CHIMIA

CHIMIA 2016, Volume 70
ISSN 0009-4293
www. chimia.ch

SCS
Swiss Chemical
Society

Supplementa to Issue 7-8/2016

SCS Fall Meeting 2016

Poster Abstracts
Session of Computational Chemistry

September 15, 2016
University of Zurich, Irchel Campus
http://scg.ch/fallmeeting/2016

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GW with Gaussian basis functions in CP2K

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We present an implementation of G_0W_0 and eigenvalue-self-consistent GW (evGW) in the Gaussian and plane waves scheme for molecules. Technically, we calculate the correlation self-energy for imaginary frequencies employing a resolution-of-the-identity approach. The correlation self-energy for real frequencies is then evaluated by analytic continuation. This technique allows an efficient parallel implementation and application to systems with several hundreds of atoms.

We employ evGW to calculate the HOMO-LUMO gaps of linear acenes, linear chains formed of connected benzene rings. Distinct differences between the closed and the open-shell (broken-symmetry) evGW HOMO-LUMO gaps for long acenes are found. In future experiments, a comparison of measured HOMO-LUMO gaps and our calculated evGW values may be helpful to determine the electronic groundstate of linear acenes.

Structure-function based screening discovers agonists for a prototypical olfactory receptor

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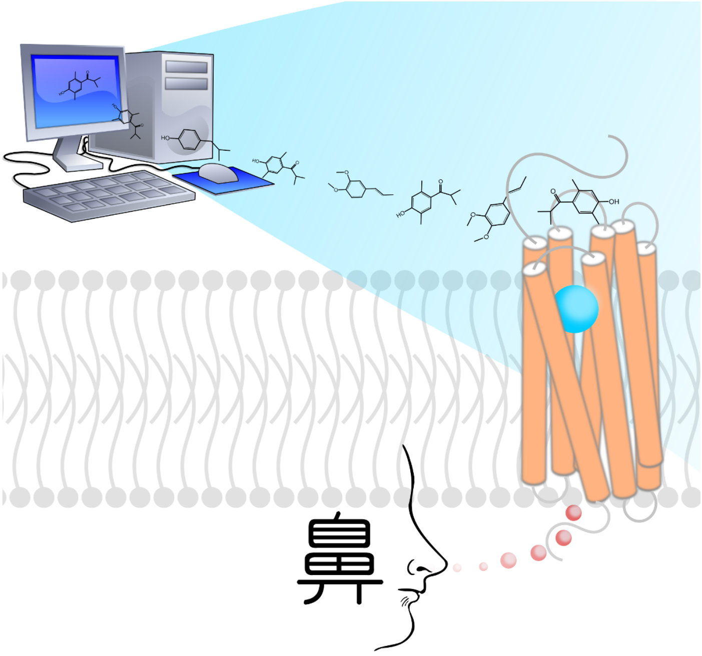
The mammalian olfactory system uses hundreds of specialized G-protein-coupled olfactory receptors (ORs), to discriminate a nearly unlimited number of odorants. Further chemosensory functions of ORs in non-olfactory organs appear of increasing medical relevance. However, the fundamental molecular principles of how odorants bind to and activate their ORs are largely unresolved, because most ORs are orphan receptors with unknown ligands. This demands for accelerated compound screening. Available methods do not allow functional screening of the huge chemical range of OR-activating compounds. Here we show for the prototypical OR Olfr73 that structure-based molecular dynamics simulations together with computer-based virtual screening can efficiently select active compounds from a library of 1.6 million molecular species. Our approach predicted 25 potential agonists, of which 17 activated Olfr73 in cell-based assays. Our findings provide important insights into the molecular mechanism of agonist induced activation of ORs and might help to identify OR targeting drugs.



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Potential Energy Surface-Based Conformational Analysis: Automatic Deduction of Conformational Reaction Route Maps at the Quantum Mechanical Level

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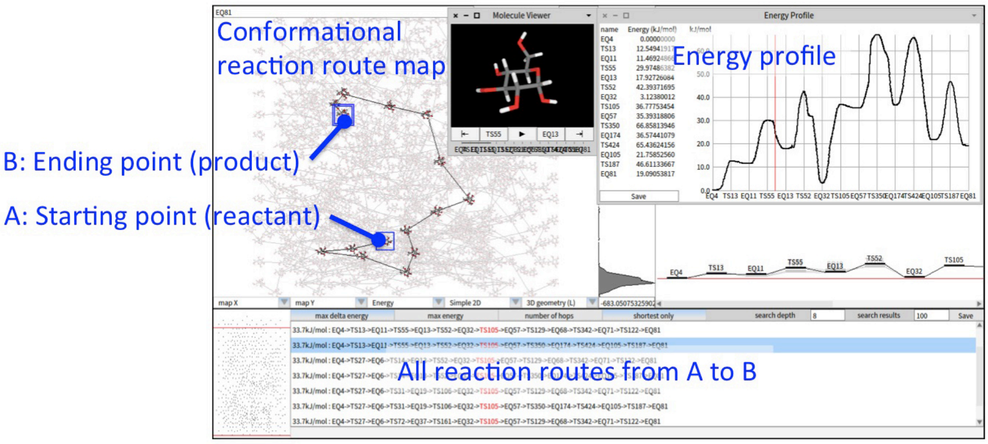
We introduce the PES (potential energy surface)-based conformational analysis approach. This approach searches a conformational space with PES-based sampling based on the GRRM (Global Reaction Route mappings) method [1], which explores a PES with the SHS (Scaled Hypersphere Search) of the ADDF (Automatic Downward Distortion Following) method. An advantage of this approach is that it automatically performs sampling only rational structures purely regarding the mathematical feature of PES without any a priori specification of variable internal coordinates. The PES-based conformational search automatically deduces a conformational reaction route map (r-map) consisting of equilibrium (EQ) and transition state (TS) conformers, connected by reaction routes confirmed using the intrinsic reaction coordinate (IRC) method. The obtained conformational r-map should be interactively analyzed using the RMapViewer software [2] we have developed. We applied this method to conformational analysis of α- and β-D-glucoses at the quantum mechanical level (RHF/6-31G).



name	Energy (kJ/mol)
EQ4	0.00000000
TS13	12.54941917
EQ11	11.46924866
TS55	29.97486382
EQ13	17.92726084
TS52	42.39371695
EQ32	3.12380012
TS105	36.77753454
EQ57	35.39318806
TS350	66.85813946
EQ174	36.57441079
TS424	65.43624156
EQ105	21.75852560
TS187	46.61133667
EQ81	19.09053817

```
33.7kJ/mol : EQ4->TS13->EQ11->TS55->EQ13->TS52->EQ32->TS105->EQ57->TS129->EQ68->TS342->EQ71->TS122->EQ81
33.7kJ/mol : EQ4->TS13->EQ11->TS55->EQ13->TS52->EQ32->TS105->EQ57->TS350->EQ174->TS424->EQ105->TS187->EQ81
33.7kJ/mol : EQ4->TS27->EQ6->TS14->EQ13->TS52->EQ32->TS105->EQ57->TS129->EQ68->TS342->EQ71->TS122->EQ81
33.7kJ/mol : EQ4->TS27->EQ6->T[illegible]
33.7kJ/mol : EQ4->TS27->EQ6->TS31->EQ19->TS106->EQ32->TS105->EQ57->TS129->EQ68->TS342->EQ71->TS122->EQ81
33.7kJ/mol : EQ4->TS27->EQ6->TS31->EQ19->TS106->EQ32->TS105->EQ57->TS350->EQ174->TS424->EQ105->TS187->EQ81
33.7kJ/mol : EQ4->TS27->EQ6->TS72->EQ37->TS161->EQ32->TS105->EQ57->TS129->EQ68->TS342->EQ71->TS122->EQ81
```

The obtained conformational r-map for α-D-glucose consisted of 201 EQ and 435 TS conformers, and that for β-D-glucose consisted of 202 EQ and 371 TS conformers. By analyzing the conformational r-maps with RMapViewer, we have found multiple minimum energy paths (MEPs) between global minima of ${}^{1}C_{4}$ and ${}^{4}C_{1}$ chair conformations, where the thermodynamic and kinetic predominance of ${}^{4}C_{1}$ conformations is clearly shown.

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Protein-ligand Interaction Fingerprints of the ß$_2$-Adrenergic Receptor

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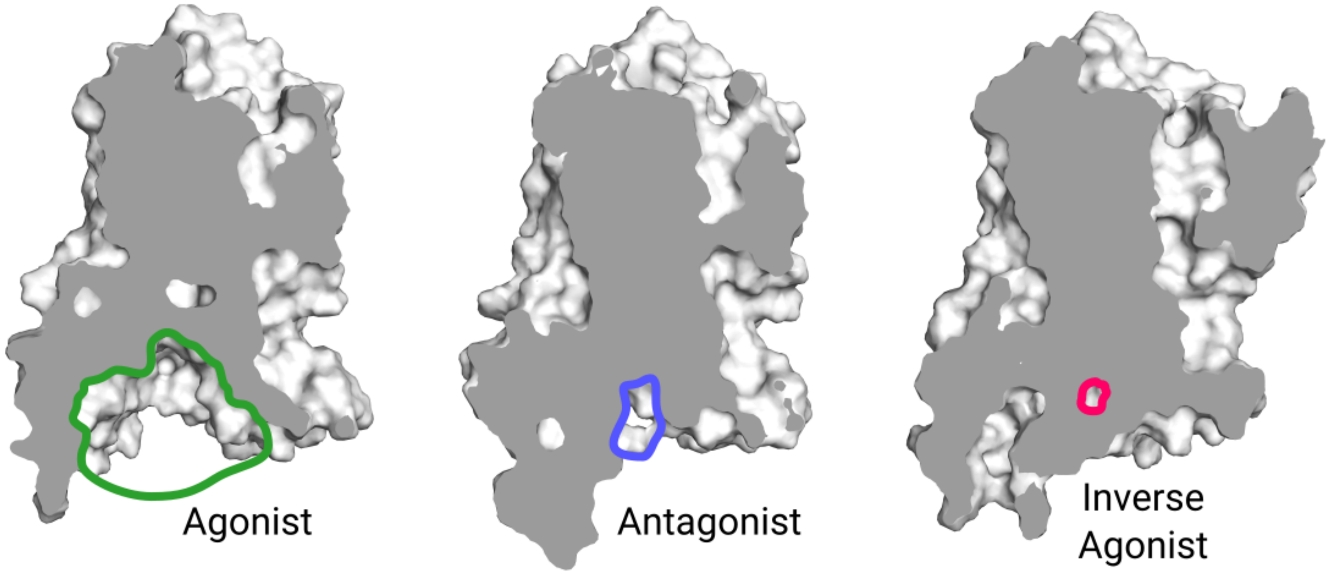
ß$_2$ adrenergic receptor (ß$_2$AR), a transmembrane protein, belongs to the family of G-protein coupled receptors (GPCRs)[1]. It regulates numerous important physiological activities in the human body, such as the relaxation of bronchial smooth muscles[2] and the hemostasis of blood glucose[3,4]. It has been a classical target for rational drug design[5]. With the recent breakthrough in experimental technology, a number of ligand-bound ß$_2$AR crystal structures have been elucidated[6], providing more atomic details of various binding modes of agonists, antagonists and inverse agonists. In this study, we selected four representative molecules from each class of compounds and investigated their impacts on ß$_2$AR through 12 x 100 ns molecular dynamics (MD) simulations[7]. From the trajectories, we generated fingerprints based on the protein-ligand interaction propensity. Among the 16 identified important residues in the binding pocket, D113$^{3.32}$ and N312$^{7.39}$ are essential for all the ligands. Furthermore, the agonistic property of a ligand is mainly attributed to its polar interactions with TM5, whilst an antagonist or inverse agonist stabilizes the receptor via the hydrophobic interactions with TM5 and TM6. Our findings provide insightful prospective into GPCR targeted drug discoveries.



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Junction Control: Modulating Conductance Channel and Length Dependence on Molecular Level

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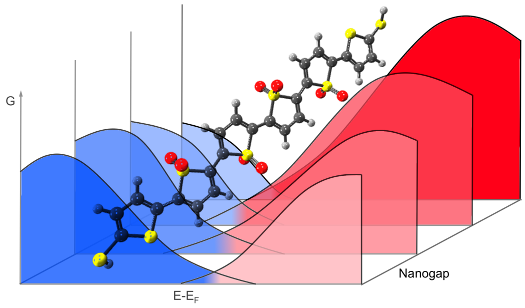
Single molecule junctions (SMJs) are unimolecular electronic devices that consist of a (organic) molecule bridging the gap between two conducting electrodes (typically gold).[1] SMJs represent a powerful tool for studying the intimate details of interface phenomena, electron and heat transport through molecules, their reactions[2] and interactions with external electromagnetic fields and mechanical forces. As components of electronic circuits, they allow ultimate downscaling and switching capabilities.[3]



Our research is aimed at gaining a deeper insight into the role of molecular structure in the SMJ in silico. We employ accurate conductance simulations using NEGF+DFT approach[4] on one hand and a multitude of physical-organic molecular descriptors on the other.[5] In this contribution, we illustrate how the interplay between the molecular length and the anchoring group can modulate the junction's conductivity channel. Our results reveal that the chemical nature of the linker groups and substituents within the molecular core, as well as the length and extent of conjugation in it can trigger change from p- to n-type conductivity and supress the decay in conductivity with increasing nanogap.

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Multiscale Analysis for Field-Effect Penetration through 2D Materials

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Gate-tunable two-dimensional (2D) materials-based quantum capacitors (QCs) and van der Waals heterostructures involves tuning transport or optoelectronic characteristics by the field effect. Recent studies have attributed the observed gate-tunable characteristics to the change of Fermi energy in the first 2D layer adjacent to the dielectrics, while the penetration of the field effect through the one-molecule-thick material is often ignored or over-simplified. We present a multiscale analysis to model penetration of the field effect through graphene in a metal-oxide-graphene-semiconductor (MOGS) QC, including quantifying the degree of “transparency” for graphene two-dimensional electron gas (2DEG) to an electric displacement field. We find that the space charge density in the semiconductor layer can be modulated by gating in a nonlinear manner, forming an accumulation or inversion layer at the semiconductor / graphene interface. The degree of transparency is determined by the combined effect of graphene quantum capacitance and the semiconductor capacitance, which allows us to predict the ranking for a variety of monolayer 2D materials according to their transparency to an electric displacement field as follows: graphene › silicene › germanene › WS_2 › WTe_2 › WSe_2 › MoS_2 › $MoSe_2$ › $MoTe_2$, when the majority carriers are electrons. Our findings reveal a general picture of operation modes and design rules for the 2D-materials-based QCs.

Low-Lying ππ* States of Heteroaromatic Molecules: A Challenge for Excited State Methods

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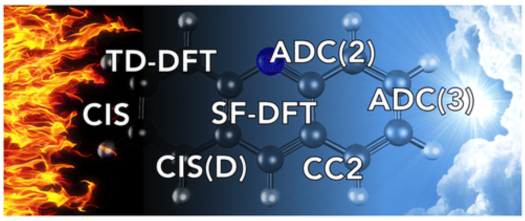
The description of low-lying ππ* states of linear acenes by standard electronic structure methods is known to be challenging.[1] Here, we broaden the framework of this problem by considering a set of fused heteroaromatic rings and demonstrate that standard electronic structure methods do not provide a balanced description of the two (typically) lowest singlet state (La and Lb) excitations.[2] While the Lb state is highly sensitive to correlation effects, La suffers from the same drawbacks as charge transfer excitations. We show that the comparison between CIS/CIS(D) can serve as a diagnostic for detecting the two problematic excited states. Standard TD-DFT and even its spin-flip variant lead to inaccurate excitation energies and interstate gaps, with only a double hybrid functional performing somewhat better. The complication inherent to a balanced description of these states is so important that even CC2 and ADC(2) do not necessarily match the ADC(3) reference.



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DORI on the move

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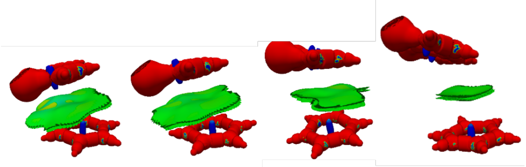
Scalar fields, which detect regions with localized electrons (e.g., ELF, LOL) or with significant density overlap give an intuitive representation of quantum electronic structures.[1] As an example, the Density Overlap Region Indicator (DORI),[2] a function recently introduced in our laboratory,reveals simultaneously different types of bonding and non-covalent interactions. Yet, these functions are generally visualized for static situations and at 0 Kelvin. Here, we analyse the benefit of exploring DORI with standard or enhanced sampling[3] ab initio molecular dynamic trajectories. We investigate systems featuring fluctuating π-stacking motifs, hydrogen bond networks and π-conductivity and compare the static and dynamic pictures.



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Mechanistic Study of Denitrification Reaction in Truncated Hemoglobin using Adiabatic Reactive Molecular Dynamics

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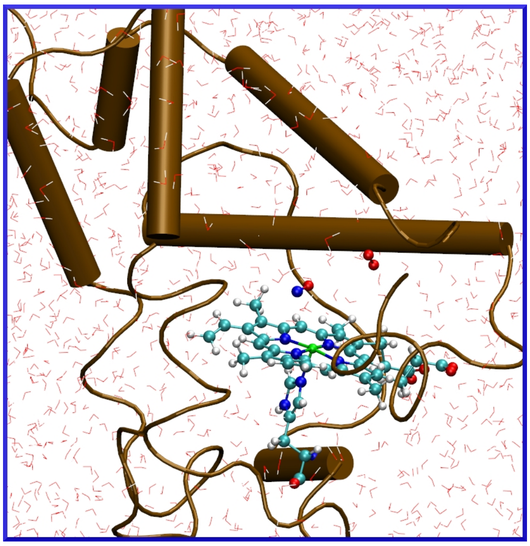
[1]University of Basel

Proteins such as truncated hemoglobin (trhbN) binds oxygen cooperatively with very high affinity and a slow dissociation rate. Along with oxygen molecule, it also binds other molecules like NO, CO etc. Understanding the kinetics of binding of nitric oxide (NO) to the oxygenated hemoglobin (trHbN) gains increased interest as it plays an important role in bacterial detoxification and nitrosative stress[1,2]. Many studies have been carried out on trHbN but it is not clear how the denitrification reaction takes place in trHbN (reaction sequence shown bellow). Mechanistic details of binding of NO to the oxygenated trHbN was studied here using force field based multi surface adiabatic reactive molecular dynamics (MS-ARMD) as implemented in CHARMM[3]. Although *ab initio* MD or hybrid QM/MM can be used to study such process. However, they do not allow to sample the phase space exhaustively because of high computational cost. On the other hand, we successfully parametrized the force field for the above process with sufficient accuracy, which allow to exhaustively sample the phase space and in turn offers meaning full energetics and rate constant for the NO replacement reaction (Expt. rate constant 4.36 X 10^7 $M^{-1}S^{-1}$)[4,5]

$\mathbf{Fe^{II}NO + O_2 \rightarrow Fe^{II}O_2 + NO \rightarrow Fe^{III} + NO_3^-}$



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Modelling the π conjugation length in aromatic antenna : A simple predictive tool for the synthesis of functional material

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[1]University of Geneva

The ability of predicting the photophysical properties of potential luminescent material presents a great interest for synthetic chemists. In this perspective, we report [1] a re-examination of the model by Yamaguchi *et al* [2] that relates the fluorescence quantum yield to the charge separation upon electronic excitation. To verify the applicability of the proposed model, we chose a series of substituted terpyridines the photophysical properties of which were recently reported [3]. Terpyridine derivatives are attractive aromatic antenna since the effect of substituents on the photophysical properties as well as the fluorescence quenching upon metal complexation can be very large. The charge separation upon excitation is modelled with the help of two different quantities, namely the change in dipole moment and the exciton size [4]. Both reflect charge separation and show S-shape dependence on the measured fluorescence quantum yield, hence verifying the proposed model.

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Computational Investigation and Design of Cobalt Aqua Complexes for Homogeneous Water Oxidation

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[1]University of Zurich

We study the water oxidation mechanism of the cobalt aqua complex $[Co(H_2O)_6]^{2+}$ by means of density functional theory. Assuming a water-nucleophilic-attack mechanism, we investigate how the oxidation and spin states of the metal center change during the catalytic cycle. Additionally, we explore how the substitution of one water ligand by a halide, pyridine or a derivative thereof influences the thermodynamics of the water oxidation process. We show in detail how different substituents alter the stability and symmetry of the frontier orbitals and correlate these findings by comparing the computed free energy profiles with the one of an “ideal” catalyst. This allows to identify the most promising cobalt aqua complex for water oxidation and gives an indication how to further improve the thermodynamics of this catalyst.

M. Schilling, G. R. Patzke, J. Hutter, S. Luber J. Phys. Chem. C, **2016**, 120 (15), pp 7966–7975

Theoretical Investigation on the Nature of Xe Migration in Truncated Hemoglobin N

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In heme proteins, the efficient transfer of O_2, NO and CO to the active site is achieved via ligand migration networks. These networks contain cavities (pockets), where the ligand successively localizes as it diffuses through the protein. It has also been suggested that migration networks can detain O_2, NO and CO in their pockets for storage or detoxification purposes [1]-[3]. A thorough understanding of the nature of ligand migration is essential for better assessing the function and importance of these networks. Under this scope, the migration of Xe in truncated hemoglobin N (TrHbN) of *Mycobacterium Tuberculosis* was investigated using classical molecular dynamics (MD) simulations. It was found that Xe transitions between different pockets and intra-pocket relaxation occur on similar time scales (10 ps and 20 ps respectively), consistent with the low free energy barriers for NO/O_2 migration in TrHbN (1-2 kcal/mol) that have been previously reported [4]-[6]. In addition, the comparison of transition probabilities showed that Xe migration in TrHbN is not a Markovian process. Further analysis revealed that memory effects should be attributed to the protein’s rearrangement as Xe moves through it. Finally, the very frequent observation of back and forth transitions supports the suggestion that TrHbN can detain NO molecules in its pockets, prior to their subsequent detoxification in its active site [3].

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Replacing Porphyrins with Pyrphyrins: Adsorption and Metalation on Au(111)

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Pyrphyrin, a tetradentate bipyridine based macrocycle, represents an interesting but widely unexplored molecular ligand. An alternative to pyrrole-based macrocycles, which are known as porphyrins, pyrphyrins have the ring systems consisting of four pyridines as donors. A high stability of pyrphyrin and its corresponding complexes is suggested. Metal complexes based on pyrphyrin ligands have recently shown promise as water reduction catalysts in homogeneous photochemical water splitting reactions [1]. In another study, it is shown that Co-ligated pyrphyrin on TiO_2 can act as a molecular photosensitizer[2].

In this study, we examined the adsorption and metalation of pyrphyrin on a single crystalline surface by means of low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), density functional theory (DFT) and Metadynamics (MTD) simulations. Pyrphyrin coverages of approximately one monolayer and less were obtained by sublimation of the molecules on a Au(111) surface at room temperature. Cobalt deposition and subsequent annealing led to the formation of Co-ligated pyrphyrin (CoPyr) molecules. DFT calculations show that the molecules are physisorbed, however preferred adsorption sites are identified where Co and N are optimally coordinated to reconstructed surface Au atoms, see Figure 1. The effect of herringbone reconstruction of the surface on CoPyr adsorption is also clarified by DFT [3].

Possible metalation steps are identified using monolayer covered surface by MTD simulations. Results suggest that metalation of pyrphyrin from the top is a downhill process, whereas, since Co adatoms on the Au(111) surface form also a stable state, the process from underneath needs to be activated, since it occurs over an energy barrier. Several intermediate states of the metalation reaction were observed and the reaction steps for the Co metalation of pyrphyrin molecules on Au(111) were established by combination of experiment and theory [4].

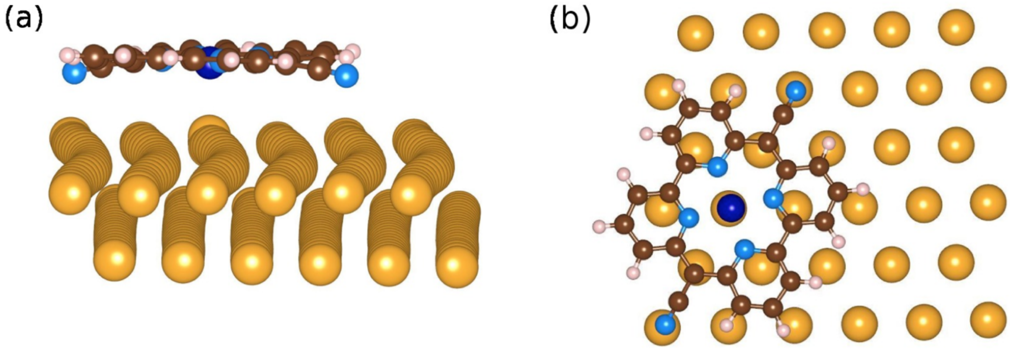

Figure 1. Side view (a) and top view (b) of optimized structure of CoPyr on reconstructed Au(111) surface. Color code: dark blue:Co, blue: N, brown:C, pink: H, and yellow: Au.

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Exploiting A Tactic for Tuning the Plasmonic Properties of Thiophene Derivatives

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The light absorption energy and strength of a series of thiophene-derivatives can be tuned via structural and chemical manipulations. We here provide means to alter and control the plasmonic properties [1] of these heteroaromatic units. These promising results offer an appealing strategy for designing molecules for applications in which light absorptions/emissions are involved, e.g. organic dye-sensitized solar cell and light emitting diodes. With the goal of enhancing solar light capture, the potential of the approach is demonstrated through identifying dyes with improved light absorption strength and coverage [2]. The absorption spectra of the proposed chemical motifs are computed using linear response time-dependent DFT (TDDFT) validated against high-level algebraic diagrammatic construction in third order (ADC(3)) computations.

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Improving the exploration of free energy landscapes at the electronic structure levels

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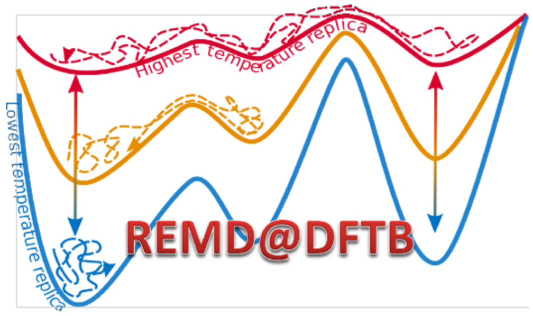
Recently, our laboratory exploited the DFTB electronic structure framework and combines it with replica exchange molecular dynamics (REMD). Whereas, neither DFTB nor REMD is new, the potential of performing replica exchange molecular dynamics at an electronic structure level (REMD@DFTB) was successfully demonstrated through revisiting several computational organic chemistry problems and discovering many new facets of their chemistry that remain hidden because conformational entropy is not generally considered and the phase space is not explored enough.[1]We now discuss a more general implementation of replica exchange relying upon bias potentials. The Hamiltonian[2] REMD variant will serve to overcome the limitation associated with the use of high temperatures needed in the more standard enhanced sampling scheme. Within this context, we will also show that the decoupling of the DFTB energy and the dispersion energy correction can serve to accelerate the sampling. These extensions of REMD@DFTB are tested on both chemical reactions and free energy landscape of molecular complexes.



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A potential model for molecular dynamics simulations in organic - inorganic halide perovskites

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The dynamical properties of organic - inorganic halide perovskites at finite temperature can be examined via first-principles molecular dynamics simulations. However the accessible size and time windows of this approach are very limited. Recently, an interatomic model potential for molecular dynamics was derived from first-principles and used to study the properties of methylammonium lead halide at zero and finite temperature.[1] However this model is not taking polarization effects into account. In case of halide perovskites the anions have a large polarizability and in addition they are surrounded by a polarizable medium, the perovskite cage. A reliable and higly-accurate force-field for these materials could be used to tackle several open issues. For instance, due to the liquid processing of hybrid organic-inorganic lead halide perovskites, there is only limited control of the crystal phase that is formed. Experiments proved the presence of multiple phases (cubic, tetragonal, orthorhombic).[2] To predict reliably the structure of a material a method that is able to provide an accurate potential energy surface, as well as an algorithm which can find the low-energy local minima on this potential energy surface are required. In the present work a novel polarizable model potential is used as the force field of molecular dynamics simulations to describe the potential energy surface, accurately.

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Quantum Molecular Dynamics and Cryogenic Spectroscopy Determine the Structure of Cyclic Intermediates Involved in Peptide Sequence Scrambling

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Collision-induced dissociation CID is a key technique used in mass spectrometry based peptide sequencing. Collisionally activated peptides undergo statistical dissociation, forming a series of backbone fragment ions that reflect their amino acid (AA) sequence. Some of these fragments may experience a “head-to-tail” cyclization, which after proton migration, can lead to the cyclic structure opening in a different place than the initially formed bond. This process leads to AA sequence scrambling that may hinder sequencing of the initial peptide.

In this presentation we report our work combining state-of-the-art theoretical and experimental techniques to identify the precise structures of key intermediates in the scrambling process. We combine simulated annealing ab initio molecular dynamics (SA-AIMD) with IR-UV (infra red – ultra violet) double-resonance spectroscopy in a cryogenic ion trap to reveal detailed structural information of b6 fragment ions of the biomolecule FAGFAG, *b6*-FAGFAG, produced by CID. [1,2]

The most stable *b6*-FAGFAG fragments show intriguing symmetric cyclic structures in which the proton is situated on a C2 symmetry axis and forms exceptionally short H-bonds (1.20A) with two backbone oxygens. See figure 1. Other non-symmetric cyclic structures also exist, one of which is protonated on the amide nitrogen, where ring opening is likely to occur.

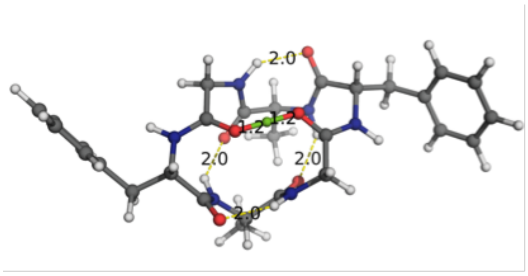

Figure 1- Symmetric cyclic *b*6-FAGFAG.

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Rigorous approach to the cellularization of the Herman–Kluk semiclassical propagator

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The Initial Value Representation of the Herman--Kluk propagator (HK-IVR) method is a well-established semiclassical approximation to the quantum evolution operator based on classical trajectories, which includes quantum effects such as tunneling, coherence and zero-point energy into the dynamics. However, the application of the HK-IVR approach to large scale systems has been very limited due to the oscillatory nature of the integrand involved which results in unfeasible number of classical trajectories required to obtained converged results. A common way of dealing with this problem is based on application of the Filinov filtering(cellularization) technique to smooth out the oscillatory behavior of the integrand.

Here we present a novel rigorous cellularization scheme employing the inverse Weierstrass transform and optimal scaling of the cell size with the number of cells. The main advantage of the new methodology is that the size of the sampling weight for the cell centers correlates with the size of cells, allowing for effective sampling of the phase space covered by the initial state of the system. It can be shown analytically that the presented approach, unlike the standard Filinov filtering, converges to the original HK-IVR result in the limit of infinite number of trajectories. We illustrate the performance of the new methodology by calculating autocorrelation functions and spectra of several model systems.

Quantum chemistry meets kinetic modeling: Predicting the evolution of chemical processes occuring on multiple time scales

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Systematic explorations of high-dimensional energy surfaces are essential to detect thermodynamically relevant chemical products in complex reaction networks [1]. However, chemical species observed in the course of a synthetic process and with it the pathways leading to a desired product can only be explained in a time-resolved framework. The development of kinetic modeling methods has been considerably promoted by the fields of reaction engineering (e.g., computational singular perturbation [2]) and molecular dynamics (e.g., Markov state models [3]). The approaches are quite complementary, yet they focus both on the occurence of the multiple time scale problem, which is a rule rather than an exception regarding physical processes. In chemical mechanisms, for instance, we encounter fast conformational changes versus slow associative reactions. So far, special numeric solvers for stiff differential equations are necessary to study the evolution of such systems. Here, we present a new approach [4] based on linear algebra, which allows us to model the kinetics of complex reaction networks extracted from electronic structure calculations. Our *Markovian Network Analysis* has been developed to understand why a reaction leads to certain products and how to control the probability of certain mechanistic pathways.

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Accelerating equilibrium isotope effect calculations by stochastic integration with respect to mass[1]

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We accelerate calculations of equilibrium isotope effects with a novel Monte Carlo procedure that involves changing particle masses stochastically during the calculation. We demonstrate that if combined with thermodynamic integration with respect to mass[2,3] this procedure eliminates the integration error in a manner similar to the lambda dynamics,[4,5] while if combined with the so-called direct estimators,[6] it decreases the statistical error of the calculation. The method is tested on a harmonic model system and on deuterated species of methane. For the latter system we also show how the new Monte Carlo procedure allows to calculate all equilibrium isotope effects of the form $CH_{4-x}D_x/CH_4$ during a single simulation with a reasonable statistical error.

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Computational Rationalization of the selectivity of Ru(II) and Os(II) anticancer agents in HIS/HER binding to the histone components of the Nucleosome Core Particle

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Cancer is a widespread disease in developed countries. Over the last twenty years, metal-based antitumor drugs have emerged as effective chemotherapeutic agents.[1] Indeed, the success of platinum complexes (i.e., cisplatin and carboplatin) paved the way for exploiting the unique physico-chemical properties of organometallic complexes in medicinal chemistry.[2] The resistance and the severe side effects of cisplatin, prompted for the development of alternative metal-based anticancer agents, such as ruthenium(II) and osmium(II) based compounds that exhibit low toxicity and selective activity against specific cancer cells types.[3,4] In collaboration with the group of Prof. P. J. Dyson at EPFL and Prof. C. Davey at Nanyang Technical University, we are working on the design of novel potential Ru(II) and Os(II) anticancer drugs acting at the Nucleosome Core particle (NCP) level.[5] X-ray crysrallographic structures show that these compounds bind to the histone components of the NCP, which is the basic repeating unit of chromatin. By looking at the binding of a series of Ru(II) and Os(II) compounds in crystals of the NCP, we found that these compounds bind either exclusively to His side chains (i.e., HIS sites) or to highly electronegative regions (i.e., HER sites), which are characterized by the presence of at least one negatively charged side chain (Glu/Asp). Understanding and determining the binding selectivity of Ru(II) and Os(II) compounds for either HIS or HER sites of the NCP is of great interest to rationalize the design of future potential anticancer drugs. Here, classical molecular dyanmics (MD) and hybrid qunantum mechanics/molecular mechanics (QM/MM) simulations are used to unravel the selection mechanism at molecular level. Thermodynamic Integration (TI) is used to determine the binding free energies, thus allowing the discrimination of the HIS vs. HER preferred binding site. Overall, our computational and experimental efforts could provide novel insights for the discovery of new anticancer drugs targeting the NCP.

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Targeting Multiple Reactions by Protein Engineering: Hydration of CO_2 and Tetrazole Formation

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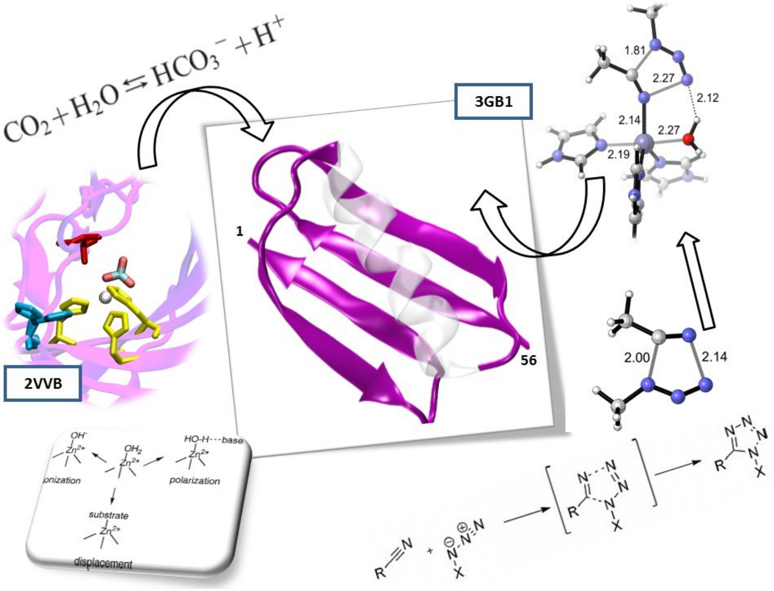
Designing proteins capable of catalysing chemically and biologically important reactions is of considerable interest in view of promising applications in fields, such as biomedicine and materials science. In this project, we target hydration of CO_2 to mimic Nature's enzyme human carbonic anhydrase II[1] and a (3 + 2) cyloaddition reaction to form tetrazoles[2,3] in the presence of a zinc binding site as Lewis acid. To design an efficient enzyme, the 56-residue B1 domain of streptococcal protein G (GB1)which is well-known for its unusual thermostability was used as a starting point.[4,5] Subsequently, the scaffold was (re)-engineered through a series of mutations to introduce the zinc active site while retaining the original fold. Three novel zinc binding sites were created successfully by computational design. The structural and catalytic properties were characterized by performing classical molecular dynamics (MD), quantum mechanics/molecular mechanics (QM/MM) simulations in combination with metadynamics to enhance sampling. Computational evidence suggests a promising CO_2 and acetonitrile binding site on the same variant. Besides, theoretical predictions revealed that the use of zinc fingers may lead to a more facile cycloaddition.[6] To validate the computational findings, wild-type protein and mutants are expressed and purified. Structural characterizations and enzymatic assays are currently ongoing.



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DFT studies on a well-defined Re-oxo complex grafted on Al-modified silica active in olefin metathesis

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Studies on well-defined rhenium complexes grafted on supports using surface organometallic chemistry (SOMC) provide useful information to obtain molecular understanding of the industrial analogues.[1] Recently, catalytic activity in olefin metathesis was reported for a rhenium catalyst grafted on silica having aluminum sites in close proximity.[2] Nevertheless, the role of how such Lewis acid centers can activate this catalyst to undergo metathesis is still not fully understood.

In this contribution, we present a computational study of the rhenium oxo complex on the surface of silica-alumina active in olefin metathesis. Firstly, the chemical shift and quadrupolar constant of Al sites on the surface is calculated with and without the presence of the Re catalyst in order to determine the nature of the active site by comparison with the experimental signals in 27Al NMR. Afterwards, the reactivity of this catalyst in olefin metathesis was evaluated by means of DFT calculations. We explored the role of the Lewis acidic Al sites of the surface, showing how activation of such catalyst can occur, which then enables the initiation process for metathesis. Finding out the role of Lewis acid in metathesis, might help to improve the understanding of industrial catalysts.

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Exploration of Complex Chemical Reaction Mechanisms

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For the systematic exploration of the chemical space for a specific purpose, the identification of relevant intermediates and products in complex reaction networks is decisive. Currently, we are developing three complementary approaches to achieve this goal.

In our heuristics-guided approach, molecular structures are generated automatically based on rules derived from conceptual quantum mechanics. Recently, we showed at the example of Schrock's nitrogen fixation catalyst that heuristic guidance combined with electronic structure calculations allows for the identification of new reaction paths plausible at room temperature [1].

In our inverse approach [2], molecular structures are generated based on the concept of gradient-driven molecule construction [3]. We have fully automatized this framework as shown for the example of carbon dioxide activation to rationalize a known CO2-binding complex [4].

In our interactive approach, molecular structures are generated interactively by real-time manipulation of the studied system with a computer mouse or a haptic device [5-8]. We showed that molecules with more than hundred atoms can be studied in real time with quantum chemical methods [7], which significantly speeds up the exploration process.

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Integral evalution of contracted solid harmonic Gaussian functions

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[1]University of Zurich, [2]University of Copenhagen

An integral scheme based on solid harmonic Gaussians is introduced for the efficient calculation of two-center integrals and their derivatives. The integral expressions are derived using Hobson's theorem and the differentiation rules of the spherical tensor gradient operator. Our integral scheme is applicable for different operators $O(|\mathbf{r}_1\text{-}\mathbf{r}_{2|)}$. Furthermore, integral expressions are derived for overlap integrals where two functions are located at center A and B . The latter integrals are important for local resolution of identity approaches that employ an overlap metric. The method presented herein is superior to Cartesian Gaussian-based methods. This is especially true for deeply contracted basis sets where a speed-up factor of at least an order of magnitude is observed.

Second Generation Car-Parrinello MD: Application to supported nanostructures

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A growing interest is devoted nowadays to nanostructured quasi two dimensional systems formed at the surface of crystalline solids. In particular, graphene or hexagonal boron nitride (h-BN) supported on transition metals, like Rh, Ru, Ni, and Cu attract an incresing interest. Despite the important effort made in their synthesis and characterization, the atomistic mechanisms that play a key role in self-assembly and manipulation of such films are still a matter of debate, since they cannot be resolved experimentally. To this end, density functional theory based atomistic simulations have become key tools to support the experimental investigation. Atomistic modelling of nanostructures can give valuable insight on their properties and their dynamical behavior. However, the simulation of the above mentioned systems requires rather large scale slab models to accommodate the supercell of the reconstructed monolayers and the correct pattern of the adsorbates' assemblies. The metallic substrate, in turn, makes the computational effort even more demanding, due to the slow converging wavefunctions. These aspects establish severe limitations on the time scale of the simulations affordable with standard ab-initio methods. A possible route to overcome these limitations is to employ a recently developed Car-Parrinello-like approach to Born-Oppenheimer MD. In the spirit of the Car-Parrinello scheme the wavefunctions are not self-consistently optimized during the dynamics. However, in contrast to CP, large integration time steps can be used in the simulation. This scheme leads to a slightly dissipative dynamics but it has been shown that within a Langevin thermostat it is possible to compensate for this dissipation and obtain a correct canonical sampling. We report on the application of this MD scheme to h-BN on Rh(111), which we simulated at different temperatures to investigate its thermal stability and the possible nanomesh migration mechanisms.

Frozen-density embedding theory with average solvent charge densities from explicit atomistic simulations

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Besides molecular electron densities obtained within the Born–Oppenheimer approximation ($\rho_B(r)$) to represent the environment, the ensemble averaged density ($\rho_B(r)$) is also admissible in frozen-density embedding theory (FDET) [Wesolowski, *Phys. Rev. A*, 2008,**77**, 11444]. This makes it possible to introduce an approximation in the evaluation of the solvent effect on quantum mechanical observables consisting of replacing the ensemble averaged observable by the observable evaluated at ensemble averaged $\rho_B(r)$. This approximation is shown to affect negligibly the solvatochromic shift in the absorption of hydrated acetone. The proposed model provides a continuum type of representation of the solvent, which reflects nevertheless its local structure, and it is to be applied as a post-simulation analysis tool inatomistic level simulations.

Influence of empirical van der Waals dispersion correction on the DFT description of alkaline-earth fluorohalides

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Alkaline-earth fluorohalides *MFX* are receiving much 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 [1]. 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. Due to the layered nature of their structures and especially the presence of the stacking $−X^{-}−X^{-}−$ anionic layers, 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 [2]. This deficiency of standard approximate functionals could indeed explain the overestimation of the *c* parameter reported for PbFI [3]. To investigate this question, periodic DFT calculations have been performed to study the crystal structures, the vibrational frequencies, the bulk modulus (B_0) and its derivatives (B_0'), and the mode Grüneisen parameters of the *MFX* compounds (*M* = Ca, Sr, Ba, Pb and *X* = Cl, Br, I). The PBE and B3LYP functionals [4] and their DFT-D2 dispersion-corrected variants [5] were employed. For these layered ionic compounds, it proved necessary to modify the semi-empirical D2 dispersion correction.

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Spin crossover in mixed [Co(bpy)$_3$][Li$_x$Na$_{1-x}$Cr(ox)$_3$] crystals

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The electronic ground state of hexacoordinated d^7 Co(II) complexes is either a low-spin (LS) state of octahedral ligand-field $^2E_g(t_{2g}^6e_g^1)$ state parentage, or a high-spin (HS) state of octahedral ligand-field $^4T_{1g}(t_{2g}^5e_g^2)$ state parentage. Spin crossover (SCO) is observed for Co(II) complexes with a LS ground state and a close-lying HS state: it consists in the entropy-driven thermal population of the metastable HS state.

[Co(bpy)$_3$]$^{2+}$ (bpy = 2,2’-bipyridine) is usually a HS species, as in the polymeric three-dimentional compound [Co(bpy)$_3$][NaCr(ox)$_3$] (ox = $C_2O_4^{2-}$), where it occupies the cavities formed by the trisoxalate network [1]. Upon the substitution of Na$^+$ by the smaller Li$^+$ ion, there is a decrease of the volume available to [Co(bpy)$_3$]$^{2+}$, which causes [Co(bpy)$_3$][LiCr(ox)$_3$] to exhibit SCO [2]. The influence of the Na$^+$-Li$^+$ substitution can be rationalized in terms of an increase of the chemical pressure experienced by the complex, which destabilizes the HS state of larger molecular volume with regard to the LS state [3].

In this poster we report the periodic DFT study of the magnetic behavior of the [Co(bpy)$_3$][Na$_{1-x}$Li$_x$Cr(ox)$_3$] mixed crystals as a function of their chemical composition and also of pressure. The equivalence between chemical and physical pressure will be discussed.

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Computational Study of the Quantum Dynamics of Tunneling and Electroweak Parity Violation in 1,2-dithiine

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Measuring the parity-violating energy difference $\Delta_{\mathrm{pv}}E$ between enantiomers of chiral molecules is one of the frontiers of highest resolution molecular spectroscopy and a considerable challenge, which has not been met with success so far [1-4]. Over the last decades, much progress has been made in the accurate theoretical description of molecular parity violation [5-7], its possible implications for the origin of molecular chirality and biomolecular homochirality, and its role in the stereomutation dynamics of chiral molecules [1-4]. Accurate theoretical predictions of molecular parity violation importantly assist in a search for the most suitable molecular system. Moreover, tunneling must be studied for candidate molecules, as one must have $\Delta_{\mathrm{pv}}E \gg \Delta E_{\pm}$ (the tunneling splitting).

We present calculations of the parity-violating potential and tunneling splittings for 1,2-dithiine (1,2-dithia-3,5-cyclohexadiene, $C_4H_4S_2$). Our computations utilized the quasi-adiabatic channel reaction path Hamiltonian method [8] and our coupled-cluster singles and doubles linear response (CCSD-LR) approach [7] to electroweak quantum chemistry. Our theoretical investigations predict that the parity violating energy difference in the ground state ($1.1\cdot10^{-11}$ (*hc*) cm^{-1}) is in principle measurable as it is much larger than the calculated tunneling splitting ($4\cdot10^{-25}$ (*hc*) cm^{-1}) for the symmetrical potential. With a planar transition state for stereomutation at about 2500 cm^{-1} tunneling splitting become appreciable above 2300 cm^{-1}. This makes levels of well-defined parity accessible to parity selection by available powerful infrared lasers and thus useful for one of the existing experimental approaches towards molecular parity violation [9]. We also demonstrated that the high resolution spectroscopic analysis needed for designing the parity violation experiment is becoming feasible for this molecule, thus we conclude that 1,2-dithiine is a promising candidate for detecting molecular parity violation, for which the basic experimental capabilities have been demonstrated in our laboratory [10]. If time permits , we shall present numerical investigations of certain fundamental mechanisms of the kinetics stereomutation processes including parity violation (see also [3] and references therein).

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As if They Were Transition Metal Compounds: the Amazing Electronic Structure and Reactivity of Hypervalent Iodine Reagents

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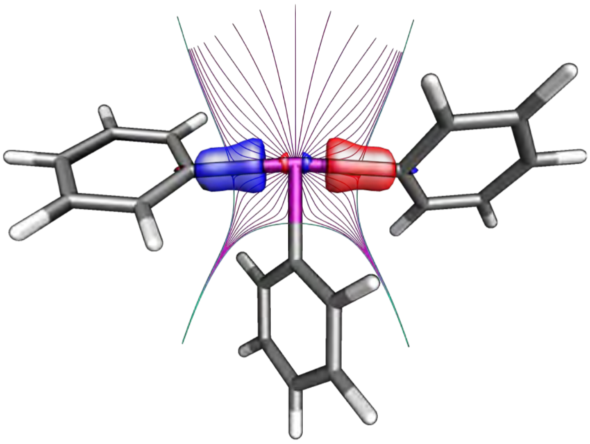
Hypervalent iodine compounds, in particular trivalent iodine species (I^3 iodanes), have become important reagents for the transfer of electrophilic substituents to arenes and other nucleophiles. However, relatively little is known about the mechanism of these transfers. Our research has shown that iodanes show a rich and often complex reactivity, reminiscent of the one of organometallics. Whereas many aspects of the reactivity of these compounds can be expressed by simple “back-of-the-envelope-rules”, the prediction of activation energies may require extended dynamics simulation as entropy contributions may determine the course of a reaction [1].

In this presentation, we explore fundamental aspects of the structure, the bonding and the reactivity of these compounds, whose electronic structure is usually described in terms of a 3-center-4-electron (3c-4e) bond model, involving the iodine central atom and its two trans-substituents; the third substituent is bound by a classical 2-center bond (see figure). Using the Domain Averaged Fermi Hole method, we are able to show which factors govern the formation of 3c-4e bonds, the heart of the iodane reactivity [2].



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CHIMIA

CHIMIA 2016, Volume 70
ISSN 0009-4293
www. chimia.ch

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Industrial Impact of Computational Chemistry and Materials Science

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The combination of powerful theoretical concepts, advanced computational software and today’s extraordinary computational capabilities opens unprecedented opportunities for the industrial application of computational chemistry and materials science. This talk will highlight current capabilities in the areas of advanced functional and structural materials as well as molecular systems. In the case of Li-ion batteries, *ab initio* calculations of electrochemical and structural properties have been successful in identifying candidates for low-strain cathode materials [1]. Simulations of Li diffusion in the solid state electrolyte $Li_{10}GeP_2S_{12}$ (LGPS) on crystalline *vs*. polycrystalline and amorphous structures have revealed the effect of structural changes on ion conductivity. Hydrogen embrittlement of metal alloys has its origins in chemical interactions, diffusion, and formation of metal hydrides. Detailed computational investigations of these phenomena have led to deeper insight as well as quantitative materials property data, which form the basis for systematic improvements of structural materials [2]. The systematic prediction of thermodynamic and thermochemical properties of molecular systems and fluids illustrates another aspect of the value of theoretical and computational approaches [3]. All of the above applications are facilitated by advanced capabilities implemented in the MedeA® software [4]. An assessment of the current state of the art and the challenges for future research will conclude this talk.

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Balancing London dispersion and the delocalization error with DFT functionals

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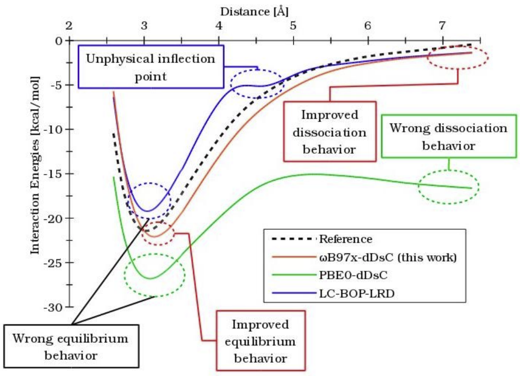
π-dimer radical cations are the simplest model systems for the computational description of charge carriers in organic electronic materials. In 2012, Steinmann and Corminboeuf introduced a benchmark database of π-dimer radical cations (Orel26rad) and demonstrated that none of the most widely-used dispersion corrected density functionals are able to achieve accurate binding energies together with a correct dissociative behavior [1]. In the same work the authors concluded that the challenging nature of these compounds originates from the inability of the functionals to properly account for London dispersion interactions and simultaneously avoid spurious charge delocalization [1]. Here, we propose the development and the optimization of a new dispersion corrected, range-separated hybrid density functional (ωB97x-dDsC), specifically conceived to achieve a balanced description of both delocalization error and long-range dispersion interactions. In particular, inspired by the overall satisfactory performance of ωB97x-D [2] on the Orel26rad dataset, we jointly-fitted the parameters that tune the damping function of the dDsC dispersion correction with the ones that regulate the core of the functional (ωB97x). ωB97x-dDsC was found able to provide highly accurate binding energies for the π-dimer radical cations not only around the equilibrium structure, but also in the asymptotic region towards the dissociation limit of the dimers. Our functional shows no significant deterioration of the description of other chemical properties when compared to existing functionals of the same family (e.g. ωB97x-D).



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A fast scheme for approximated Fock exchange potentials in plane wave implementations of Kohn-Sham Density Functional Theory

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With the considerable increase in sampling efficiency of Kohn-Sham density functional theory (KS-DFT) based first-principles molecular dynamics, the availability of more accurate but cost-effective exchange-correlation functionals has become of central importance to the field.

Plane wave/pseudo potential based first-principles molecular dynamics simulations are typically limited to the use of generalised-gradient approximation (GGA) exchange-correlation functionals. While hybrid functionals, which combine a certain amount of Hartree-Fock exchange with a (semi-)local KS-formalisms, are more accurate for a wide range of applications, the computational burden associated with the evaluation of the exact exchange integrals substantially limits the accessible time scales.
Here, we present a novel multi-grid scheme for the evaluation of Fock exchange integrals in a plane wave basis based on the combined direct/momentum space implementation used in the CPMD code, where orbital pair products are computed in real space and their corresponding Coulomb potential is obtained in momentum space. Direct and momentum space representations are linked via fast Fourier transforms (FFTs).
In the proposed scheme, high frequency components of the momentum space representation of orbital pair products are mapped onto analytic or numerical atom-centred auxiliary functions. These functions have a (pseudo) compact domain in direct space, which allows for an efficient calculation of their overlap with orbital pair products. The residual obtained from subtracting overlap-weighted auxiliary functions from the orbital pairs obtained on the standard FFT grid is mapped on a coarse, commensurate grid, and the associated Coulomb potential is calculated using the standard algorithm, but with a considerably lower plane wave cutoff. The Coulomb potential associated to the auxiliary functions is precomputed at the beginning of every SCF cycle on the full FFT grid. The residual Coulomb potential is interpolated onto the standard grid in direct space, and then added to the precomputed auxiliary Coulomb potential and, subsequently, the forces acting on the plane wave coefficients are determined via a further FFT.

This scheme allows for two Fourier transforms, which are usually calculated at the full density cutoff, to be carried out with a cutoff value typically 16-fold lower than the full density cutoff, corresponding to a four-fold increased grid spacing during the transforms of the residual. We will present speed ups compared to the standard algorithm and discuss issues linked to the choice of optimal auxiliary basis functions that guarantee sufficient smoothness of the residual function.

Quantitative Reaction Energies from an Automated Multi-Configurational Approach

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Quantum-chemical multi-configurational methods yield qualitatively correct wave functions for molecules with close-lying frontier orbitals. This class of methods, however, requires the manual selection of a subset of so-called active orbitals within which all possible configurations are considered. A poor choice of this subset leads to the exclusion of important configurations and therefore to wrong results. Quantitative data further requires perturbation theory to consider the dynamic electron correlation which makes the active orbital selection even more delicate. Currently, these active orbitals are selected based on empirical rules[1] or natural orbital occupation numbers of a precedent calculation.[2]

Here, we propose selection criteria that additionally take entropy based orbital entanglement measures into account.[3] We therefore exploit the ability of the density matrix renormalization group (DMRG) algorithm to approximate the entanglement information of a large number of active orbitals. The orbital selection protocol based on these criteria is fully automated and applied for the calculation of the heterolytic dissociation energy of four metallocenes $M(Cp)_2$, with M = V, Mn, Fe and Ni.[4]

The final energies are obtained from complete active space self-consistent field calculations with second-order perturbation theory. We compare the results of these multi-configurational calculations with those of a highly accurate coupled-cluster approach.

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FDE-ADC: Multiscale density embedding with an accurate wavefunction method.

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In the presence of an environment, excitation energies, properties and sometimes even reactivity of the target molecule may change drastically. Thus, including environmental effects into quantum chemical calculations either by implicit or explicit models is necessary for an adequate description of these systems. Frozen-Density Embedding Theory (FDET) [1;2] provides a formal framework in which the whole system is described by means of two independent quantities: the embedded wavefunction (interacting or not) and the density associated with the environment. The FDET approach can conveniently be combined with pertubative wavefunction methods, e.g. the Algebraic Diagrammatic Construction (ADC) scheme for the polarization propagator.

We present the new multiscale variant FDE-ADC [3] as a combination of FDET and ADC. The current implementation of FDE-ADC uses the Linearized FDET formalism [4], which in comparison to FDET, is significantly less expensive computationally and more importantly leads to self-consistency between the energy and embedding potential preserving simultaneously the orthogonality of the embedded wavefunctions for each electronic state.

Three molecular model systems were studied using two different FDE-ADC techniques in which the environment consisted of up to five water molecules. The molecular test systems were chosen to investigate molecule - environment interactions of varying strength from dispersion interaction up to multiple hydrogen bonds. The overall difference between the supermolecular ADC calculations and the FDE-ADC calculations in excitation energies is lower than 0.09 eV (max) and 0.032 eV in average. Also oscillator strengths are reproduced in good agreement with the supermolecular calculation. Initial results show that the FDE-ADC method is a promising approach for considering environmental effects on electronically excited states.

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Industrial modeling aspects of 1,3-dicarbonyl compounds

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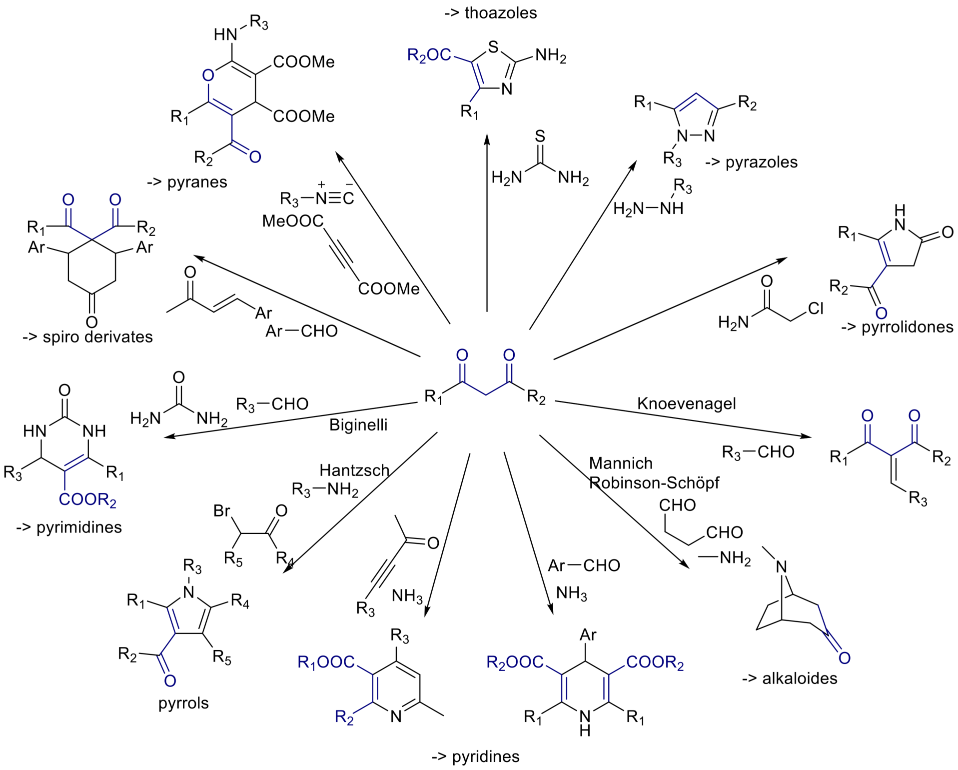
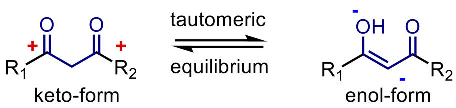
[1]Lonza AG

1,3-Dicarbonyl compounds are an important class of intermediates used in the pharma and agrochemical industry as well as in material sciences. As a manufacturer of over 100 intermediates of this class, LONZA Ltd provides a large assortment of these compounds to serve numerous industrial applications [1].



In order to provide a state-of-the-art service, a fundamental knowledge of this class of compounds is essential, which is obtained by measurements and increasingly, by molecular modeling.



In this talk, some aspects of the properties and the insights gained by *in silico* experiments of 1,3-dicarbonyl compounds are discussed.

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Is oxide hydrogenation equivalent to reduction?Fundamental differences between TiO_2 and Al_2O_3 from DFT

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TiO_2 and Al_2O_3 are universally employed supports in heterogeneous catalysis[1]. Depending on the support, however, there are sensible performance differences, the origin of which, at present, is poorly understood. In addition, reduced oxides, in particular TiO_2 , hold great promise as a support for efficient photocatalytic devices[2]. Hydrogen spillover from a supported metal cluster is widely employed in hydrogenation reactions and could also be adopted as a convenient way to introduce ”engineered disorder” in the titania structure[3], thus enhancing its light adsorption properties and electrical conductivity[4].

Here the interface reactivity and electronic structure of hydrogen-reduced TiO_2 and Al_2O_3 are investigated with GGA and hybrid DFT methods, including ab initio thermodynamics and Nudged Elastic Band (NEB) calculations. The calculations results are also compared and integrated to data obtained from a novel approach based on top-down nanofabrication and spatially-resolved in-situ X-ray absorption spectro-microscopy.

We demonstrate that, upon H_2 adsorption, two protons are bound to surface oxide anions, while two electrons are transferred to the oxide, creating electronic trap sites (formal Ti(III) centers) that strongly interact with the surface protons. Even though surface protons are highly mobile on the titania interface (particularly in presence of coadsorbed water molecules), the same can not be said for the Ti(III) centers, and thus the combined migration rate (e-/H+) of adsorbed H atoms is slower. As demonstrated in a previous study [5] defect concentration effects are also relevant: stronger H-oxide interaction is obtained at lower concentrations, as modelled with a realistic titania slab (~ 1000 atoms) and hybrid functionals.

The case of gamma-Al_2O_3 is instead quite different: instead of homolytic H_2 splitting and oxide reduction, on Al_2O_3 the hydrogen molecule split in a heterolytic manner, with formation of a proton, bound to a surface oxide anion, and of an hydride moiety, bound to particularly reactive surface Al tricoordinated (Al3c) site. On the other hand, the electronic structure of the oxide is only marginally altered, without formation of defect states in the oxide band gap. In addition, the mobility of the hydride moiety is limited, in particular in presence of coadsorbed water molecules. Hydrogen spillover from a Pt cluster to TiO2 has also been modelled, demonstrating that the spillover rate depends on the cluster hydrogen load and on the thickness of the oxide acceptor layer.

To conclude, even if hydrogen molecules can exothermically adsorb on both TiO_2 and Al_2O_3 surfaces, only in the first case oxide reduction, with formation of polaronic states, is achieved, while for alumina reducing species are confined at the interface, and demonstrate a lower mobility.

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Interatomic many-body representation improves molecular machine learning models

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We introduce an improved molecular representation based on expanding the total energy of the system in interatomic many-body interaction potentials (MBP) including bags of atoms (BoA), and bags of pairs (BoP), triplets (BoT), and quadruplets (BoQ) of atoms. Specific values correspond to the Universal Force Field[1]or other well established potentials. When considering only BoA+BoP, with BoA and BoP being the respective diagonal and off-diagonal elements in Coulomb matrix (CM), the resulting descriptor performs as well as BoB[2]. Inclusion of BoT and BoQ systematically improves the off-set as well as the learning rate. Out-of-sample prediction errors for G4MP2 quality properties of thousands of constitutional isomers decay systematically, reaching unprecedented chemical accuracy (~1 kcal/mol) for machine learning models trained on 5k molecules.

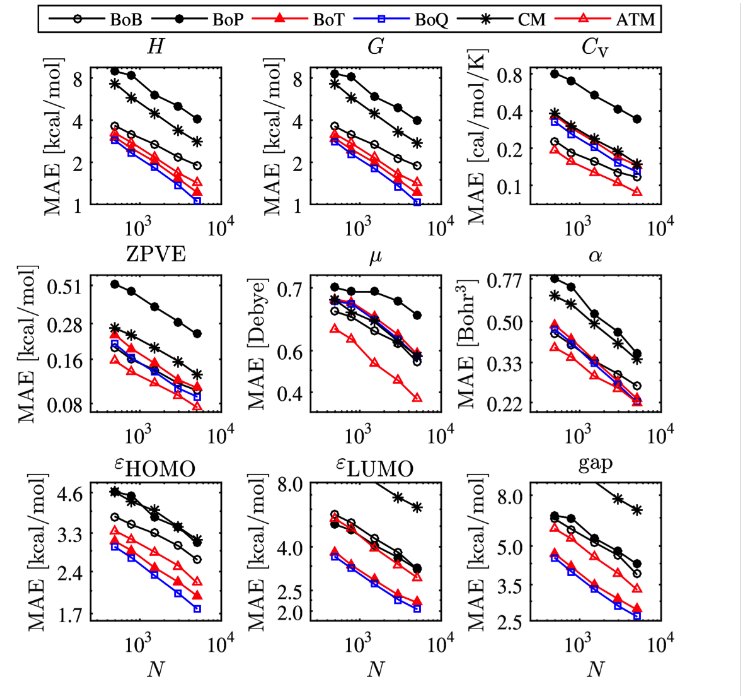

Figure 1. Single kernel[3] learning curves for *H*: enthalpy, *G*: free energy, *Cv*: heat capacity, ZPVE: zero point vibrational energy, *μ*: dipole moment, *α*: polarizability, ε_{HOMO}: HOMO energy, ε_{LUMO}: LUMO energy and HOMO-LUMO gap. Mean absolute errors are shown as a function of training set size for out of sample property predictions of the remainder of 6095 constitutional isomers of C7H10O2[4], drawnfrom GDB-17[5] database. MAEs are shown for 6 different representations: CM[2], BoB[2], BoB+ATM (Axilrod-Teller-Muto vdW potential)[6], BoP, BoT and BoQ.

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Reactive Molecular Dynamics and Infrared Spectra of Double Proton Transfers with Coupling Effects

Z.-H. Xu[1], K. Mackeprang[2], Z. Maroun[2], H. Kjaergaard[2], M. Meuwly[1]*

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For simulating double proton transfer (DPT) reactions of formic acid in dimeric forms, the previously developped Molecular Mechanics with Proton Transfer (MMPT) method has been further improved by introducing coupling effects which accurately provides an energetic description for the DPT reactions in atomistic simulations. From the experiments, the infrared spectra of formic acid dimer (FAD) and its deuterated isotopologues have been reported at the gas phase with low pressures by using spectral subtraction. And the broad OH-stretch spectral signatures (2600~3400 cm-1) agree well with previously recorded spectra. In order to align between the simulated and experimentally resultant spectral features in the proton transfer region, potential morphing was also carried out with the electronic structure calculations at the B3LYP and MP2 levels respectively. In this work, a barrier for DPT in FAD has been estimated as 5~7 kcal/mol which compares with a barrier of 7.9 kcal/mol from CCSD(T)/aug-cc-pVTZ calculations. Such a combination of experimental and computational techniques helps the barrier estimations for intramolecular proton transfer reactions, of which the reaction kinetics is not easy to be measured directly in experiments. And the further improvement of energetics of these reactive systems is also feasible and expected.

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On the ultrashort pulse approximation for the interaction of molecule with pulsed laser fields: Generalization of the Franck-Condon principle

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We explore several possible definitions of an “ultrashort laser pulse” and derive approximate geometric integrators for the nonadiabatic molecular quantum dynamics induced by interaction with such pulses. For a particular definition combined with the time-dependent perturbation theory, we are able to derive an analytical expression for the quantum evolution operator, which enormously speeds up numerical calculations. Our analytical formula can be understood as the generalization of the Franck-Condon principle to ultrashort pulses of arbitrary shapes. Finally, we show that in the limit of the pulse width going to zero, we recover the widely used and surprisingly accurate δ-pulse approximation.

The performance of the introduced approximations is illustrated using the three-state three-dimensional vibronic coupling model of pyrazine in which it is essential to go beyond the δ-pulse limit in order to describe the dynamics correctly.

Dry Reforming and Competitive Reactions on Ni, Pd and Pt metal Surfaces from DFT Calculations and Microkinetic Modeling Simulations

A. Comas-Vives[1], L. Foppa[1], M. Silaghi[1], K. Larmier[2]*

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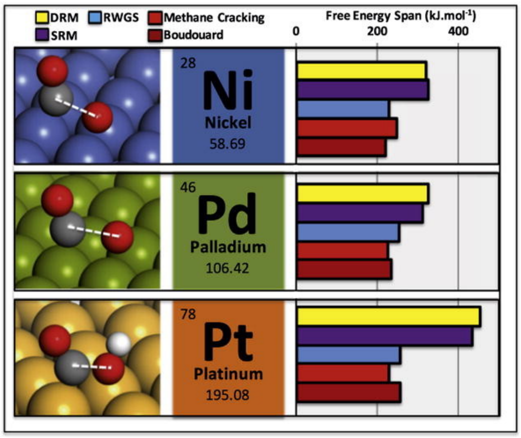
Dry (CO_2) reforming of methane converts CH_4 and CO_2 to syngas (CO and H_2), however, the high temperatures needed for the reaction and the occurrence of competitive reactions (especially coke formation) are factors that hinder their development. Herein, we provide a comparative mechanistic study of dry reforming reaction network at 700 °C on group 10 (Ni, Pd, Pt) (111) metal surfaces using periodic *ab initio* calculations and microkinetic modeling simulations.[1] While the CH_4 dissociation energy barrier is found to be metal independent, our calculations show that CO_2 dissociation is more energy-demanding following the trend Ni ‹ Pd ‹ Pt. As a consequence, the activation of CO_2 via C–O bond cleavage is less energy demanding than the CH_4 activation in the case of Ni, but not for Pd and Pt surfaces. All three metals share the same preferred dry reforming route via HCO∗ intermediate, but the overall energy span increases in the order Ni ≈ Pd ≪ Pt. Nevertheless, our microkinetic simulations suggest that only Ni (111) surface is significantly active in dry reforming, which is related to the balance between energy barriers of CH_4 and CO_2 activation processes. Another differences among these metals concern the carbon–carbon bond formation during coke production, which becomes less favorable from Ni to Pt, and the preferred reaction path for the reverse water gas shift reaction: via direct (Ni and Pd) or hydrogen-assisted (Pt) CO_2 dissociation. By comparing the reactivity of Ni, Pd and Pt surfaces, we highlight the important catalyst features needed for a good dry reforming performance in order to envisage more active and selective catalysts for this reaction.



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