminocarolein calculated using the NEMol ansatz.

Reaction-prediction scheme based on quantum chemical information and machine learning

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Predictions of products from reactants in chemical reactions are important in chemistry. Various reaction-prediction systems, which solve this problem using a computer, have been developed since 1980 [1]. Recently, the systems based on inductive data analysis methods have attracted attentions due to the high accuracy. Especially, the schemes utilizing the machine learning for organic reactions showed the great performances [2-5]. These schemes use a topological fingerprint of a molecule as a descriptor. The fingerprint is a suitable descriptor for organic molecules because of the small computational costs and its abundant information to describe variations of molecular structures. However, physical information beyond a two-dimensional molecular structure might be essential especially to predict elementary reactions including arbitrary elements such as transition metal elements.

In the present study, we extended the reaction-prediction scheme based on the machine learning [6]. The present scheme utilizes descriptors obtained by quantum chemical calculations. Polar and radical reactions extracted from a textbook in organic chemistry are predicted. The scheme gives close results to the previous studies with the topological fingerprint. Especially, the descriptors have an advantage in the prediction of radical reaction. An analysis of a relationship between descriptors and a reaction is performed in order to obtain the physicochemical knowledge in the reaction [7].

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From structure to electronic properties of poly[methyl(phenyl)silylene] with DFT approach

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Poly[methyl(phenyl)silylene] (PMPSi) belongs to a group of σ-conjugated polymers, which are valuable materials due to their unique electron-optical properties induced by σ-orbital delocalization along their single-bonded Si backbones. Therefore, these properties, e.g. absorption maximum (λ_{max}), are strongly dependent on the extent of electron delocalization and thus on conformation of the backbone chains [1]. Maximal σ-conjugation is related with helical arrangement of PMPSi. However, various disruptions of ideal conformation, such as bends of backbones, which are connected with adoption of semi-crystalline structure, are normally found in its chains. This evoked the aim of the investigation of the structural disruptions in backbone and their effect on the electronic properties [2, 3]. A kink of approximately *gauche* (60°) conformation that consists of four consecutive Si atoms was virtually introduced to several oligo[methyl(phenyl)silylene] ($OMPSi_n$, n=1-10) backbones and these molecules were subjected to DFT and TDDFT study with B3LYP, M06 and ωB97X-D functionals, and 6-31G* basis set.

It was discovered that delocalization of molecular orbitals is affected by the presence of the kink because it causes their asymmetric distribution to non-disrupted parts of the backbone and to phenyl (Phe) rings in the kink vicinity. A position of the kink in Si chain also influences the value of HOMO-LUMO gap and therefore λ_{max}. Bandgap becomes wider as the kink shifts closer to the center of the backbone that reflects in experimental and calculated spectra. Further, the employment of π-π interactions between Phe groups was confirmed on decamers and tetramers by Phe-Phe angle-distance dependence and molecular energy. It was found that the kink is viable folding element in PMPSi polymer.

Acknowledgement

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$[Sb_nAu_nSb_n]^m$ (n= 4,5,6; m= -2, -1, -2) sandwich complexes as host of elements from groups I and II of periodic table.

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Sandwich complexes have been widely explored during the last sixty years, since the ferrocene was synthesized in the early 1950s; its discover gave rise to a new area of research in chemical and materials sciences, having abundant applications as catalysts, nanodevices, polymers or as building block for new materials. Sandwich compounds are not only confined within carbon-containing ligands, but have also been synthesized carbon-free metallocenes and poly-metallic sandwich compounds, as is the case of $[Sb_3Au_3Sb_3]^{3-}$ in 2015; the first all-metal layer sandwich species; which has inspire the design of new nanoscale building blocks with hollow structure, since that can increase their functional features, and depending on the size cavity, they can encapsulate a second material. In these sense, Zhu *et al*. theoretically have studied the Sb-Au sandwich complexes increasing the size of their metal rings from 3 up to 6, keeping the integrity of sandwich and thus growing up their hollow interior.[1-3]

In this work, we evaluate the capacity of the $[Sb_nAu_nSb_n]^m$ (n= 4,5,6; m= -2, -1, -2) sandwich complexes to capture inside them elements from groups I and II of the periodic table. Within density functional theory framework, the neutral and charged structures were optimized and characterized as minima by frequency analysis, we use the non-empirical exchange-correlation functional PBE0 and the def2-TZVP basis sets with the corresponding pseudopotential for heavy atoms.

Our results shown that in most of the cases, the guest is located in the center of the gold ring causing its elongation and therefore modifying the stacking of the three metal layers, preserving thus the sandwich integrity.

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Energetics of ion binding of the Na^+/H^+ antiporter MjNhaP1

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Sodium proton transport is essential for the viability of the cell by controlling pH and salt concentration, and maintaining volume homeostasis. Originally described as Na^+/H^+ exchangers, several cation/proton antiporter (CPA) were recently shown to also transport K^+[1,2]. By contrast the electroneutral NhaP1 of *Methanocaldococcus jannaschii* (MjNhaP1) does not transport potassium ions [3]. To understand the ion selectivity of MjNhaP1, we estimate the free-energy of ion binding using classical free-energy perturbation (FEP) calculations. In a fully atomistic molecular-dynamics (MD) simulation, a sodium ion is alchemically transformed to a potassium ion, which sheds light on the molecular mechanism of ion specificity.

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Embedded Multireference Coupled Cluster Theory

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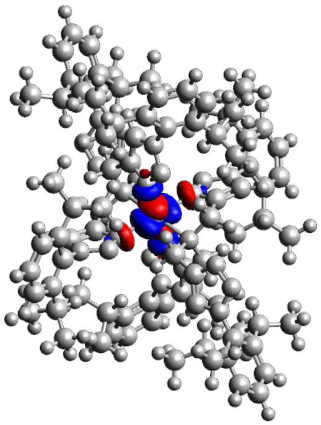
Many chemical reactions are dominated by a small number of atoms and electrons in an active region of the molecule. This has led to the development of embedded electronic structure methods, which strive to combine an accurate description of the active region with a computationally less expensive approach for the rest of the system. This is of particular importance for multirefererence systems, which require more complex and expensive theories, for example internally contracted multireference coupled cluster (icMRCC) theory[1]. We have implemented an embedding procedure that uses truncated sub-spaces of the occupied and virtual molecular orbitals, rendering expensive multireference calculations viable by restricting them to the active region of the molecule. The occupied molecular orbitals are localised and partitioned into active and environment regions, and a reduced virtual space made by merging projected atomic orbitals within the active region. Embedded icMRCC calculations are further incorporated into less expensive perturbative methods [2] using a simple subtractive approach. We present benchmark calculations for the embedding procedure using small molecules, including homolytic bond breaking and carbenes. Further application to much larger systems is also demonstrated, including transition metal complexes consisting of hundreds of atoms and thousands of basis functions (see figure).



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Computational study of biologically active naphthylisoquinoline alkaloids: an overview of obtained results

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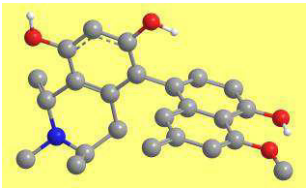
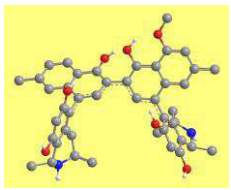
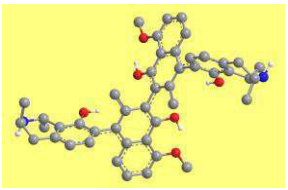
Naphthylisoquinoline alkaloids are alkaloids found in plants of the *Ancistrodaceae* and *Dioncophyllaceae* families. They exhibit remarkable biological activities - antimalarial, anti-HIV, anti-trypanosomal, anti-leishmanial and others [1-2]. Their molecules may contain one unit consisting of one isoquinoline moiety and one naphthalene moiety (monomeric structures) or two such units (dimeric structures). The presentation offers an overview of the results obtained for 33 monomeric alkaloids with antimalarial activity [3] and two dimeric alkaloids – jozimine A2 [4], with antimalarial activity, and michellamine A [5], with anti-HIV activity. Calculations were carried out at the HF/6-31G(d,p) and DFT/B3LYP/6-31+G(d,p) levels in vacuo and in three different solvents. The results show that the conformational preferences and other molecular properties are influenced by intramolecular hydrogen bond (IHB) patterns, i.e., the number and type of IHBs present in a conformer, and by the mutual orientations of the moieties, with preference for mutual perpendicularity [3-5]. The solvent shows non-negligible effects on the molecular properties, mostly depending on the solvent nature and on the conformer's IHB pattern.



Ancistrocongoline



Michellamine A



Jozimine A_2

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Modern Coupled Cluster Approaches for the Spin-State Energetics of Carbenes

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Carbenes constitute a large class of organic compounds that are not only of high practical interest because of their rich and varied chemistry, but also of fundamental interest owing to the complexity of their electronic structure. The stability and accessibility of the spin singlet and triplet states determines to large extent their physical and chemical properties. It is therefore of great importance to have widely applicable quantum chemical methods that can accurately predict the relative energies of these states for any given carbene. This often presents a challenge because of the fundamentally different closed or open-shell electronic configurations that contribute to the each possible state, the presence of near-degeneracies, and the substituent effects. In the present work we compile a benchmark set of aryl carbenes that span a range of singlet-triplet gaps and include both singlet and triplet ground state species. The performance of various correlated wave function methods is evaluated for the prediction of the ground spin state and the singlet-triplet gap. The comparison includes modern linear-scaling domain-based local pair natural implementations of coupled cluster theory, and critically examines the convergence and reliability of explicitly correlated F12 coupled cluster methods for open-shell species.

Modelling the electronic states of polyphenylene-ethynylenes

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Hydrocarbon dendrimers are macromolecules experimentally well-known for their exceptional optoelectronic properties [1]. Polyphenylene-ethynylene (PPE) dendrimers behave as light-harvesting antennae in which unidirectional exciton transfer occurs along a series of linear, conjugated building blocks connected *via* the *meta*-substitution of phenylene rings. Thus, PPE dendrimers have received much interest as artificial photosynthetic systems. Recent theoretical investigations based on semi-classical dynamics simulations [2] have indicated that the unidirectional energy transfer involves a cascade of conical intersections between excited states localized on different linear fragments. Yet, the calculations of full-dimensional potential energy surfaces (PES) remains out of reach for any level higher than semi-empirical, due to the size of the systems.

Different types of calculations (TDDFT, extended Hückel) enlightened a strong hierarchy within the interactions governing the electronic structure of *meta*-PPEs; in particular, their first excited states result from weak couplings among the excited states of the corresponding *para*-PPEs. This allows us to build a new type of diabatic representation for the PES under the form of a Hubbard matrix, whose eigenvalues are expected to reproduce the adiabatic energies at a TDDFT level of theory. The dependence on the nuclear coordinates will be expressed through the Hubbard parameters that are involved in the energies of the diabatic states (diagonal) and their couplings (off-diagonal); as all are local, each will only depend on a few nuclear coordinates, thus simplifying drastically the potential energy functions. The explicit expression of the Hubbard matrix elements through their constituting parameters as functions of the nuclear coordinates will be based on a multiscale approach.

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Relativistic calculations for identifying new chemical species at ultra-trace concentrations: $AtO(OH)_2^-$ and $IAtBr^-$ revealed

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Revealing the occurence of and identifying new chemical species at ultra-trace concentrations may turn out to be practically impossible from the sole experimental point of view. In such conditions, standard analytical chemistry tools such as spectroscopy ones cannot be used, and little information can be convincingly obtained. The molecular charge of a given species can be determined with electromigration experiments or chromatography, and speciation changes can be indirectly characterized by means of competition experiments.
In this work, we will focus on the identification of new astatine (At, $Z = 85$) species. Actually, this work is of fundamental interest owing the high potential of the ^{211}At radionuclide in radiotherapy and the current lack of knowledge on the chemistry of astatine [1]. Note that due to the minute quantities of astatine than can be produced in cyclotrons, one is in this case obliged to work at ultra-trace concentrations. Since At is a heavy element and since its $6p$ shell may not be fully occupied in the compounds it can form, calculations must account for relativistic effects and in particular for spin-orbit coupling (SOC).
In this presentation, we will first show that the spin-orbit DFT (SO-DFT) method is accurate enough to compute or predict equilibrium constants of reactions between astatine basic units and inorganic ligands [2]. Then, we will show that SO-DFT calculations can discriminate two hypotheses arising from experiments concerning the identification of a new species belonging to the Pourbaix (E-pH) diagram of astatine, leading to the firm identification of $AtO(OH)_2^-$ [3]. Finally, we will show that SO-DFT calculations can be used to target the tiny experimental domain to be covered for evidencing an "exotic" interhalogen compound, $IAtBr^-$ [4].

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Potential energy surfaces for dissociative collisions of atmospheric molecules

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We are developing potential energy surfaces for collisions of atmospheric molecules. Reactions of atmospheric molecules like O_2, N_2, and NO play an important role in atmospheric chemistry and are also of interest for re-entry chemistry in aerospace applications. Hypersonic vehicles, spacecraft, and re-entry vehicles are in the atmosphere for extended periods of time, and their surface is exposed to interactions with high-temperature gases. The currently applied chemical models in hypersonic flow simulations are partially based on outdated data and assumptions. Accurate global potential energy surfaces (PESs) are needed for realistic computational fluid dynamics (CFD) simulations of shock layers around hypersonic vehicles.

Construction of potential energy surfaces involves electronic structure calculations and fitting of potential energy surfaces and their couplings. These surfaces can be further used for to calculate reaction rates and energy transfer. Due to the highly multi-reference characters of the reactants, intermediate structures, and products, construction of the PESs is very challenging from the theoretical point of view and requires application of expensive methods and significant amounts of computational time. A global ground-state potential energy surface describes all kinds of collisions of two diatomic molecules, as well as a triatomic molecule interacting with an atom, and a triatomic surface as a sub-surface of the four-body PES. Although the spin state of the whole system is constrained in a four-body system, the spin states of sub-systems are not conserved. Thus, individual three-body PESs are also important for the investigation of atom-diatom collisions. The surfaces are based on electronic structure calculations by multi-state complete-active-space second-order perturbation theory with minimally augmented correlation-consistent polarized valence triple-zeta basis sets. Potential energy surfaces are obtained by fitting the many-body interaction to electronic structure data points with a fitting function that is a permutationally invariant polynomial in terms of bond-order functions of the six interatomic distances. The resulting surfaces are used to carry out dynamical simulations that allow one to get reaction rate constants and energy transfer rate constants to model heat transport.

The authors are grateful to Tom Schwartzentruber and Graham Candler for collaboration on the overall project. This work was supported in part by the Air Force Office of Scientific Research by grant no. 3002-11098-00056269.

Computational Approach to Organic Reactions Mechanisms in Ionic Liquids

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Ionic Liquids have extended, remarkably, the possibilities of tuning organic reactions taking advantage of the environmental effects [1]. Although only a small part of all hypothetic ionic liquids has been effectively synthetized and used as reaction media they are enough to provide a large variability of effects on reactions affecting reaction efficiency and selectivity not easy to rationalize. Ionic liquids cannot be localized along the classic coordinates of polarity, acidity, etc. used for molecular solvent classification. These categories can be used but they are not sufficient to full classify and rationalize them.

Ionic liquids can be considered as an equimolar mix of an anion and a cation. The effect of ions' net charges is quenched at macroscopic level but can be important at molecular level. This weaken one of the axioms of the solvent polarity theory: the importance of the dielectric constant value is limited in this context. Specific chemical properties of anion or cation or both can influence the reaction mechanism while their combination determines the physico-chemical nature of the ionic liquid.

Here we will present some computational studies [2] about reaction mechanisms in ionic liquids. The aim of these studies is to rationalize the experimental observed effects in terms of specific chemical roles taken by anion or cation or both. These effects influence heavily mechanism and selectivity of the reaction studied.

The chemical nature of these effects is related to phenomena like hydrogen bond, steric hindering, inductive effect, acid/base properties, etc. Some mechanism in which ionic liquids present catalytic effects in molecular solvents will be also presented.

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DFT MECHANISM OF CHELATING RUTHENIUM CATALYSTS NEW FOR RING OPENING METATHESIS POLYMERIZATION (ROMP).

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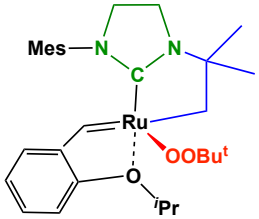
The Ring Opening Metathesis Polymerization (**ROMP**) is nowadays a highlighted area to the production of novel polymeric materials.[1] In this direction, the polynorbonadiene has been widely studied through well-defined Schrock catalysts. For instance, [Mo(NR)(=CHR_2)(biphenolate)$_2$] give to rise to *cis*-isotactic polymers, while the called MAP catalysts [Mo(NR)(=CHR_2)(OR_1)(Pyr)] produce the highly stereoregular or *cis*-syndiotactic polymers.[2,3] On the other hand, in the 2013 was reported the first Grubbs catalysts **1** that also conduce to *cis*-syndiotactic polymers.[4] This belongs to the *Z*-selective catalyst´s family for Cross Metathesis (**CM**) which has allowed to obtain in the last decade high yield of *cis*-olefins.[5,6] In sense, we recently have studied the ancillary and chelating ligand effect on ruthenium complexes and found that the catalysts **2** and **3** are also *Z*-selective.[7] Therefore, these new catalysts that have similar characteristic to **1** could also lead to highly stereoregular polymers. For research this premise, we studied the **DFT** mechanism of these catalysts on **ROMP** reactions using norbornadiene as substrate. Specifically, were found the initiation and propagation step, and the rotameric change of the metal-carbene bond on the 14e- propagation specie, which has been postulated as the determinant step in the stereoregular polymer formation using Mo-complexes. All calculations were performed in the Gaussian 09 program, using the M06 functional. The Ru was described by the pseudopotential, called MWB28, which replaces the 28 inner electrons by a nonlocal effective potential. The others elements were described by the 6-31+G(*d,p*) basis sets. Finally, we carried out the vibrational analysis of all located stationary points to ensure their nature as intermediate or transition structure.



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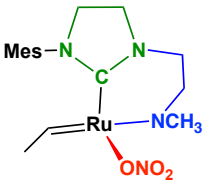

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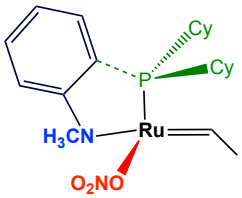

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Towards an Accurate First-Principles Description of Excited States in Dielectric Environments: The Versatile ADC(0-3)/SS-PCM Approach

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We present a combination of the state-specific polarizable-continuum model (SS-PCM) with the ADC family of excited-state methods (ADC: algebraic-diagrammatic construction for the polarization propagator). Using a self-consistent scheme for "long-lived" solvent-equilibrated states as well as a perturbation-theoretical approach (ptSS-PCM) for vertical transitions in the non-equilibrium limit, ADC/SS-PCM can rigorously model all common photophysical processes. These include ground- and excited-state (one and two photon) absorption, fluorescence and phosphorescence. The SS-PCM is available for all variants of ADC implemented in Q-Chem 5.0, i.e, canonical ADC, spin-flip ADC for multi-reference problems, CVS-ADC for core-valence excitations, as well as ri- and SOS-ADC(2) for increased efficiency and accuracy. By computing excited-state wavefunctions via the efficient intermediate-state representation formalism, the computational overhead for the SS-PCM is kept small, such that applications to systems with 500+ basis functions are possible with riADC(2). One example is the large (ca. 400 bf.) push-pull system (ZMSO2, Fig. 1), for which we demonstrate how solvent-polarity governs the extent of charge-separation in the lowest excited state. Modeling the solvent-relaxed excited-state PES of DMABN in polar and non-polar solvents, we establish that ADC(2)/SS-PCM affords excellent agreement with experimental fluorescence data. However, the observed solvent-dependent dual fluorescence can only be explained at the ADC(3)/SS-PCM level of theory.

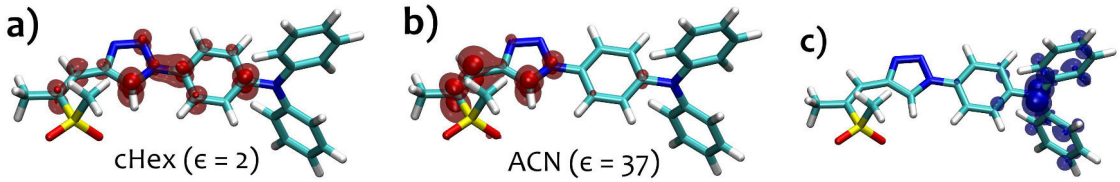

Figure 1: Isodensity plots of electron (red, a&b) and hole (blue, c) for the solvent-relaxed lowest excited state of ZMSO2 in cyclo-hexane and acetonitrile @ riADC(2)/SV(P)/SS-PCM

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Thermochemical Properties of $BaXO_3$ (X=Mn, Zr, Ce) Perovskite Materials using First Principles Phonon Calculations

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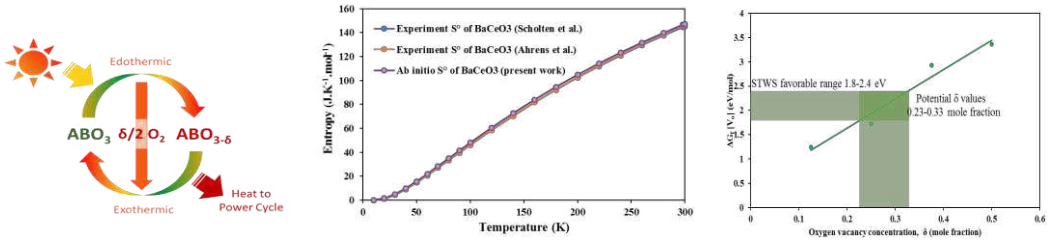
Perovskites metal oxides (ABO_3) are attractive candidates for energy applications such as solar thermal water splitting (STWS), solar fuel production and photocatalysis due to their mixed oxidation states [1]. In STWS process, these materials can be reduced under solar-driven, high-temperature conditions, to produce reduced perovskite metal oxides ($ABO_{3-\delta}$) and oxygen ($\delta/2O_2$) (Figure 1(a)). This reduced metal oxide can subsequently be oxidized by water, to release heat and hydrogen (H_2) via an exothermic reaction. The performance of such metal oxides as redox materials is dominated by their free energy associated with the formation/removal of oxygen vacancies in the reduction/oxidation reactions, respectively. Here, we predict the redox thermochemistry of $BaXO_3$ (X = Mn, Zr, Ce) using density functional theory (DFT). Thermochemical properties obtained here are in excellent agreement with experimental data (Figure 1(b)). For $BaCeO_3$, our calculations show that energetically optimal formation energies ($\Delta G_f[V_0]$) are achieved with vacancy concentrations of δ = 0.23-0.33. Furthermore, our predicted $\Delta G_f[V_0]$ values for $BaCeO_{3-\delta}$ demonstrate, for the first time, that $BaCeO_3$ is a potentially useful, yet unexplored, perovskite for solar thermal water splitting applications. Comparison of $BaCeO_3$ with $BaMnO_3$ and $BaZrO_3$ reveals the electronic and structural origins of this improved performance.



(a) **(b)** **(c)**

Figure 1: **(a)** STWS redox reaction, **(b)** PBE-PAW+U+J, entropy S° of present and experimental work (J K^{-1} mol^{-1}) of bulk $BaCeO_3$ [2,3], **(c)** PBE-PAW+U+J, $\Delta G_f[V_0]$ of $BaCeO_{3-\delta}$ (298.15 K, 1 atm) as a function of δ. The green zone indicates the optimum $\Delta G_f[V_0]$ range 1.8-2.4 eV [4].

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Behavior of finite uniform electron gases at high and low density.

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Traditional concept of uniform electron gas consists of a homogeneous system of electrons at constant density contained in an infinite volume. In spite of its simplicity many real phenomena in solid-state physics can be adequately explained by this model,[1] i.e. electronic structure of metals, superconductivity and quantum hall effect.

Similarly, the importance of uniform electron gas to chemistry cannot be overstated. After all, at the crudest level an electron cloud in a molecule is just a collection of minuscule chunks of uniform electron density. This is the main idea behind local density approximation and forms a starting point for most density functionals. However, is an infinite electron gas the best starting point for studying a finite molecular system?

Recently, a new paradigm of finite uniform electron gases has been introduced by Loos and Gill.[2, 3] It consists of electrons confined to the surface of (n+1)-dimensional ball, or an n-sphere, with fixed radius. Two electron systems in such space have been studied extensively, and behavior of electrons on a 3-sphere is most reminiscent of realistic systems.[3, 4] However, practical utilisation of this paradigm in density functional theory necessitates going beyond just two electron systems and requires solving the many body problem.

This presentation will give a brief introduction to finite uniform electron gases, and our progress in finding methods for solving the corresponding many body problem, with particular emphasis on high and low density regimes.

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Is a post-self-consistent-field addition of the non-local correlation kernel in van-der-Waals density functionals sufficient?

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Addressing the inability of Kohn-Sham density functional theory (KS-DFT) to properly describe London-dispersion forces has attracted a lot of attention in recent years. One technique for DFT that describes London-dispersion forces is the addition of a non-local correlation kernel to the exchange-correlation density functional. The resulting functional is then called a van-der-Waals density functional (vdW-DF), and various formulations exist.

Adding the non-local correlation functional in a post-self-consistent-field (post-SCF) fashion can be accurate [1], which is beneficial to reduce computational cost. Yet, implementations of newer functionals recommend a fully self-consistent usage of the non-local correlation term[2].

To the best of our knowledge, there has not been any thorough assessment of whether or not adding the non-local correlation kernel in the post-SCF fashion is accurate for a broad range of chemical problems (including large systems), compared to employing it during the SCF procedure.

In this work, we thoroughly investigate this issue by examining various exchange-correlation functionals augmented with the accurate[3] VV10 non-local correlation kernel for an extended database that encompasses general main-group thermochemistry, kinetics and non-covalent interactions.

Our results suggest that the accuracy of vdW-DFs is not compromised when the non-local correlation functional is added to the exchange-correlation functional after the SCF procedure. Finally, we also conduct an in-depth analysis of how using a non-local correlation functional influences other molecular properties, such as electron densities. Our findings provide insights for future method developments.

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Exciton Transference in Natural and Hypothetical Bacteriochlorophyll Arrangements. Is Singlet Fission a Possible Photosynthetic Mechanism?

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Several excitation energy transfer (EET) processes are known to occur during the first stages of photosynthesis, with timescales ranging from a few fs to several tens of ps, however their full assignment is still a matter of controversy [1]. Singlet fission (SF) is a photochemical in which an exciton in a singlet state decays to two coupled–degenerate triplet excitons with half the energy of the original excited singlet [2]. The resulting multiexcitonic (ME) state can later decouple in vicinal molecules, thus propagating the original excitation. SF has been extensively observed in polyaromatic hydrocarbons [3] but not in chlorophyll–related photosynthetic pigments.

Bacteriochlorophylls (Bchl) *–a* through *–d* are the light–harvesting pigments used by anaerobic photosynthetic bacteria; the structural simplicity of their photosystem II complexes makes them attractive for electronic structure calculations [3]. Time Dependent Denstiy Functional Theory (TD–DFT) at the CAM–B3LYP/6-31G(*d*) level of theory and Restricted Active Space–Spin Flip (RAS-SF) calculations were undertaken to get a full description of the excited states on each pigment molecule and their dimers at various conformations. Pigment dimers in the Fenna–Matthews–Olson (FMO) complex and the bchQRU chlorosome from *C. tepidium* (a 600 Bchl–*d* toroid) were studied as candidates for SF in photosynthesis.

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An efficient method for calculating effective core potential integrals.

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[2]*Q-Chem Inc., 6601 Owens Dr, Pleasanton, CA 94588, USA*

Effective core potential (ECP) integrals are one of the most difficult one-electron integrals due to their constituent projected integrals. Several authors[1] have provided methods to compute these difficult projected integrals yet there remains no dominant method that is both efficient and reliable.

Taking inspiration from efficient algorithms to calculate two-electron repulsion integrals, we develop efficient recurrence relations and rigorous upper bounds for ECP integrals. Our recurrence relations are founded upon a previously derived simple fundamental projected integral[2] and our rigorous upper bounds reduce the number of total ECP integrals from $O(M \times N^2)$ to $O(M)$ significant ECP integrals, where N and M are the the number of basis and ECP functions, respectively. We implement the present method into Q-Chem 5.0 and demonstrate significantly faster ECP integral computation as compared to Q-Chem 4.4[3] and GAMESS (US).[4]

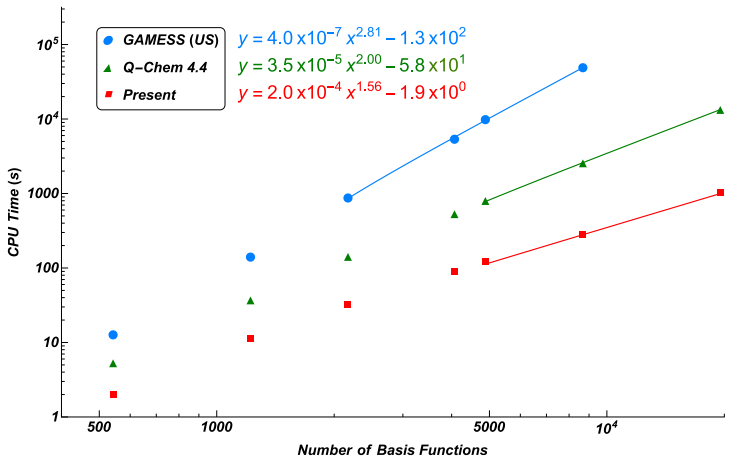

Figure 1: ECP integral timings for a Pt SBKJC slab.

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Evaluation of aromaticity based on magnetically induced current using the GIMIC method for open-shell molecules

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Aromaticity is a familiar concept for chemists that can help probing the electronic structures of π-conjugated molecules. So, when applying an external magnetic field perpendicular to the plane of an aromatic molecule, both diatropic and paratropic currents, associated with aromaticity and antiaromaticity, respectively, are induced. The magnetically induced current (MIC) strength, *J*, is a quantitative indicator of aromaticity. The gauge including magnetically induced current (GIMIC) method has recently been developed for various levels of electronic structure theory and quantum chemistry packages to evaluate such currents for a variety of electronic states including open-shell systems [1].

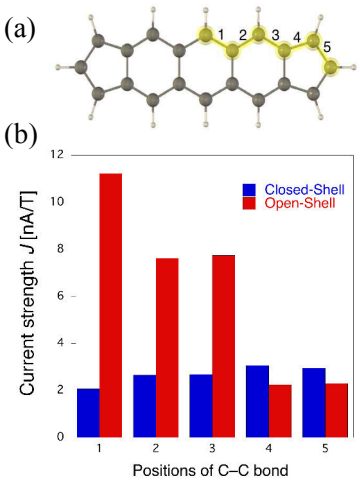

Fig. 1 (a) Molecular structure of DPA(5). (b) Current strength *J* across each C–C bond of DPA(5) for closed-shell (blue) and open-shell (red) solutions.

We investigate here at the DFT level the aromaticity of open-shell singlet molecules, dicyclopenta-fused acenes (DPA) [2] and polyacenes (PA), for clarifying the relationships between open-shell character and the MIC. For DPA, *J* values are significantly different between closed-shell and open-shell wave-functions (Fig. 1): open-shell show larger aromaticity in the 6-membered rings than closed-shell ones. We also present the results on PA together an analysis of the relationship between the spatial current and odd electron distributions.

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Chiral glycine methyl ester – Chirality transfer in matrix-isolation vibrational circular dichroism (MI–VCD) spectroscopy

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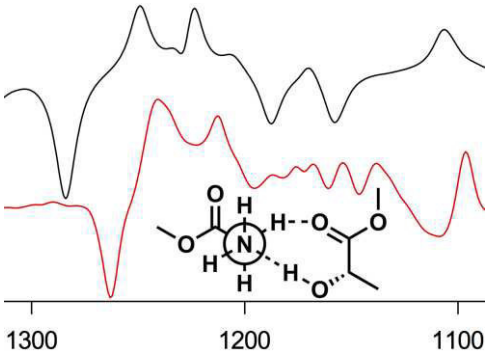
The origin of homochirality of even the most fundamental biomolecules, such as amino acids or sugars, is still vividly debated. Current hypotheses often invoke the interaction of racemic mixtures with circularly polarized light (CPL), *e.g.*, preferential photolysis of one enantiomer [1]. Indeed, photolysis of various amino acids in extraterrestrial ice analogs with CPL in the UV/Vis range [2] yields small enantiomeric excesses (*ee*) similar to those found in the Murchison meteorite [3]. Since CPL has been detected in the interstellar medium [4], the initial generation of chiral biomolecules on extraterrestrial bodies, *e.g.*, on comets, is now being regarded as a viable scenario [1]: Fixation of suitable (organic) precursors in cometary ices may lead to accumulation of sufficiently high reactant concentrations and protects volatiles against evaporation.



Combination of chiroptical methods, such as vibrational circular dichroism (VCD) spectroscopy with matrix-isolation (MI) enables the investigation [5] of chiral species and their interactions under realistic model conditions. We recently found that the achiral amino acid derivative glycine methyl ester (Gly–OMe) forms binary complexes with either L- or D-methyl lactate in solid dinitrogen matrices upon mild annealing. As a result, Gly–OMe acquires unique VCD activity of its ester moiety and thus "inherits" chirality from the methyl lactate template (*cf.* inset; *red*: experimental VCD trace of L-methyl lactate:Gly–OMe complex; *black*: VCD trace of complex computed at B3PW91/aug-cc-pVTZ). In subsequent CPL-enabled transformations, this transfer of chirality may provide a means for the proliferation of chiral information even across the boundaries of different classes of biologically relevant compounds (*vide supra*).

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Surface Effects on Vacancy Diffusion in Titanate Perovskites $ATiO_3$ (A = Sr^{2+}, Ba^{2+}, Ca^{2+})

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The formation, stability and mobility of oxygen vacancy defects in ABO_3 perovskites has great influence on their potential use in energy applications, such as fuel cell electrodes and thin film technologies. Tuning $A^{II}Ti^{IV}O_3$ titanate prevoskites has attracted considerable attention in this respect due the various electronic, optical and thermal properties which are useful for hydrogen and oxygen evolution reactions. Across this prevoskite series, variation of the A-site cation results in various structural effects in the titanate crystal, inducing changes that tailor the individual titanates towards different applications. Recent studies have highlighted the importance of lattice oxygen diffusion in catalytic surface water splitting reactions,[1] while surface oxygen vacancies deprotonate adsorbed water molecules.[2] Several other simulations reported in the literature have investigated the propensity for surface defect formation and defect aggregation in bulk $SrTiO_3$.[3,4] In contrast, oxygen vacancy diffusion near the catalytic interface (i.e. the surface/subsurface region) remains unexplored, despite the fact that it potentially limits the utility of $SrTiO_3$ in most real-world energy applications. Herein we investigate oxygen vacancy diffusion at the [0001]$ATiO_3$ interface (A = Sr^{2+}, Ba^{2+}, Ca^{2+}) using PBE-PAW+U+J (Figure 1), and demonstrate how the A-site cation can promote/limit oxygen diffusion near the catalyst interface. Our results show that the size of the A-site cation has a substantial impact on the stability and mobility of oxygen defects in both the AO and TiO_2 sublattices. A geometrical energy decomposition analysis also reveals that the interaction and deformation energy contribution to the oxygen vacancy formation and migration corralates to the ease of the AO sublattice structurally housing a defect compared to the TiO_2 sublattice.

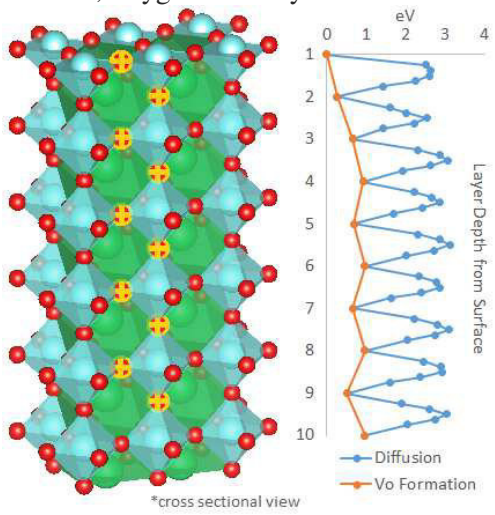

Figure 1. PBE-PAW+U+J oxygen formation energies (V_O) and diffusion barriers, eV, for the [0001]$SrTiO_3$ interface.

[1] X. Rong, J. Parolin, A. M. Kolpak, *ACS Catal.*, **6**, 1153 (2016).
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Short-Range Spin-Dependent Interaction Energies between Chiral Molecules

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The interaction between two closed-shell chiral molecules has been investigated for enantioselective discrimination in the long-range region[1]. To find a discriminating and non-negligible energy difference for the interaction in homo- and hetero-chiral dimers, a method for short- and medium-range interaction energies has to be employed[2]. The group function approach allows for the direct calculation of the interaction energy, decomposed into contributions whose physical interpretations are discussed in Ref. [3]. The overlap region of electron distributions of the interacting systems becomes accessible by suspending the strong-orthogonality condition between their individual wave functions. Expanding the non-orthogonality contributions in order of transpositions between the systems, spin-dependent terms arise via a coupling of the corresponding spin tensor operators[4]. The implementation of this scheme starting from broken-symmetry Hartree-Fock determinants is presented with applications to simple systems. The convergence of the expansion and the interpretation of the arising contributions is discussed.

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Concerted Proton Transfer in Mixed Acid-Water Clusters: $[(HCl)(H_2O)]_2$ and $[(HF)(H_2O)]_4$

Itay Zakay[1], Mychel E. Varner[2], R. Benny Gerber[1,3]

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Molecular dynamics simulations using directly *ab initio* potentials are carried out for the ionically-bonded clusters: $[(Cl^-)(H_3O^+)]_2$ and $[(F^-)(H_3O^+)]_4$, to explore their transitions to the hydrogen-bonded structures: $[(HCl)(H_2O)]_2$ and $[(HF)(H_2O)]_4$, respectively. Both the ionic and H-bonded structures are highly symmetric for both clusters. It is found that proton transfers are concerted in all trajectories for $[(Cl^-)(H_3O^+)]_2$, whereas for $[(F^-)(H_3O^+)]_4$ the four-proton concerted transfer is highly dominant but not exclusive. It is suggested that the high symmetry of the ionic and the H-bonded structures plays a role in the preference for concerted transfers. The results predict a major role of collective effects in ionization of acid molecules in concentrated systems.

Insights into the formation of catalytically active metal-substituted polyoxometalates in the presence of proteins

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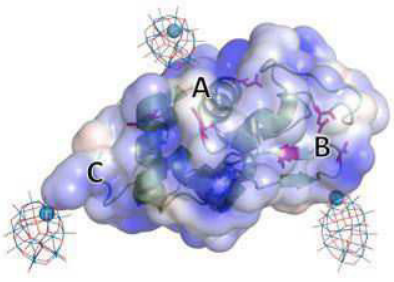
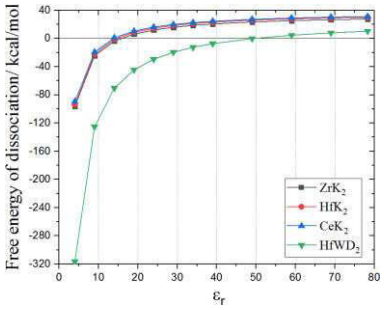
Several metal-substituted polyoxometalates (MSPs) of MX_2 type (M = Zr(IV), Hf(IV), Ce(IV) and X = Keggin (K), Wells-Dawson (WD) polyoxometalates) have demonstrated a remarkable selectivity towards peptide bond hydrolysis in proteins under mild conditions [1]. The hydrolytic activity has been attributed to the MX species, presumably formed through dissociation of the starting MX_2 compounds [1]. However, the existence of MX species in water solutions, at near neutral pH, have not been evidenced experimentally so far. Recently, a monomeric ZrK polyoxometalate was identified in a co-crystal with hen egg-white lysozyme (HEWL) [2]. Here, we report on the successful co-crystallization between HEWL and a catalytically active HfWD polyoxometalate, which is the first crystallographic evidence for the existence of this species. The crystal structure showed three binding sites (the Figure on the left), one of which lays in the proximity of three cleavage sites. Since in both experiments MX_2 species were used as staring compounds, the X-ray results strongly suggest that in the presence of a protein the dissociation reaction $MX_2 \rightarrow MX + X$ becomes favorable, while it is unfavorable in the absence of a protein. Previous studies showed that the dielectric constant ε_r at the protein surface is much lower as compared to bulk water, ranging from $\varepsilon_r \approx 6\text{-}7$ inside the protein to $\varepsilon_r \approx 20\text{-}30$ at the surface of the protein [3]. To examine the influence of ε_r on the reaction thermodynamics DFT calculations were performed on a series MX_2 type MSPs. The results (the Figure on the right) suggest that binding of the MSPs to the protein surface (with low ε_r) may promote dissociation by increasing the Coulomb repulsion between the negatively charged X moieties of the MX_2 complexes, which is otherwise effectively screened in the bulk water.





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Conformational Analysis and Accurate Prediction of Molecular Properties for Highly Flexible Chiral Natural Products

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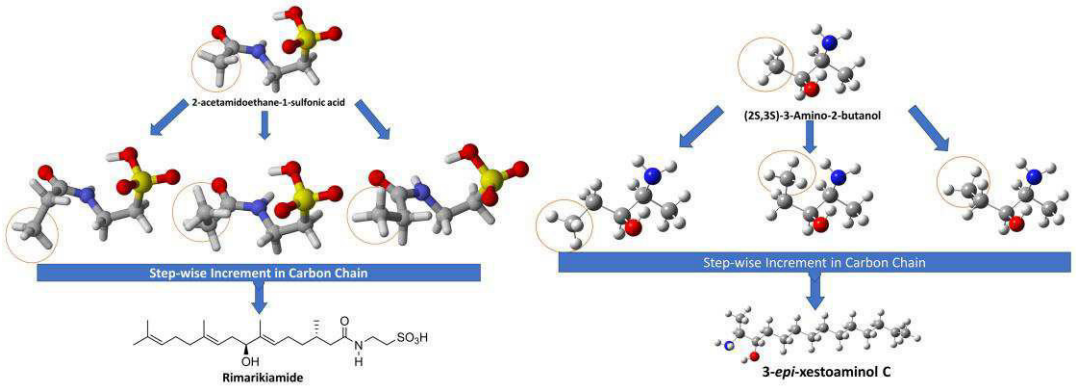
Despite advances in electronic structure theory, the theoretical prediction of spectroscopic properties remains a computational challenge. This is especially true for natural products that exhibit very large conformational freedom and hence need to be sampled over many different accessible conformations. We report a strategy, *MICE-PES* (Method for the Incremental Construction and Exploration of the Potential Energy Surface) which can predict NMR chemical shifts and more elusive properties like the optical rotation with great precision, through step-wise incremental increases of the conformational degrees of freedom. This method maps the potential energy in a systematic incremental approach using high level quantum chemical calculations in a much shorter time than a normal systematic conformational search will take even at a very low level of theory. The application of this method is demonstrated for 3-*epi*-xestoaminol C [1] and rimarikiamide. Both compounds are chiral natural products, one with a long, linear alkyl chain of 14 carbon atoms, the other also includes intramolecular hydrogen bonding and unsaturated carbon-carbon bonds. Comparisons with experimental NMR and $[\alpha]_D$ values are reported to validate the results of the Density Functional Theory calculations.



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Density-Functional Tight-Binding Molecular Dynamics Simulations of Proton Diffusion in the Bulk Ices and Liquid Water

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A fast proton diffusion in the bulk water is governed by the combination of vehicular and Grotthuss diffusion processes[1]. Fluorescence quenching study confirmed that hydronium ion moves faster in the ice I_h phase rather than in the liquid one[2]. However, current theoretical study of the proton transfer in the ice phase is limited to the empirical molecular dynamics simulation, which is only specific for the ice I_h phase[3]. Extension of molecular dynamics simulation at the ab-initio level is difficult due to the limitation of the computational cost. In the present work[4], the structural, dynamical, and energetic properties of the excess proton in the bulk water, low-density (I_h and I_c), and high-density (III and melted VI) ice phases were studied using the density-functional tight-binding (DFTB) method, which has a good balance between computational cost and accuracy. Moreover, divide-and-conquer scheme in DC-DFTB-K[5] code enables to perform large size simulations of the bulk water systems. The estimated proton transfer rates in the low-density ice structures are faster than in the high-density one. It is owing to the low density ices conserve the perfect tetrahedral structure of hydrogen bond networks, which are necessary for facilitating the proton transfer. The present study has reproduced the experimental tendency of the proton transfer rate in the ice phases.

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Accurate Prediction of One-Electron Reduction Potentials of Transition Metal Complexes.

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Many chemical transformations that involve metalloenzymes are very closely related to the redox properties of their metal sites. Those arise from variability in transition metals that are involved in reactions, different oxidation, spin and protonation states, total charges, types of ligands and ligand field geometries, different solvent (protein) environments, etc. The calculations of such electronic properties are therefore invaluable in understanding the above biochemical processes. Accurate prediction of reduction potentials is still a formidable task that is complicated by many factors among which solvation of highly charged species plays a crucial role. Herein, we present a robust and efficient theoretical methodology for the calculation of reduction potentials of transition metal complexes. The validation has been done on nearly 50 non-heme iron complexes, where the experimental electrochemical data are known and which often serve as biomimetic models of non-heme iron enzymes. For the subset of these non-heme iron complexes, the redox properties were also investigated along with their effects on H-atom abstraction reactivity. Last but not least, the accurate protocol for calculation of charged species in aqueous solution is presented. Here we introduce the novel H-atom addition/abstraction methodology used to neutralize charged species through several followed thermodynamic cycles. The accuracy has been evaluated on the set of 15 different transition-metal complexes that are considered as extremely challenging systems for computational electrochemistry. It is shown that the absolute error of calculated reduction potentials in comparison with the experiment is in most cases less than approx. 200 mV, which makes our methodology highly useful also in the interpretation of complicated electrochemical data, as well as in the description of electronic and spin state properties of transition metal complexes.

Concentration dependence of sound velocity in water and methanol mixtures using molecular-dynamics simulations.

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It is experimentally known that the ultrasonic velocity of water-methanol mixture depends on the methanol concentration X_{m} and it takes a maximum when X_{m} is about 15% [1]. However, the microscopic mechanism of these features has not yet been elucidated. In our previous study, we had performed molecular-dynamics (MD) simulations of water and methanol mixtures for various concentrations X_{m} and calculated the wavenumber-dependent sound velocity $v(k)$, where k is the wavenumber [2]. In that study, SPC/E and TIP4P models for water and OPLS-AA model for methanol were used. The MD simulations were carried out with 10000 molecules for a period of 0.1ns. Though the simulation time of 0.1ns was not long enough to calculate $v(k)$, we had obtained the following preliminary results: For a fixed X_{m}, with increasing wavenumber from about 1 nm^{-1} to about 7 nm^{-1}, the value of $v(k)$ increases. When the wavenumber k is about 5~7 nm^{-1}, with increasing X_{m} from 0 to 100%, $v(k)$ changes almost linearly from the value of pure water to that of pure methanol. With decreasing wavenumber, the concentration dependence of $v(k)$ changes and when the wavenumber is as small as 2 nm^{-1}, $v(k)$ shows a maximum near X_{m}=20%.

The purpose of the present study is to calculate the sound velocity with high accuracy from longer time MD simulations and to assure the previous results. To show the results above shown is independent with potential model, we employed a different water model, TIP4P-Ew. The simulations were performed at room temperature for 11 methanol concentrations X_{m} from 0 to 100% in steps of 10%. The number of molecules was determined so that the length of the side of the cubic simulation box became 6.28nm. To improve statistical average the MD simulation for a period of 1ns were conducted three times for each X_{m}. The wavenumber-dependent sound velocity $v(k)$ was calculated from the relation $v(k) = \omega(k)/k$, where $\omega(k)$ is peak frequency of $\omega^2 S(k,\omega)$. Here, $S(k,\omega)$ is the dynamic structure factor and ω is the angular frequency. We found that sound velocity of several nanometer wavelength in water-methanol mixture shows similar concentration dependence to that of ultrasonic wave. We also discuss temperature dependence of sound velocity.

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