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Molecular Energy and Electron Transfer

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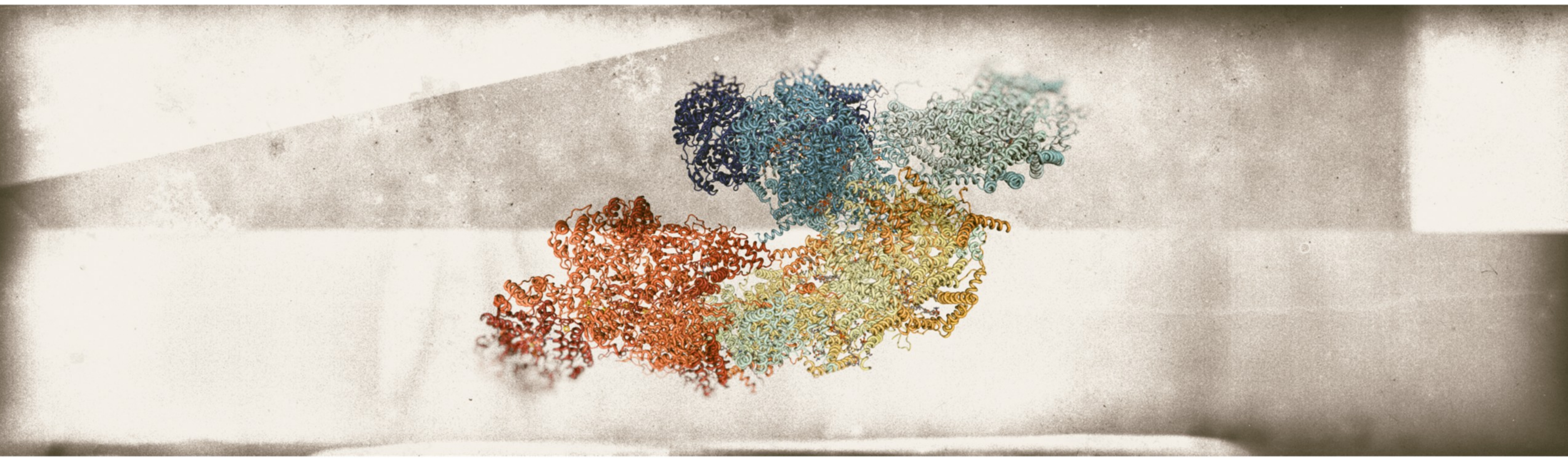

Book of Abstracts

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Theoretical Investigation of Glutinic Acid: Molecular Structure, Electronic and Vibrational Properties

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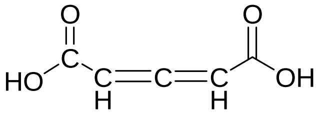
Fatty acids are a carboxylic acid with a long unbranched aliphatic tail (chain), which is either saturated or unsaturated. Fatty acids are a carboxylic acid with a long unbranched aliphatic tail (chain), which is either saturated or unsaturated. Moreover, the dienes in which two double bonds share a single carbon, sp-hybridized as in alkynes, are called 'Allenes' or 'Cumulenes' and these kinds of double bonds are named as 'Cumule double bonds'.

The first allenic dicarboxylic acid, called glutinic acid (**1**, named as 2,3-pentadienedioic acid, Scheme1) was isolated from leaf resin of Alnus glutinosa in 1908 by Hans [1]. Its structure (**1**) was confirmed in 1958 [2], and its absolute configuration was established in 1962 [3]. It has been used as a starting substrate for synthesizing natural allenes, heterocyclic prostanoids, alkaloids, nucleosides and other heterocyclic compounds [4].



(**1**)

Scheme 1. Glutinic acid (**1**)

Initially the theoretical study involves obtaining the optimized geometries of glutinic acid (**1**) at B3LYP/6-31+G(d,p), X3LYP/6-31+G(d,p), and MP2/6-31+G(d,p) levels with the help of Gaussian09 [5]. Then DFT quantum mechanical calculations (charge distribution, angles between bonds, bond lengths, theoretical IR and NMR spectra) were carried out at the corresponding levels. The complete vibrational assignments of wavenumbers have been made on the basis of potential energy distribution (PED). From this analysis, it is seen that the vibrational frequencies obtained from B3LYP method are in good agreement with the experiment, when compared to other methods used herein. Nonlinear optical properties and thermal properties are also calculated.

This work was partially supported by Balikesir University, The Center of Scientific Research Projects (Project Code: BAP-2016–151).

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Calculation of vibrationally resolved absorption spectra of acenes and pyrene

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Abstract

Generally, absorption spectra of molecules are simulated by computing the vertical electronic excitation energies and oscillator strengths based on the fully relaxed ground state structure.[1] This results in sharp peaks making a comparison with experiment that typically consists of broad bands challenging. The reason for the band broadening observed in experiment is related to solvent and vibrational effects implying also structural changes of the underlying molecular geometry, which is hard to model theoretically.[2, 3, 4]

In the present work we investigate benefits, challenges and limitations of the new approach suggested by Tapavica *et. al.*[5] by applying the latter to aromatic hydrocarbon molecules such as naphthalene, anthracene, pentacene and pyrene aiming at resolving their vibrational UV absorption as well as their emission fluorescence spectra. Three different possible inclusions of vibrational effects to the UV spectra are investigated and compared. First the displaced harmonic oscillator approximation (DHOA) has been tested, followed by the frequency-shifted displacement harmonic approximation (FS-DHOA). Finally a full Duschinsky formalism has been applied (DUSCH). All calculated vibrationally resolved spectra are analysed and compared to experiment.

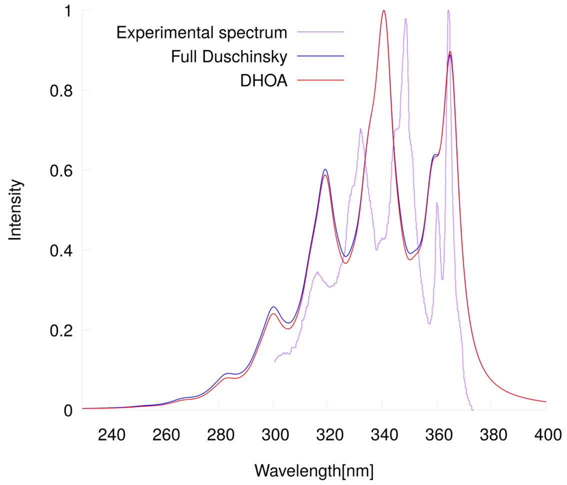

Figure 1: Simulated and experimental spectrum of the $1B_{2\mathrm{u}}$ state of anthracene. The 0-0 transition energy is shifted by -50.3 nm (-0.41 eV)

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DFT Benchmarking for the Correct Description of Spin States in Bioinorganic Centers. 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.

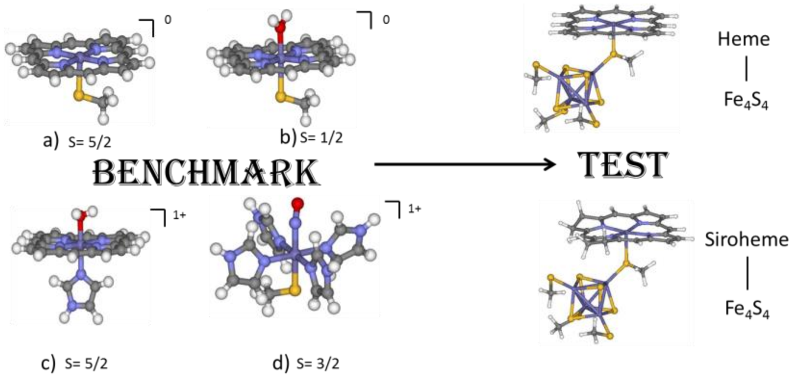

Fig.1. Left: Bioinorganic models derived from the active sites of the following proteins: ferric cytochrome P450 with a vacant distal position (a) and aqua-bound (b), ferric haemoglobin (c) and ferrou-nitrosyl Superoxide Reductase (d). Right: heme-[Fe_4S_4] and siroheme-[Fe_4S_4] systems

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 high-spin states, while pure functionals overestimates 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 give more insights on nature’s preferences for the former system over the latter.

Resonance Lifetimes in Large Systems

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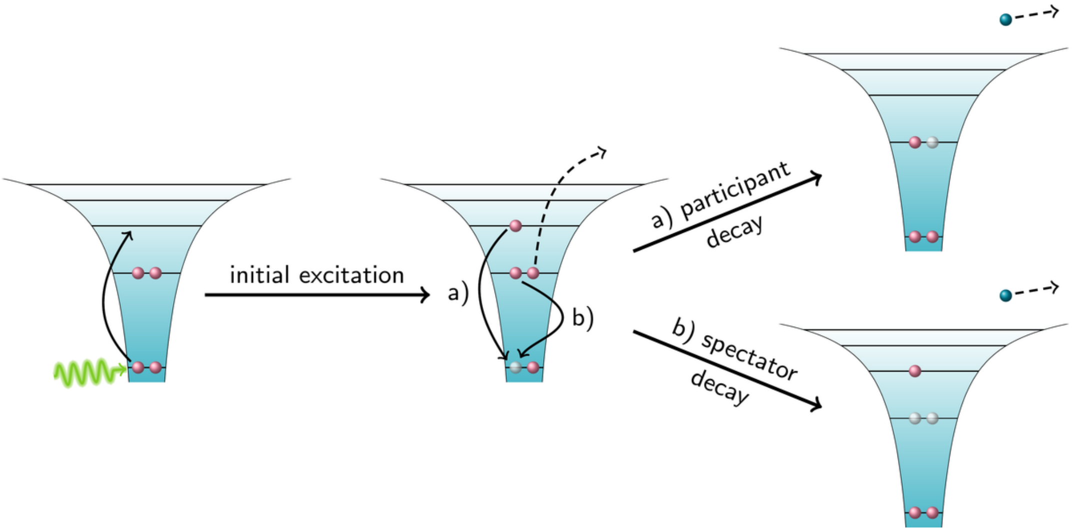
Atoms or molecules can be electronically excited to states possessing an energy higher than the ionization potential of the respective species. Such so-called resonance states are generally not stable and can undergo electronic decay processes as shown in the figure below, giving rise to possibly low-energetic free electrons, which are known to cause damage to tissues in living matter.

A characteristic number of resonance states is their *lifetime* or *decay width*, connected to each other via the Heisenberg uncertainty relation. Due to the unbound nature of the involved electronic states, the theoretical description of lifetimes is challenging, especially in the context of available electronic structure codes making use of square-integrable basis sets.

Different approaches to this problem have been proposed so far, one of which is constituted by the *Fano-ADC-Stieltjes* method, using the *Algebraic Diagrammatic Construction* (ADC) scheme for the polarization propagator for electronic state modeling. Here, we present an efficient implementation of this method, applicable up to mid-sized organic molecules. As an example, the calculation of a resonance width in naphthalene is shown.



Schematic illustration of possible resonant Auger processes of high-energetic excited electronic systems.

Symmetry-related Proton Transfer Pathways in Respiratory Complex I

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Abstract

Complex I functions as the initial electron acceptor in aerobic respiratory chains of most organisms. This gigantic redox-driven enzyme employs the energy from quinone reduction to pump protons across its complete *ca*. 200 Å membrane domain, thermodynamically driving synthesis of ATP. Despite recently resolved structures from several species, the molecular mechanism by which complex I catalyzes this long-range proton-coupled electron transfer (PCET) process, however, still remains unclear. We perform here large-scale classical and quantum molecular simulations in order to study the function of the proton pump in complex I from *Thermus thermophilus*. The simulations suggest that proton channels are established at symmetry-related locations in four subunits of the membrane domain. The channels open up by formation of quasi-one dimensional water chains that are sensitive to the protonation states of buried residues at structurally conserved broken helix elements. Our combined data provide mechanistic insight into long-range coupling effects, and predictions for new site-directed mutagenesis experiments.

Magnetically induced currents in organic boron-nitrogen polycyclic molecules and organic ring systems containing metal ions.

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The aromatic character of a molecule correlates with the current pathways induced in an external magnetic field. Calculations using the gauge-including magnetically induced currents (GIMIC) program are a reliable method to evaluate the induced current densities and compare the aromaticity in molecular rings [1]. Our recent work covers annelated-ring systems and compares the effect of boron and nitrogen on the induced current strengths. We confirm that in spite of possessing 16 π electrons, the dibenzo[a,e]pentalene shows little resemblance to the antiaromatic pentalene core [2]. The introduction of boron and nitrogen heteroatoms further increases the aromaticity of the molecular rings. A recent research topic involves the aromaticity of dicupra[10]annulenes with 10 π electrons. Lithium ions situated above and below each of the rings yield nearly planar rings, which makes the rings aromatic. The substitution of all hydrogen atoms of the molecular rings with trimethylsilyl and phenyl substituents distorts the rings, especially when two Li^+ lie on the same side of the molecule. Very strong currents flow around the copper atoms, however, the ring current is lost. The results were recently published [3].

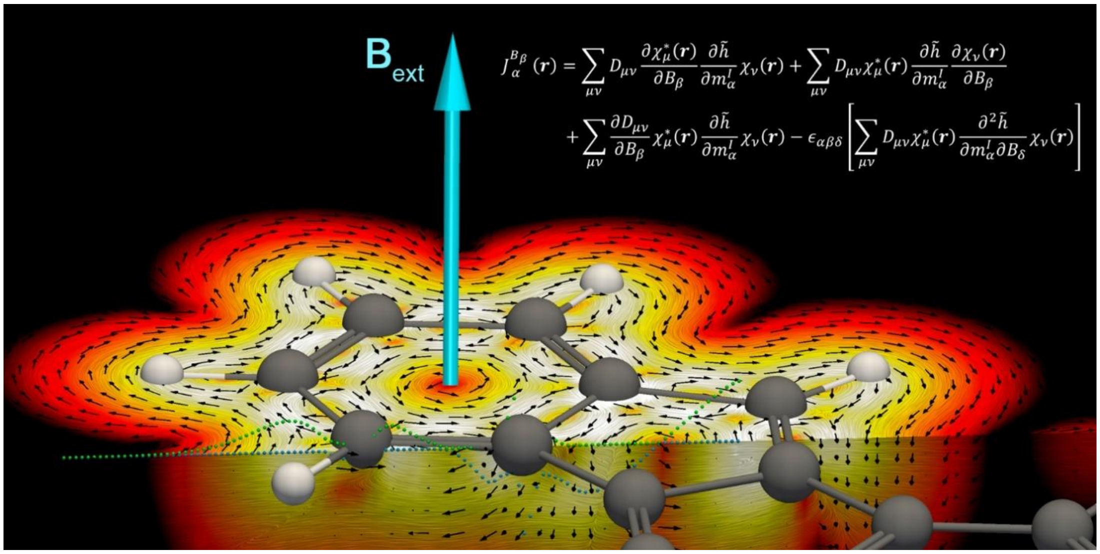

Fig. The induced current densities in the dibenzo[a,e]pentalene molecule [2]. The mathematical expression is the working equation of the GIMIC [1] program.

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Spin–vibronic coupling from TDDFT spin–orbit matrix elements

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Intersystem crossing (ISC) rates are important properties needed to understand excited state processes. For calculating ISC rates spin–orbit matrix elements (SOMEs) are sufficient in many cases, but if states of same character ($\langle \pi\pi^* | \hat{H}_{SO} | \pi\pi^* \rangle$ or $\langle n\pi^* | \hat{H}_{SO} | n\pi^* \rangle$) are involved, vibronic contributions to SOMEs get important. Therefore one has to calculate derivatives of SOMEs to get accurate ISC rates.

In the present work we show an inexpensive approach for calculating SOME derivatives using accurate SOMEs from time dependent density functional theory (TDDFT) by the SPOILER [1] program. For the calculation of numerical SOME derivatives we extended the frequency analysis program SNF [3] to include the SPOILER calculations at each distorted step.

The approach is applied to free-base-porphyrin (FBP) and gives good results in comparison with SOME derivatives accuired at DFT/MRCI level [2].

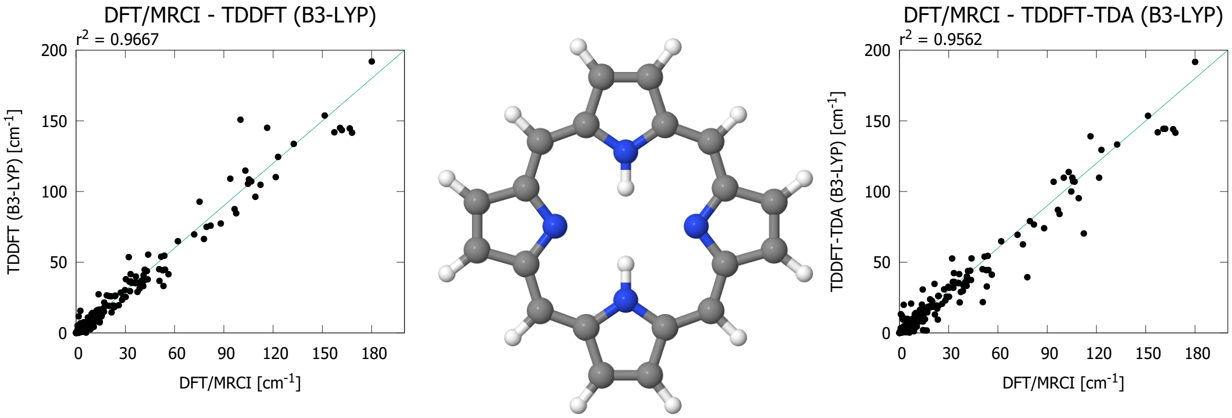

Figure 1: Structure of free-base-porphyrin (FBP) and correlation plots of DFT/MRCI and TDDFT(TDA) SOME derivatives.

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Using Multireference Quantum Chemistry for Photochemistry and Photophysics of Large Molecules

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Large molecules play a great role in organic electronics, photonics, and photovoltaics. They are used as media for charge and exciton migration, light emitters or light harvesters, chemical sensors, etc. Simulating their phorochemical and photophysical properties in amorphous organic layers is an important step in the virtual design of organic electronic devices. These computational problems are usually addressed with the relatively cheap and fast density functional theory, which allows for large-scale calculations. However, this approach has intrinsic deficiencies that lead to qualitatively wrong results. Among these are overestimation of charge delocalization in extended molecular systems, underestimation of the energy of charge-transfer states, and different errors in the energies of singlet and triplet states, which lead to wrong transition probabilities of nonradiative processes.

Multireference methods, such as CASSCF/XMCQDPT, provide qualitatively correct and accurate description of the processes of interest. In particular, they correctly describe charge and exciton localization in extended systems. They also provide a balanced treatment of states of different multiplicity and different orbital character. Therefore, multireference methods give deeper insight into the nature of the systems under study. Understanding the mechanism of the target process will help one to find simple molecular descriptors that can be calculated by cheap methods in large scale.

I outline the problems in which multireference treatment is necessary and demonstrate the application of multireference computational methods to the problems of photophysics and photochemistry of some materials used in organic electronics.

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Electron transfer through iron-sulfur centers in respiratory Complex I

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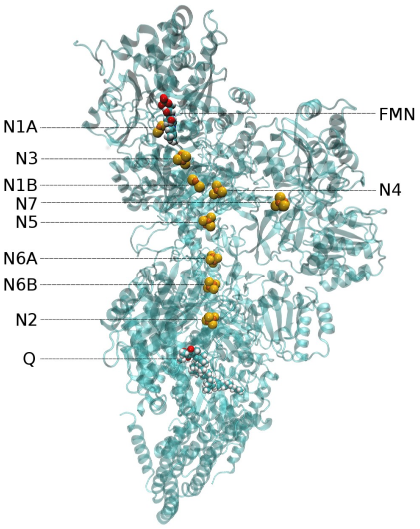
Complex I functions as a redox-driven proton pump in aerobic respiratory chains. It takes electrons from NADH via FMN and transfers them through 8 to 9 iron-sulfur centers (ISC) before reducing quinone (Q) to quinol (QH_2). Redox potential measurements of ISCs show that they are almost isoenergetic, nevertheless, it is not well understood how this process is possible since each ISC is ligated in a particular conformation to the protein and their protein environment is different. Here, we have performed molecular dynamics (MD) simulations and DFT calculations of all possible combinations of oxidized/reduced state of each ISC relevant in the electron transfer chain. This allows us to estimate the reorganization of the protein upon change of oxidation state. We also calculate the redox potential using Poisson-Boltzmann electrostatic calculations of the whole protein, obtaining a good agreement with experimental values. Moreover, we have also performed a DFT analysis of the spin energetics of each ISC obtaining that the different spin arrangements affect around 5 kcal/mol the total energetics. Our combined data provided information that can be used to estimate the electron transfer rates in complex I.



The figure shows the hydrophilic domain of Complex I and its cofactors, starting from FMN, two electrons move along the iron-sulfur cluster (ISC) chain until it reaches quinone (Q).

Gamiz-Hernandez AP, Jussupow A, Johansson MP, Kaila VRI (2017) Terminal Electron–Proton Transfer Dynamics in the Quinone Reduction of Respiratory Complex I. *J Am Chem Soc* 139(45):16282-16286.

Establishing Semi-Empirical QM/MM Strategies for Proton Transfers between Glycans 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 are currently conducting 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 stepwise gas-phase proton affinities of the different groups (cf. Fig. 2), with ωB97XD/6-311++g(d,p) calculations as reference. In the first two steps the bisulfate and carboxyl groups are deprotonated in either order; the hydroxyl or amide groups are deprotonated in the third step. 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]

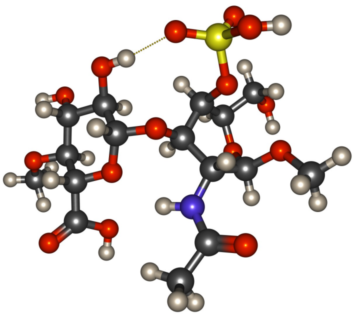

Figure 1: Model compound.

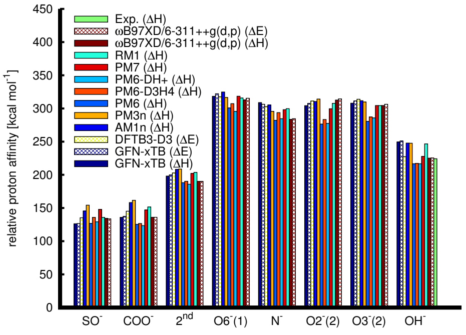

Figure 2: Comparison of gas-phase proton affinities.

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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Calculation of the nuclear spin-spin coupling constants in a series of acetylene derivatives $HC{\equiv}CXH_3$ where X = C, Si, Ge, Sn and Pb.

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We present the results of calculation of the nuclear spin-spin coupling constants in a series of acetylene derivatives $HC{\equiv}CXH_3$, where X is C, Si, Ge, Sn, Pb employing both coupled cluster theory (CC) and density functional theory (DFT), the latter in nonrelativistic and relativistic four-component approach with different exchange-correlation functionals and basis sets.

The available experimental data refers to ethylene substituted acetylene derivatives $HC{\equiv}CX(C_2H_5)_3$, whereas the discussed coupling contants have been calculated for compounds containing hydrogen atoms instead of ethylene groups. Therefore, the influence of the substitution of H atoms with ethylene groups on the coupling constants was studied by comparing the values obtained by nonrelativistic DFT calculations for both types of molecules.

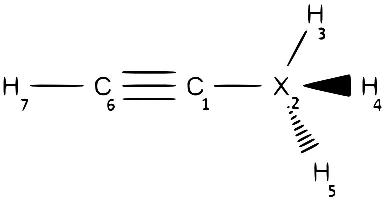

Figure 1: The general structure of studied series of acetylene derivatives, where X = C, Si, Ge, Sn, Pb.

In this particular case electron correlation seems to have greater impact on the calculated values than the relativistic effects. Generally, the CC method reproduces the experimental values better than the DFT method, for which the performance of B3LYP functional was the most satisfactory. The relativistic effects become noticeable only for tin- and lead-containing molecules for the couplings including heavy atoms.

As for the basis set choice, the use of ATZP basis set gives results in better agreement with the experiment than the aug-cc-pVTZ-J basis set, probably conincidentally, since aug-cc-pVTZ-J was specially modifed for spin-spin coupling calculations.

Another factor contributing to the difficulty of calculations of the spin-spin coupling constants is their strong dependence on molecular geometry and, consequently, relatively large rovibrational effects. The calculations of the derivatives of the coupling constants with respect to the C≡C and C-H bond lengths have been performed and it seems that the derivatives of the coupling constants with respect to bond lengths are much more sensitive to the relativistic effects than the coupling constants. Furthermore, zero-point-vibrational corrections to spin-spin coupling constants have been calculated with the use of nonrelativistic DFT method. The differences between the vibrational averaged values and the values for optimized geometry constitute up to 10% of the values and in most cases the addition of the ZPV correction leads to improved agreement with the experimental values.

The applications of the Hückel-Su-Schrieffer-Heeger method.
I. Carbon-carbon bond lengths in policyclic benzenoid hydrocarbons.

Jan Kwapisz[a] **and Leszek Z. Stolarczyk**[b]

October 26, 2017

Abstract

The variation of the carbon-carbon bond lengths in π-electron hydrocarbons is a consequence of the presence of mobile electrons residing on the valence orbitals of the π-symmetry. In the coming paper by Stolarczyk and Krygowski a simple quantum approach, the Augmented Hückel Molecular Orbital (AugHMO) model, is proposed for the qualitative, as well as quantitative, study of this phenomenon. The simplest realization of the AugHMO model is the Hückel-Su-Schrieffer-Heeger (HSSH) method, in which the β parameters of the HMO model depend linearly on the bond lengths. With a proper parametrization, the HSSH method is capable of fairly accurate description of the bond lengths in a variety of π-electron hydrocarbons and carbon systems, including polyacetylene, fullerene C_{60}, and graphene.

We have applied the HSSH method is applied in a study of carbon-carbon bond lengths in a set of 34 selected policyclic benzenoid hydrocarbons (PAHs). This is exactly the set of molecules analyzed by Rieger and Müllen (*J. Phys. Org. Chem.* **2010**, *23*, 315) in the context of their electronic-excitation spectra. These PAHs have been obtained by chemical synthesis, but in most cases no diffraction data (by X-rays or neutrons) of sufficient quality is available to provide us with their geometry. On the other hand, these PAHs are rather big (up to 96 carbon atoms), and *ab initio* methods of quantum chemistry are too expensive for reliable geometry optimization. That makes the HSSH method a very attractive alternative. The poster will cover both the general method and the specific calculations.

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Efficient Linear-Scaling Implementation of Local-Hybrid Density-Functionals

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Local hybrid functionals, i. e., functionals with local dependence on the exact exchange energy density (see for example refs [1–4]), generalize the popular class of global hybrids and extend the applicability of density functional theory to more 'difficult' electronic structures that require an accurate description of static correlation (e. g., transition state and multi-reference ground states).

However, the lack of efficient implementations restrained their wide-spread application. Here, we present the first linear scaling SCF and molecular forces implementation of local hybrid functionals employing the seminumerical integration scheme of Kaupp *et. al.* [5, 6]. A high computational efficiency is achieved by combining the preLinK-method of Kussmann and Ochsenfeld [7] with explicit screening of integrals for whole batches of grid-points to minimize the screening overhead.

The linear scaling behavior, efficiency, accuracy and multi-node parallelization of our implementation in the FermiONs++ program package [7, 8] is demonstrated for large molecules with up to 1052 atoms and 11230 basisfunctions. Additionally, the accuracy of the local hybrids functionals PSTS [1], Becke05 [2], Johnson13 [3], and KP16 [4] is investigated for the bond dissociation of dihydrogen, exemplifying a typical strong correlation problem.

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Coupled-cluster modeling of strong correlation

Susi Lehtola

We discuss coupled-cluster type modeling of strongly correlated systems, and present results obtained at the singlet-reference perfect quadruples (PQ) [1] and perfect hextuples (PH) [2] models, which are truncated versions of coupled-cluster theory with single through quadruple and single through hextuple excitations, respectively, using a recently developed efficient implementation thereof scalable to problem sizes up to 300 electrons in 300 orbitals [3].

We also present results obtained with the full configuration interaction and adaptive sampling configuration interaction approaches [4], where we extract the coupled cluster coefficients using a decomposition approach [5].

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Catalytic Mechanism and Molecular Engineering of Quinolone Biosynthesis in Dioxygenase AsqJ

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The Fe(II)/α-ketoglutarate-dependent dioxygenase AsqJ from *Aspergillus nidulans* is an outstanding, multifunctional enzyme. It stereoselectively catalyzes both a ferryl-induced desaturation reaction and epoxidation of quinolone alkaloids, important natural products with antibacterial and antitumor activities. We investigate here the mechanistic concepts of this unique dioxygenase using a combination of quantum chemical QM and QM/MM calculations, X-ray crystallography, and HPLC/MS analysis. Our reaction barriers for the various stages of the reaction cycle are thermodynamically and kinetically feasible, and the calculations show that intrinsic strain of the substrate is important for catalysis. We further engineer AsqJ *in silico* and *in vitro* enabling catalysis of different quinolone substrates.

Theoretical description of photodissociation of ultracold diatomic molecules with quantum state control

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Chemistry and physics of ultracold (below 1 mK) molecules is a fast growing field with wide possibilities for future applications. One of them is the control of the chemical reactions dynamics. The reaction investigated experimentally by the group of Tanya Zelevinsky at the University of Columbia in New York was a light-induced photodissociation of the diatomic strontium molecule $Sr_2 \rightarrow Sr + Sr$. The experiment was performed with the full control over the initial quantum states of the molecule and final states of the fragments. After a controlled decay, the fragments were recorded, creating 2D patterns (Fig. 1). The theoretical description of the experimental results is based on the formula for the photodissociation cross section

$$\sigma(\theta,\phi) = \sum_{l=0}^{\infty} \sum_{m=0}^{l} \beta_{lm} P_l^m(\cos\theta)\cos(l\phi), \tag{1}$$

where (θ, ϕ) are the scattering angles and β_{lm} are anisotropy parameters. In the full quantum model, the formulas for the anisotropy parameters were derived using Fermi golden rule with the appropriate transition operator.

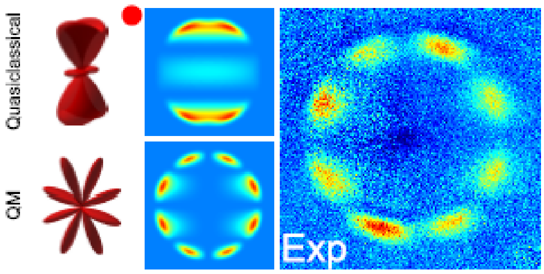

Figure 1: Experimental image compared with the quantum and quasiclassical theoretical predictions [1]

The theoretical results full explained unexpected experimental findings, such as the lack of the cylindrical symmetry of the images and the existence of a shape resonance. It was proven that the well-known quasiclassical model of the photodissociation [2] is not sufficient to describe the experiment with full quantum state control.

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First-principles analysis of electronic and optical properties of donor-acceptor type polymer photovoltaic materials

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In this work we present a tight-binding approach to estimate certain quantities of a donor-acceptor (D-A) type polymer, such as the orbital energies, ionization potential, electron affinity, and lowest optical excitation energy. D-A type polymers can be used as the donor material in the blends of bulk-heterojunction solar-cells. The main advantage of the D-A construction is better tuning of the energy level alignment with the PCBM (or any other acceptor) and optical absorption spectrum. The D-A monomer contains a couple of chemically bonded donor and acceptor moiety, each of which within a polymer chain is spatially separated from the next nearest moiety of the same type by the other one. Therefore the orbital overlap is expected to be less than in an ordinary monomer sequence. We build a tight-binding model on this idea allowing us to estimate computationally heavy to attain polymer properties from monomer and dimer calculations. We perform DFT simulations to obtain interatomic matrix elements of the tight binding Hamiltonian and also check the success of the tight binding approach for one and up to four monomer sequences. The lowest excitation energies of the singlet and triplet excited states are calculated from ΔSCF-DFT. We hypothesis that due to the cancellation of the known errors of the DFT, the Kohn-Sham HOMO-LUMO gap reasonable agrees with the optical gap although the explicit electron-hole interaction is not taken into account in the ground state DFT calculations.

Statistical assessment of prediction quality of reorganization energies of a series of indan-1,3-diones

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One of the quantities used for mobility calculations of charge carriers in organic semiconductors is the reorganization energy. It appears in the equation for mobility constant in the semi-classical variant of Marcus–Hush theory:[1]

$$k = \frac{2\pi}{\hbar} J_{DA}^2 FC = \frac{2\pi}{\hbar} J_{DA}^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left[-\frac{\lambda}{4k_B T}\left(1+\frac{\Delta G^0}{\lambda}\right)^2\right] , \tag{1}$$

where J_{DA} is transfer integral, FC – Franck–Condon factor, ΔG^0 – free energy change for the reaction (we use Gibbs free energy here, as isobaric conditions are more applicable than isochoric both to solution in open container and to a thin film), λ is the reorganization energy and k_B and $\hbar$ are, correspondingly, Boltzmann and reduced Planck constants.

Contrariwise to the transfer integral, calculation of λ is quite straightforward, with the ΔSCF scheme canonized by A. Klimkāns:[2]

$$\lambda_{ion} = E_+(R_0) - E_+(R_+) \ , \tag{2}$$

where $E_+(R_0)$ is the energy of ionized molecule, corresponding to pre-ionization geometry, and $E_+(R_+)$ represents the energy of ionized molecule with relaxed geometry. Analogically, for the recombination process

$$\lambda_{neutr} = E_0(R_+) - E_0(R_0) \ , \tag{3}$$

where $E_0(R_+)$ is the energy of neutral species with the equilibrium geometry of an ion and $E_0(R_0)$ is the ground-state energy of neutral molecule (prior to ionization).

Reliable calculations of this property with some high-level methods of classical wave-function theory is sometimes impossible for organic molecules due to high computational requirements. Density functional theory is a frequently used low-cost alternative, and applicability of different density functionals for this is frequently explored.[3][4] At the same time, one of the factors not so frequently considered is the size and quality of the basis set. We hereby provide a systematic comparison of results with Pople basis sets with results by Møller–Plesset perturbation theory, obtained by statistical method of effect decomposition which should mitigate the system-dependent error.[5] A series of 4'-substituted 2-benzylideneindane-1,3-diones was chosen for this study to be able to transfer from direct comparison of quantities of interest towards comparison of regression parameters.

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Molecular Diodes

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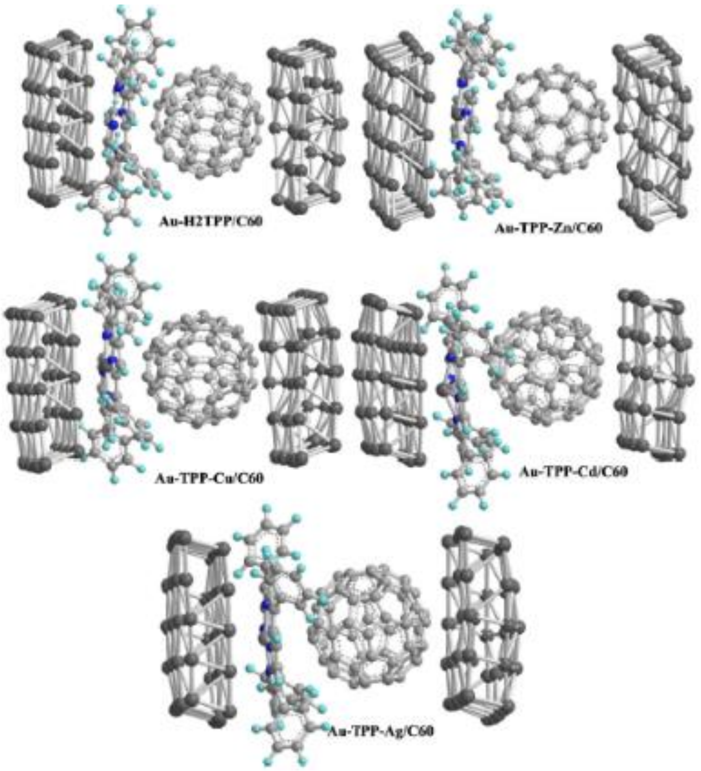
Molecular diodes based on charge transfer complexes of fullerene [60] with different metalloporphyrins have been modeled. Their current-voltage characteristics and the rectification ratios (RR) were calculated using direct ab initio method at PBE/def2-SVP level of theory with D3 dispersion correction, for voltages ranging from -2 to +2V. The highest RR of 32.5 was determined for complex of fullerene [60] with zinc tetraphenylporphyrin at 0.8V. Other molecular diodes possessed lower RR, however, all complexes showed RR higher than 1 at all bias voltages. The asymmetric evolutions and alignment of the molecular orbitals with the applied bias were found to be essential for generating the molecular diode rectification behavior. Metal nature of metalloporphyrins and the interaction porphyrin-electrode significantly affect RR of molecular diode. Large metal ions like Cd^{2+} and Ag^{2+} in metalloporphyrins disfavor rectification creating conducting channels in two directions, while smaller ions Zn^{2+} and Cu^{2+} favor rectification increasing the interaction between gold electrode and the porphyrin macrocycle.



Title: Investigation of the Adsorption of Phosphonic Acid on the Rutile TiO_2(110) Surface for Water Splitting Applications

Authors: Dr. *Tiziana Musso*, Dr. Marcella Iannuzzi, Prof. Jürg Hutter, René Wick and Prof. David Tilley

Photoelectrochemical (PEC) cells are used to achieve water splitting thanks to a semiconductor photocatalyst. A suitable photocatalyst should be stable and have band-edge potentials suitable for overall water splitting, as in order to have spontaneous water splitting, the band edges of the semiconductor must straddle the potentials for the hydrogen and oxygen evolution reactions [1]. Titania has been the pioneer electrode material since the discovery of its UV light-driven photocatalytic water splitting properties in 1972, but it has some intrinsic limitations like the inability to harvest visible light[2]. In this regard, functionalization of TiO_2 surfaces with functional organic molecules is considered a way to tune titania's properties.

In this joint experimental and theoretical work, the (110) surface of rutile TiO_2 has been functionalized with phosphonic acid (H_3PO_3), which has good long-term stability and high affinity towards metal oxide surfaces [3]. The exact binding of the phosphonic acid to the TiO_2 surface is not easy to assess experimentally and is still much debated [3,4]. With *ab-initio* simulations carried out with the CP2K code we show that the bidentate mode is the most favorable adsorption mode of phosphonic acid on rutile (110).
Considering that theoretical models and computational studies are fundamental to describe PEC interfacial properties, the band alignment between photoelectrode band edges and water redox potentials is of crucial interest, but still much debated [5]. An electronic analysis shows that at high H_3PO_3 coverages, the titania bands are shifted upwards, resulting in a higher photo voltage.

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Efficient (Non-)Adiabatic Molecular Dynamics for Large Molecular Systems

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Born-Oppenheimer and non-adiabatic molecular dynamics (BOMD and NAMD) simulations have become a powerful and established tool for the calculation of ground and excited state properties. They can, for example, be used for sampling potential energy surfaces, predicting experimental spectra, calculating thermodynamic properties, and exploring photochemical reaction pathways. Here, we discuss efficient and accurate schemes within our FermiONs++ program package for ground-state BOMD and NAMD, that can even be applied to large molecular systems.

For the first scheme [1], we combine (a) the corrected small basis set Hartree-Fock (HF-3c) [2], (b) the extended Lagrangian BOMD (XL-BOMD) method [3], and (c) efficient methods for calculating Coulomb and exchange terms (with PreLinK) on graphics processing units (GPUs) [4, 5]. We present timings and high-quality vibrational spectra (extracted from simulated trajectories) of several molecular systems comprising up to 500 atoms.

NAMD simulations are carried out, using the fewest switches surface hopping algorithm [6] together with linear response time-dependent density functional theory (TDDFT). Different approaches to access the non-adiabatic couplings and the use of simplified TDDFT schemes [7, 8] are investigated. We discuss their performance on GPUs and show illustrative examples of NAMD simulations.

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Exploring Strategies for Labeling Viruses with Gold Nanoclusters through Non-equilibrium Molecular Dynamics Simulations

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Bio-compatible gold nanoclusters have recently been utilized as site-specific contrast agents for virus imaging in electron microscopy.[1] Two strategies have been shown to be successful: covalent binding to cysteine groups in the viral capsid[1a] or non-covalent binding to hydrophobic pockets.[1b] The latter strategy is expected to prove useful for dynamic studies of virus uncoating.

We have estimated the binding affinities of the natural pocket factor, Pleconaril (antiviral drug) and an in-house synthesized drug-like molecule (Kirtan) into the hydrophobic pocket of Echovirus 1 by using molecular dynamics simulations combined with non-equilibrium free energy calculations.[2] We have also studied the binding of $Au_{102}p\mathrm{MBA}_{44}$ nanocluster/Kirtan complex to the pocket. Although the absolute binding affinities are overestimated for all the systems, the trend is in agreement with recent experiments.[1b] While the gold nanocluster does not decrease the affinity of Kirtan molecule to the virus, the affinity is sensitive to the protonation state of the nanocluster.

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Designing ligands for metal complexes using machine learning methods

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Interest in the application of machine learning (ML) in chemistry has increased among the recent successes of ML in other fields[1]. ML has been successfully applied to solving the direct problem of mapping chemical structures to properties. This results yielding linearly scaling methods with good accuracies under the condition that the molecule is represented correctly [2].

The task of molecular design is central to chemistry and is an inverse problem of finding of chemical structures with wanted properties. This is an optimization problem over practically infinite chemical space. Genetic algorithms (GA) have been used for optimizing molecules as iterative process of random mutations and filtering of suitable candidates for future generations [3-4]. The recent very successful methods in deep learning have been transformed to the language of chemistry. Several generative models have been applied to design libraries of new molecules which optimize some metric [5-8].

In this work, generative ML models are applied to the design of new ligands for transition metal complexes. The used ML methods, generation of a training data set, and some preliminary findings are presented.

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Energetics of proton coupled-electron transfer reactions in the NADH-binding site of respiratory complex I

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Complex I functions as a redox-driven proton pump in aerobic respiratory chains. It catalyzes the two electron transfer from NADH to quinone through a series of iron-sulfur (FeS) centers. The free energy released is employed to pump protons across the membrane domain, localized *ca*. 200 Å away from the quinone-binding site. The process is initiated by a hydride transfer from NADH to FMN, followed by the subsequent release of the oxidized NAD^+. During this process, the two electrons are introduced into the FeS centers chain, followed by their sequentially transfer to the quinone, which is reduced to quinol. Two of the FeS centers, N1a and N3, are located in the proximity of the NADH-binding site, but only N3 has been proposed to directly participate in the electron transfer to quinone, whereas the exact role of N1a is still unclear. To understand the molecular mechanism, energetics, and dynamics of this proton-coupled electron transfer (PCET) process linked to the NADH/FMN chemistries, we have employed here multi-scale quantum and classical molecular simulations. We have merged together different quantum mechanical subsystems including the initial electron donor, NADH/FMN, and acceptors, N1a/N3 in the calculations. We present energetics of likely PCET steps in these processes, and discuss their mechanistic implications for the function of complex I.

Interactions and chemical reactions in ionic three-body systems: $A^+ + AB$, $AB^+ + A$, and A_2B^+

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The poster concerns interactions, energetics, and chemical reactions in ionic three-body systems A^++AB, AB^++A, and $A_2B^+$of alkali-metals in the context of modern experiments with cold hybrid ion-atom systems. Ground-state electronic properties of diatomic AB^+ and triatomic A_2B^+ molecular ions consisting of Li, Na, K, Rb and Cs atoms are calculated using coupled-cluster method and possible channels of chemical reactions are indentified.

Heteronuclear alkaline metal molecular ions are shown to have significant permanent electric dipole moments that depend nonlinearily on internuclear distances due to charge delocalization.

The present results open the way for investigating more comlex molecular ions important in chemistry as well as chemical reactions controlled by external laser or magnetic fields and other applications of molecular ions formed in cold hybrid ion-atom systems.

Advanced Simulations of Electronic Spectra using Path Integral Molecular Dynamics: The Case of Criegee Intermediates

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This work focuses on the development of reliable *ab initio* computational protocol for simulations of absorption cross sections on the case of Criegee intermediates. Criegee intermediates are formed by ozonolysis of alkenes and they play a pivotal role in atmospheric chemistry as they are responsible for the removal of volatile organic compounds from the troposphere.[1] However, their experimental characterization is difficult due to their short lifetime and difficult preparation.

Absorption spectra are modelled using the *ab initio* based reflection principle. Quantum effects are incorporated by combining the path integral molecular dynamics and a quantum thermostat based on the Generalized Langevin Equation.[2] The calculated UV spectra are efficiently processed with the kernel density estimation method. We found that commonly used electronic structure methods are inadequate to describe Criegee intermediates due to their complex electronic structure. Single-reference wavefunction based methods become reliable only once the triple excitations components are included. Therefore, we introduce composite EOM-CCSD/T and CC2/3 methods providing excellent absorption cross sections for all C1 and C2 Criegee intermediates at reasonable computational cost. Our absorption spectra for C2 Criegee intermediates are the first to provide absolute intensities for individual conformers.

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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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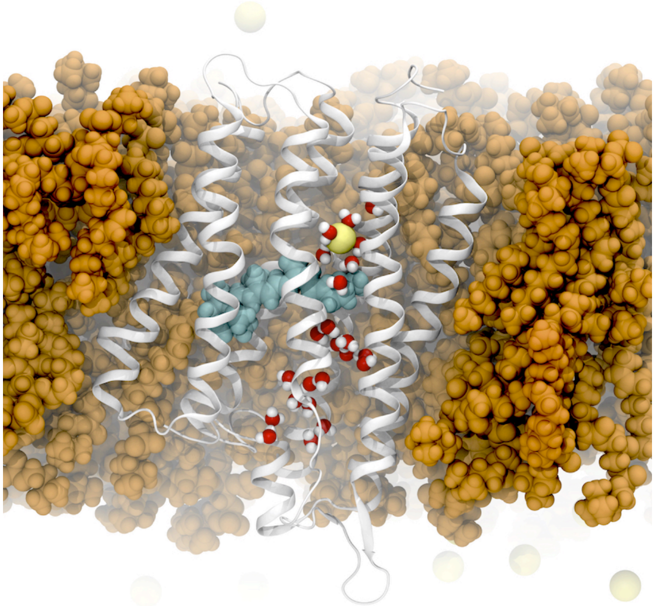

Electronic structure analysis of [Fe^{III}N$_3$(cyclam-acetato)]$^+$ as a model complex for dinitrogen photocleavage

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Nitrogen is the most prevalent gas in the Earth's atmosphere and an essential element for life. Molecular nitrogen is almost inert due to the dinitrogen triple bond having one of the largest naturally occurring bond dissociation energies (944.87 kJ mol^{-1}).[1] Few organisms possess the nitrogenase enzyme required to make use of this abundant resource, and the only synthetic equivalent at industrial scale is the Haber-Bosch process. While the Haber-Bosch process has been optimised for efficiency there are drawbacks: the dihydrogen source used comes from fossil fuels and the whole process only produces one product, ammonia. Research into molecular catalysts capable of N_2 activation is thus ongoing, and a relatively new approach is the photochemical activation of N_2, using light from the solar spectrum as the primary source of energy. This process has been investigated in experimental and computational studies over the last few years,[2] as a stable and efficient photocatalyst holds promise for processes more sustainable and with a more diverse range of products than the Haber-Bosch process.[3] Computational studies in particular are used to better understand, and therefore optimise potential catalysts.

As model complexes for the dinitrogen photocleavage reaction, iron azido complexes with a Fe-N-N-N bonding motif will be studied. These complexes have been previously synthesised and characterised in the literature.[4] There are two different bond cleavage reaction pathways which are observed upon photoexcitation of the complex at different wavelengths: (i) Fe-N bond scission which results in $N_3^{\bullet}$ or N_3^{-} and the 5-coordinate Fe complex (photoreduction or redox-neutral photodissociation), and (ii) N-N bond cleavage forming N_2 and an iron nitrido complex (photooxidation). We use quantum mechanical methods to better understand the electronic structures of these systems. By predicting UV/VIS spectra and comparing with available experimental data, we assign the character of the electronic excitations responsible for the two different pathways and identify computational methods that are accurate yet affordable.

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The computation of intramolecular photophysical rate constants using TDDFT and XMC-QDPT2 methods and Plotnikov's theory

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The internal conversion (k_{IC}) and intersystem crossing (k_{ISC}) rate constants calculation was carried out for the set of most representative organic and organometalic compounds using the XMC-QDPT2, TDDFT methods and the Plotnikov's theory within adiabatic and Franck-Condon approximation. We have considered a set of molecules that are characterized by the specific and well-known spectroscopic properties: these are pyrromethene 567, psoralene, hetero[8]circulenes, free base porphyrin, naphthalene and higher acenes, OLED-important *fac*-Alq_3 and *fac*-$Ir(ppy)_3$ compounds. For the most of studied systems both FC and adiabatic approximation provides the reasonable results for the k_{IC}, k_{ISC} and fluorescence quantum yield values comparing with the experimental data. The exceptions are polyacenes and free base porphyrin for which we need to overcome the common FC and adiabatic approximation and operating beyond them.

Our computations show that in the case of IC process the energy of electronic excitation expended mainly for the activation of high-frequency stretching vibrations of X-H bonds (X=C, N and O atoms). This fact generally supports the earlier proposed Plotnikov's theory for the mechanisms of non-radiative processes in polyatomic molecules.

CYTOCHROME C PEROOXIDASE CATALYSIS: BEYOND THE POULOS-KRAUT MECHANISM

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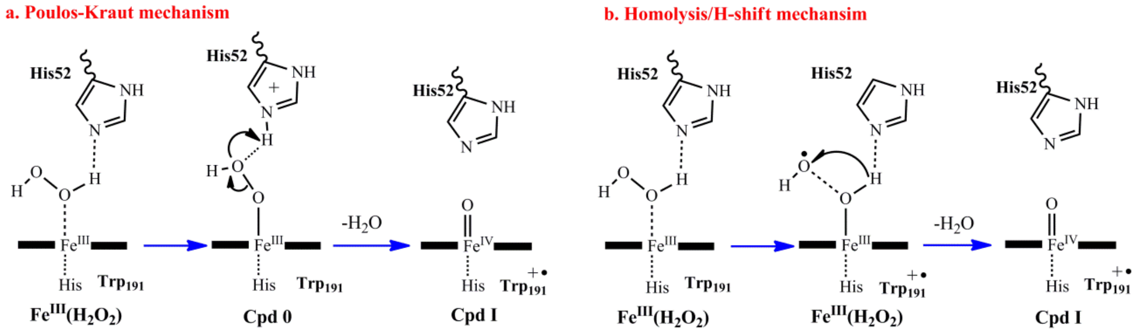
Cytochrome c peroxidase (CcP) catalyzes the reduction of H_2O_2 to water by using additional electrons and protons, and numerous efforts have been devoted to studies of its structure/functions, especially the formation of the active species Compound I (Cpd I). In the widely-accepted Poulos-Kraut mechanism, the proximal H of H_2O_2 first shifts to His 42 to form compound 0 (Cpd 0), and the following proton transfer from His42 to distal O triggers the heterolytic cleavage the O-O bond.[1-3] Intriguingly, the recent experiment by Casadei et al. proposed a proton-catalyzed O-O activation mechanism[4]. Herein, the combined molecular dynamics (MD) simulations and quantum-mechanical/molecular mechanics (QM/MM) calculations are used to address this enigma. Our calculations demonstrate the widely-accepted Poulos-Kraut mechanism is highly unfavourable in wild type CcP, and at the same time identify a novel "homolysis/H-shift mechanism" for Cpd I formation, which is enhanced by electron transfer from a nearby Trp residue to the iron centre. The present findings have far-reaching implications for the interplay of H_2O_2 activation and electron transfer in peroxidases in general.



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