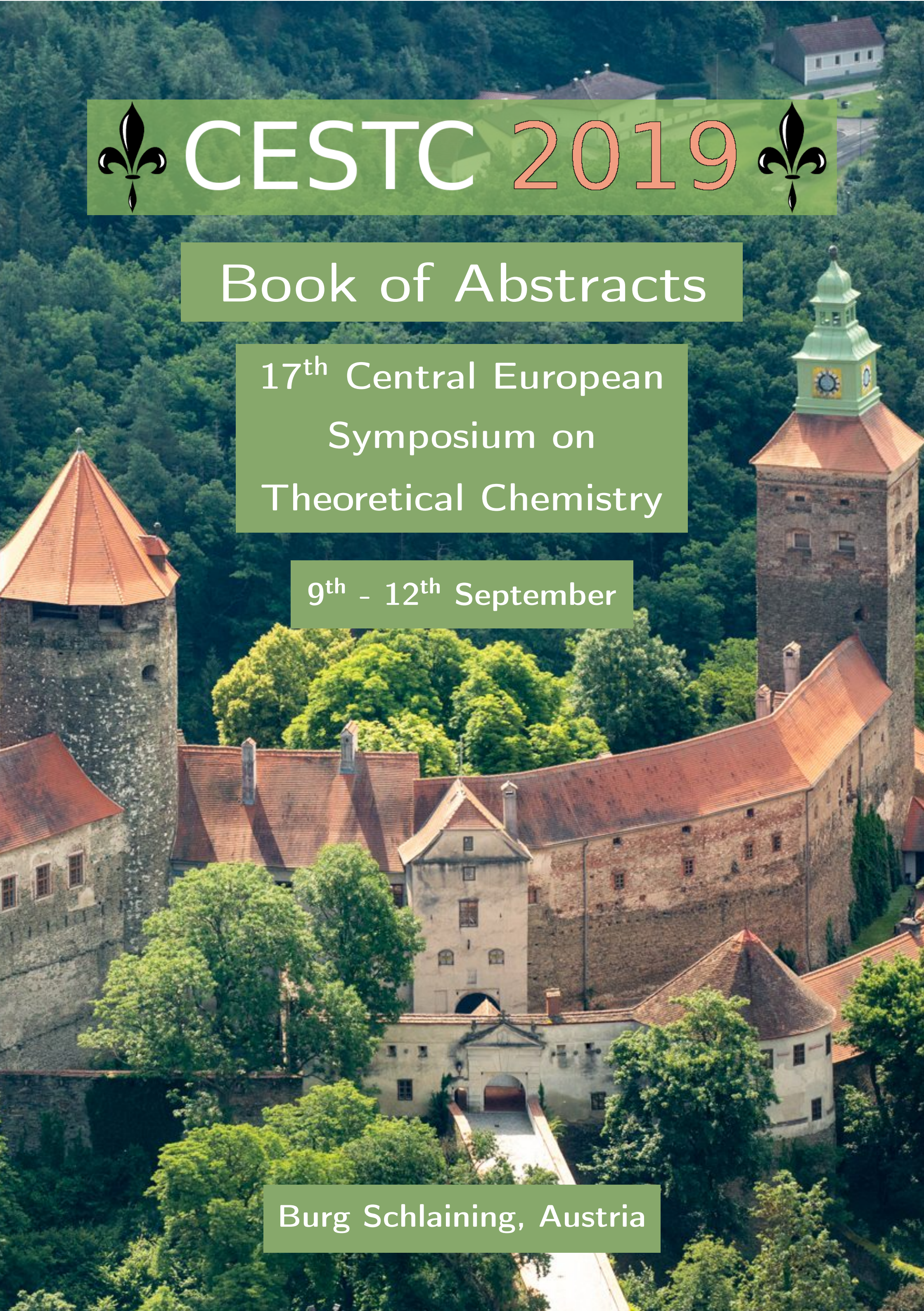

CESTC 2019

Book of Abstracts

17th Central European Symposium on Theoretical Chemistry

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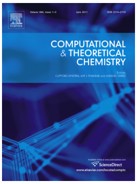
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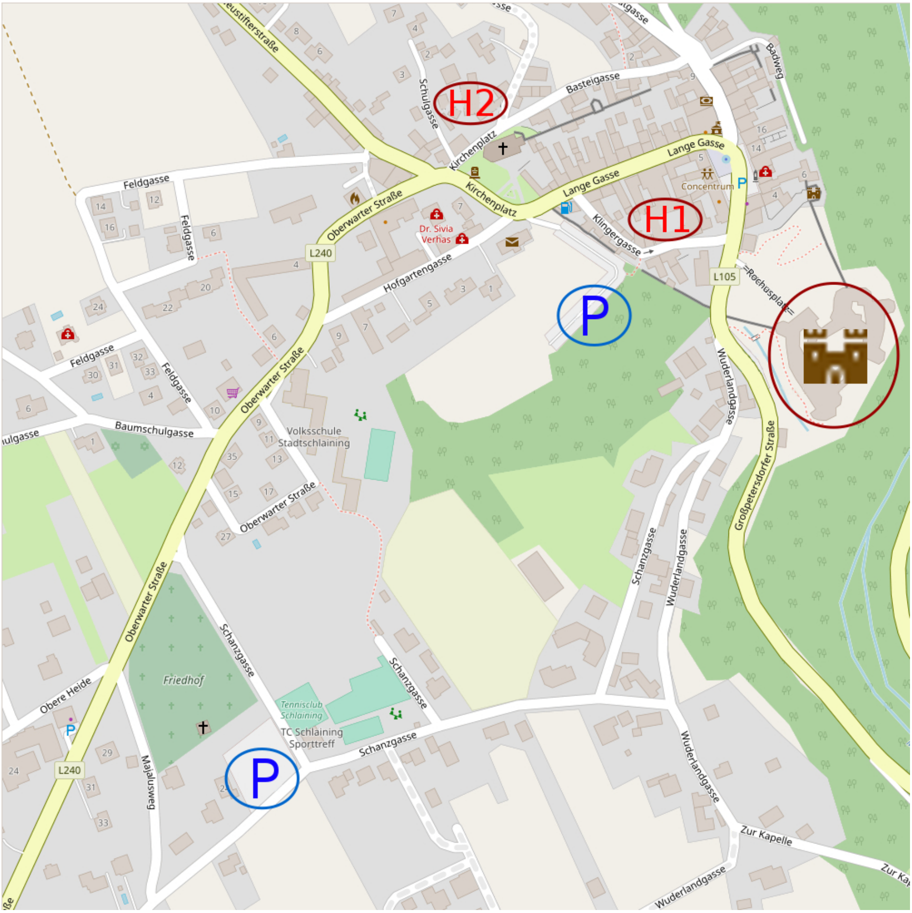

Program Overview

		Monday, 09.09.2019	Tuesday, 10.09.2019	Wednesday, 11.09.2019	Thursday, 12.09.2019
09:00	09:40		I4 – BEHLER	I8 – PAVLÍKOVÁ PŘECECHTĚLOVÁ	I11 – CSÁSZÁR
09:40	10:00		C4 – COE	I9 – KUBAS	C17 – SLAVÍČEK
10:00	10:20		C5 – WESTERMAYR		C18 – SULIMAN
10:20	10:50		Coffee break		
10:50	11:30		I5 – PITTNER	I10 – SZABADOS	I12 – DERZSI
11:30	11:50		C6 – FREITAG	C14 – MUSIAŁ	C19 – DARU
11:50	12:10		C7 – HOLZER	C15 – MIHÁLKA	C20 – NAGY
12:10	12:30		C8 – KELTERER	C16 – PRZYBYTEK	C21 – HRIVNÁK
12:30	14:00		Lunch	Lunch	Lunch/ Departure
14:00	14:20	Registration	I6 – BICZYSKO	Excursion	
14:20	14:40				
14:40	14:50		C9 – MONARI		
14:50	15:00	Welcome & Introduction			
15:00	15:20	I1 – REIHER	C10 – TÓTH		
15:20	15:40		Coffee break		
15:40	15:50	I2 – KREWALD			
15:50	16:00		I7 – KOMOROVSKY		
16:00	16:20				
16:20	16:30	Coffee break			
16:30	16:50		C11 – ONČÁK		
16:50	17:10	I3 – GRUDEN	C12 – CVITAŠ		
17:10	17:30		C13 – ESSEFFAR		
17:30	17:50	C1 – ROZGONYI	BM		
17:50	18:10	C2 – BENEDEK			
18:10	18:30	C3 – RYBICKI			
18:30	20:00	Dinner	Dinner		
20:00	22:00	PS I	PS II	Conference Dinner	

I … Invited Speaker

C … Contributed talk

PS … Poster session

BM … Board Meeting

Scientific Program

Monday, 9. September

14:00		**Registration**
14:50		**Welcome & Introduction**
15:00		Session 1 - Chair: Leticia González
15:00	I1	**Markus Reiher** – ETH Zürich *Matrix product states for electronic and vibrational structure*
15:40	I2	**Vera Krewald** – Technical University Darmstadt *Orbital entanglement analysis of magnetically coupled transition metal complexes*
16:20		**Coffee break**
16:50		Session 2 - Chair: Szalay Péter
16:50	I3	**Maja Gruden-Pavlović** – University of Belgrade *Spinning around in transition metal chemistry*
17:30	C1	**Tamás Rozgonyi** – Hungarian Academy of Sciences *Studying ultrafast photorelaxation in functional Fe(II) complexes*
17:50	C2	**Zsolt Benedek** – Budapest University of Technology and Economics *Exploring the mechanism of biomimetic nitrogen fixation and its side reactions*
18:10	C3	**Marcin Rybicki** – Humboldt-Universität zu Berlin *Ab initio description of heterogeneous catalysis - monomolecular alkane cracking over H-MFI zeolite*
18:30		**Dinner**
20:00		**Poster Session I: P01 - P35**

Tuesday, 10. September

09:00		Session 3 - Chair: Philipp Marquetand
09:00	I4	**Jörg Behler** – University of Göttingen *Understanding complex systems with high-dimensional neural network potentials*
09:40	C4	**Jeremy Coe** – Heriot-Watt University *Potential energy curves using machine learning configuration interaction*
10:00	C5	**Julia Westermayr** – University of Vienna *Machine learning for excited state dynamics: fitting multi-dimensional potentials for energies, forces and couplings*
10:20		**Coffee break**

10:50		Session 4 - Chair: Doslic Nadja
10:50	I5	**Jiří Pittner** – Academy of Sciences of the Czech Republic *Molecular dynamics with non-adiabatic and spin-orbit effects*
11:30	C6	**Leon Freitag** – ETH Zürich *Towards ab-initio surface-hopping dynamics with a density matrix renormalization group self-consistent field approach*
11:50	C7	**Christof Holzer** – Karlsruhe Institute of Technology *Prediction of excited state properties for sizable molecular systems including spin-orbit effects*
12:10	C8	**Anne-Marie Kelterer** – Graz University of Technology *The Förster energy transfer in metal organic frameworks*
12:30		**Lunch**

Tuesday, 10. September

14:00		Session 5 - Chair: Jin Wen
14:00	I6	**Malgorzata Biczysko** – Shanghai University *The role of anharmonic corrections in conformational analysis of flexible molecules*
14:40	C9	**Antonio Monari** – Université de Lorraine Nancy *A song of light and life. From molecular modeling to in-silico photobiology*
15:00	C10	**Zsuzsanna Tóth** – University of Chemistry and Technology Prague *Calculating ionization energy in condensed phase using a QM:QM method*
15:20		**Coffee break**
15:50		Session 6 - Chair: Bogumil Jeziorski
15:50	I7	**Stanislav Komorovsky** – Slovak Academy of Science *Relativistic theory for prediction of excitation energies of both closed- and open-shell species*
16:30	C11	**Milan Oncák** – University of Innsbruck *Photochemistry in helium droplets: state-dependent solvation effects in* $Cs_2He_n^+$
16:50	C12	**Marko Tomislav Cvitaš** – Ruđer Bošković Institute *Tunnelling splittings in water clusters using instantons*
17:10	C13	**M'hamed Esseffar** – Cadi Ayyad University *Diastereoselective synthesis and cytotoxic evaluation of new isoxazoles and pyrazoles with monoterpenic skeleton.*
17:30		**Board Meeting**
18:30		**Dinner**
20:00		**Poster Session II: P36 - P70**

Wednesday, 11. September

09:00		Session 7 - Chair: A. Daniel Boese
09:00	I8	**Jana Pavlíková Přecechtělová** – Central European Institute of Technology-Czech Republic *Computation of NMR chemical shifts in phosphorylated intrinsically disordered proteins: challenges and limitations*
09:40	I9	**Adam Kubas** – Polish Academy of Sciences *Mechanistic insights into Z-selectivity in (photo)catalytic retinoid synthesis*
10:20		**Coffee break**
10:50		Session 8 - Chair: Jozef Noga
10:50	I10	**Ágnes Szabados** – Eötvös Loránd University *Ring Coupled Cluster Doubles at the Multireference Level*
11:30	C14	**Monika Musiał** – University of Silesia in Katiwice *Intruder-free Fock space multireference coupled cluster method in the molecular studies*
11:50	C15	**Zsuzsanna Mihálka** – Eötvös Loránd University *Half-projection applied to the strongly orthogonal geminal product wavefunction*
12:10	C16	**Michal Przybytek** – University of Warsaw *Dispersion energy of symmetry-adapted perturbation theory from the explicitly correlated F12 approach*
12:30		**Lunch**
14:00		**Free afternoon**
19:30		**Get together**
20:00		**Conference dinner**

Thursday, 12. September

09:00		Session 9 - Chair: Miroslav Iliaš
09:00	I11	**Attila Császár** – Eötvös Loránd University *Quasistructural molecules*
09:40	C17	**Petr Slavíček** – University of Chemistry and Technology Prague *The concept of error in computational spectroscopy*
10:00	C18	**Siba Suliman** – Comenius University *Microhydration of HOIO: structural and thermochemical properties of* $HOIO + n\ H_2O\ (n = 1\ \text{-}4)$
10:20		**Coffee break**
10:50		Session 10 - Chair: Peter Surjan
10:50	I12	**Mariana Derzsi** – Slovak University of Technology *Exploring crystal chemistry of silver(II) with DFT modelling*
11:30	C19	**Janos Daru** – Ruhr-Universität Bochum *Restricting solvation to two dimensions: soft landing of microsolvated ions on inert surfaces*
11:50	C20	**Tibor Nagy** – Hungarian Academy of Sciences *A novel, thermodynamics-based objective function for the parameterization of molecular mechanics force fields*
12:10	C21	**Tomáš Hrivnák** – Comenius University *The rigorous local field approach for the effective calculation of linear and nonlinear optical properties of solvated systems*
12:30		**Lunch / Departure**

Abstracts
Invited Speakers

I1

Matrix Product States for Electronic and Vibrational Structure

M. Reiher[1]

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In my talk, I will describe our recent work on the density matrix renormalization group (DMRG) algorithm that optimizes wave functions in matrix-product-state format. We developed theory and algorithms for the representation of many-particle wave functions in electronic and nuclear structure theory. Our most recent developments comprise vibrational DMRG, variants of time-dependent DMRG, and DMRG for targeted excited-state calculations.

For references see our webpage www.reiher.ethz.ch

Orbital entanglement analysis of magnetically coupled transition metal complexes

C. J. Stein[1], D. A. Pantazis[2], V. Krewald[3]

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[2]*Max Planck Institute for Coal Research, Kaiser-Wilhelm-Platz 1, 45470 Mülheim/Ruhr, Germany*

[3]*Technische Universität Darmstadt, Alarich-Weiss-Str. 4, 64287 Darmstadt, Germany*

Exchange coupling interactions between open-shell ions in polynuclear transition-metal complexes define key magnetic and spectroscopic properties of these systems. The metal coordination environment, especially the bridging ligands, determine the nature and magnitude of the magnetic coupling. The interpretation of experimental data is guided by fits to phenomenological models, and is often supported by density functional theory (DFT), in particular broken-symmetry DFT (BS-DFT). However, the quality of the theoretical predictions with BS-DFT strongly depends on the density functional chosen and thus relies on extensive calibration studies. Moreover, BS-DFT is not systematically improvable and can only predict the sign and total span of spin ladders but not the exact nature of the magnetic coupling paths.

Multireference quantum-chemical calculations are in principle capable of describing each individual spin state arising from magnetic coupling of open-shell ions. With the advent of density matrix renormalization group (DMRG) the description of realistic systems with multiple centers and many unpaired electrons has become viable.[1,2] DMRG thus has the capacity to provide a thorough understanding of the magnetic coupling mechanisms in experimentally relevant transition metal complexes.[3,4]

Here, we present a simple analytic tool that allows us to identify exchange coupling pathways in polynuclear transition metal complexes from a wavefunction constructed in a polarized pseudo atomic orbital basis.[5] This tool is based on an entanglement analysis of the interacting orbitals in the DMRG wavefunction. The orbital entanglement analysis constitutes a visually intuitive comparison of the magnetic interactions among different structures and coordination environments. The capabilities of the entanglement analysis are showcased with a series of manganese dimers with different bridging ligands.

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[2] C. J. Stein, M. Reiher, J. Chem. Theory Comput. 2016, 12, 1760-1771.
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[4] V. Krewald, D. A. Pantazis, in Transition Metals in Coordination Environments: Computational Chemistry and Catalysis Viewpoints (Eds.: E. Broclawik, T. Borowski, M. Radoń), Springer International Publishing, Cham, 2019, pp. 91-120.
[5] C. J. Stein, D. A. Pantazis, V. Krewald, "Orbital Entanglement Analysis of Exchange-Coupled Systems", *submitted*.

I3

Spinning around in Transition Metal Chemistry

Maja Gruden[1]

[1] *University of Belgrade-Faculty of Chemistry, Studentski trg 12-16, 11001 Belgrade, Serbia*

Elucidating the role and effect of different spin states on the properties of a system is presently one of the most challenging endeavors both from an experimental and theoretical point-of-view. Computational studies, including Density functional theory (DFT) have shown that a correct description of the spin state is not trivial, and it is not always straightforward to predict the orbital occupation pattern. Although the DFT, in principle, gives an exact energy, a universal functional is still unknown, leading to density functional approximations (DFAs).

For the reliable prediction of the correct spin ground state from a number of close lying states, OPBE, SSB-D and S12g have emerged to be one of the best DFAs for the task. Some of our recent validation studies [1-3] on a diverse class of first row transition metal complexes in different oxidation states, as well as, rationalization of the connection between the spin state and the structure, properties and reactivity will be presented. For the excitation energies TD-DFT together with Ligand-Field DFT have been used.

The reaction mechanism of the catechol cleavage catalysed by biomimetic iron complexes with L-N_2H_2 and L-N_2Me_2 ligands, with all accessible spin states and two possible pathways, intradiol and extradiol, will be discussed. Using the validated level of theory in previous studies, we have elucidated the mechanism of the catalytic cycle for two biomimetic complexes, and explained the difference in the experimentally obtained products [4].

Furthermore, applicability of density functional tight binding (DFTB) to transition metal ions will be discussed .

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[2] M. SWART, M. GRUDEN: Acc. Chem. Res. **49**, 2690-2697, (2016).

[3] C. DAUL, M. ZLATAR, M. GRUDEN-PAVLOVIC AND M. SWART: *Application of Density Functional and Density Functional Based Ligand Field Theory to Spin States,* Book chapter in Spin states in biochemistry and inorganic chemistry: Influence on Structure and Reactivity, Wiley, (2015)

[4] S. STEPANOVIC, D. ANGELONE, M. GRUDEN AND M. SWART: Org. Biomol. Chem., **15**, 7860-7868, (2017)

Understanding Complex Systems with High-Dimensional Neural Network Potentials

J. Behler

[1]*Institute for Physical Chemistry, Theoretical Chemistry, Georg-August-Universität Göttingen, Tammannstr. 6, 37077 Göttingen, Germany*

A lot of progress has been made in recent years in the development of atomistic potentials employing machine learning (ML) [1]. In contrast to most conventional potentials, which are based on physical approximations to derive an analytic functional relation between the atomic configuration and the potential energy, ML potentials rely on simple but very flexible mathematical terms without a direct physical meaning. Instead, in case of ML potentials the topology of the potential energy surface is "learned" by adjusting a number of parameters with the aim to reproduce a set of reference electronic structure data as accurately as possible. Due to this bias-free construction they are applicable to a wide range of systems without changes in their functional form, and a very high accuracy close to the underlying first-principles data can be obtained.

Neural network potentials (NNPs), which have first been proposed about two decades ago [2], are an important class of ML potentials. While the first NNPs have been restricted to small molecules with only a few degrees of freedom, they are now applicable to high-dimensional systems containing thousands of atoms [3,4], which enables addressing a variety of problems in chemistry, physics and materials science. In this talk the fundamental concepts of NNPs are discussed with a special focus on constructing NNPs for high-dimensional condensed systems. Applications for different types of systems, from bulk materials via liquid water to processes at interfaces are presented.

[1] J. BEHLER: Perspective: Machine Learning Potentials for Atomistic Simulations, J. Chem. Phys. **145**, 170901, (2016)
[2] T. B. BLANK, S. D. BROWN, A. W. CALHOUN, D. J. DOREN: Neural Network models of potential energy surfaces, J. Chem. Phys. **103**, 4129-4137, (1995)
[3] J. BEHLER, M. PARRINELLO: Generalized neural-network representation of high-dimensional potential-energy surfaces, Phys. Rev. Lett. **98**, 146401, (2007)
[4] J. BEHLER: First Principles Neural Network Potentials for Reactive Simulations of Large Molecular and Condensed Systems, Angew. Chem. Int. Ed. **56**, 12828, (2017)

I5

Molecular dynamics with non-adiabatic and spin-orbit effects

Marek Pederzoli, Wasif Baig-Mirza, Lukasz Cwiklik, and Jiří Pittner
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Molecular dynamics (MD) represents an important tool for modeling of the behavior of molecular systems in time. When applied to problems from photochemistry, a treatment of excited states and crossings between different potential energy surfaces has to be incorporated in the MD scheme. We present efficient techniques which allow to approximately compute the non-adiabatic couplings and perform surface hopping MD with CASSCF, MRCI, TDDFT, and ADC(2) methods. The performance of the non-adiabatic MD is illustrated on the examples of photoizomerization of azobenzene and internal conversion of excited adenine.

We present also surface hopping dynamics on potential energy surfaces resulting from the spin-orbit splitting, i.e., surfaces corresponding to the eigenstates of the total electronic Hamiltonian including the spin-orbit coupling. In this approach, difficulties arise because of random phases of degenerate eigenvectors and possibility of crossings of the resulting mixed states. Our implementation solves these problems and allows propagation of the coefficients both in the representation of the spin free Hamiltonian and directly in the “diagonal representation” of the mixed states. As a test case, we applied our methodology to deactivation of thiophene and selenophene in the gas phase, ethanol solution, and bulk liquid phase.

We also studied halogenated BODIPY derivatives, which are emerging as important candidates for photodynamic therapy of cancer cells due to their high reactivity in triplet states. Unsubstituted BODIPY has no phosphorescence activity, indicating no transition to triplets after excitation to a singlet state, while incorporation of heavy halogen atoms in its molecule makes BODIPY highly phosphorescent. It can be assumed that the presence of halogen atoms induces spin-orbit coupling resulting in a higher rate of intersystem crossing from the excited singlet state to the low lying triplet states thus leading the experimentally observed high phosphorescent activity. In order to fully understand the excited state dynamics of these systems regarding the influence of halogen atoms, we performed surface hopping molecular dynamics simulations including the spin-orbit effects [3].

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[1] Plasser F., Crespo-Otero R., Pederzoli M., Pittner J., Lischka H., Barbatti M.: J. Chem. Theor. Comp. 10, 1395 (2014)

[2] Pederzoli M., Pittner J.: J. Chem. Phys. 146 114101 (2017)

[3] Marek Pederzoli, 1,2 Mirza Wasif Baig, 1,2 Mojmir Kyvala, 3 Jiri Pittner, 1* Lukasz Cwiklik, JCTC, submitted (2019)

I6

The role of anharmonic corrections in conformational analysis of flexible molecules

M. Biczysko[1]

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Conformational analysis represents a first step toward a detailed characterization and understanding of the structure-function relationships of molecular systems. In this respect spectroscopic experiments on isolated bio- and organic-molecules allow detection of different binding schemes and three-dimensional (3D) conformations without perturbing effects of environment. Detection of multiple 3D-geometries concomitantly present in an experimental mixture can be facilitated by “in situ” structural changes induced either by thermal variations, or the interaction with near-IR (NIR) to ultraviolet (UV) light. These sophisticated experiments need to be supported by accurate and reliable computational studies allowing to link the rich experimental data to the desired information on the structure and properties of complex molecular systems.

Computations based on the second order perturbation theory (VPT2) allow accounting for the anharmonicity of both wave function and properties. This results in a correct description of the intensity of non-fundamental transitions and more accurate band-shapes. Moreover, the same anharmonic force fields as employed in the determination of vibrational spectra allow considering vibrational corrections to molecular properties or thermodynamic functions. The most reliable structural, spectroscopic and energetic results can be obtained combining various computational methods ranging from density functional theory (DFT) to coupled cluster (CC).

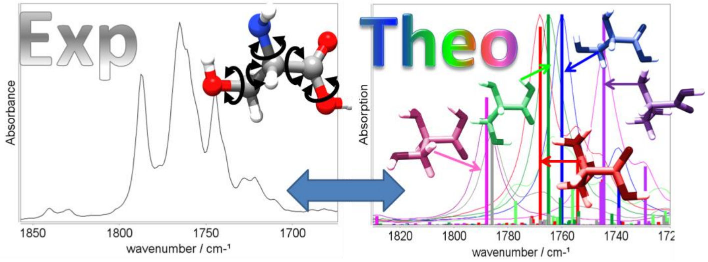

Figure 1: Computed spectra of different conformers help to analyze experimental data.

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[2] H. ZHANG, J. KRUPA, M. WIERZEJEWSKA, M. BICZYSKO: The role of dispersion and anharmonic corrections in conformational analysis of flexible molecules: the allyl group rotamerization of matrix isolated safrole, Phys. Chem. Chem. Phys. **21**, 8352-8364 (2019)

Relativistic theory for prediction of excitation energies of both closed- and open-shell species

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The accurate prediction of absorption and emission spectra of heavy-element containing compounds requires inclusion of both scalar and spin-orbit (SO) relativistic effects into consideration. At the scalar relativistic level of theory, the triplet states are degenerate and thus the singlet-triplet transitions are forbidden by the symmetry. However, when SO effects are included into the description of the system, the triplet degeneracy is lifted [so-called zero-field-splitting effect] and the singlet-triplet transitions become possible. Thus, the inclusion of SO into consideration is, for example, crucial in the description of photochemical properties of organic light-emitting diodes (OLEDs), in the prediction of L-edge X-ray spectra, or other spin-related phenomena in magnetic materials.

In this contribution, the relativistic four-component method for calculation of the excitation energies in the framework of time dependent density functional theory (TDDFT) will be presented.[1] The method treats relativistic effects on equal footing across periodic table of elements, and it is therefore ideal for performing accurate benchmark calculations. The implementation of approaches in our in-house ReSpect program allows treatment of systems with up to 100 atoms [2], which makes the method suitable for routine prediction of electronic spectra of heavy-atom containing systems.

The main outcome of this work is the use of the Kramers-restricted as well as Kramers-unrestricted reference states in TDDFT approach. The achievement of this important goal required two major improvements of existing TDDFT methodologies. First, a new algorithm for solving large eigenvalue problems had to be developed, since the commonly used algorithm was exhibiting poor convergence or did not converge at all. Second, the DFT potential and kernel resulting from the Scalmani and Frisch noncollinear ansatz [3] has been regularized to ensure correct behavior in limit cases involving small spin densities and small spin density gradients.

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[2] ReSpect, version 5.1.0 (2019) − Relativistic Spectroscopy DFT program of authors S. KOMOROVSKY; M. REPISKY; V. G. MALKIN; O. L. MALKINA; M. KAUPP; K. RUUD, with contributions from R. BAST; U. EKSTROM; M. HRDA; M. KADEK; S. KNECHT; L. KONECNY; A. KŘÍSTKOVÁ; E. MALKIN; I. MALKIN-ONDIK; R. DI REMIGIO. See www.respectprogram.org, (accessed July 26, 2019).
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I8

Computation of NMR chemical shifts in phosphorylated intrinsically disordered proteins: challenges and limitations

J. Pavlíková Přecechtělová[1,2], A. Mládek[1], V. Zapletal[1], J. Hritz[1]

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Computed chemical shifts (CSs) enable experimentalists to determine the ensemble of structures that reflect the flexibility of intrinsically disordered proteins (IDPs) and that are in accordance with experimental nuclear magnetic resonance (NMR) data. The reliable calculation or prediction of CSs is therefore a prerequisite for a successful structure characterization of phosphorylated IDPs that regulate a vast range of processes leading to neurodegenerative diseases.

The calculation of CSs by quantum chemistry methods poses many challenges that stem from the flexibility and complexity of IDPs as well as from methodological limitations or referencing problems. In this lecture, we will present our quest [1] for the design of a multiscale computational protocol that builds on the combination of (i) structural ensembles generated by molecular dynamics, (ii) a fragmentation technique based on the adjustable density matrix assembler [2], and (iii) density functional methods.

We will demonstrate the effects of conformational averaging, explicit solvent sampling, statistical sample size as well as the effects of a basis set and phosphorylation on the computed CSs. Our results indicate that good to great quantitative agreement with experiment is achieved for all nuclei provided that the systematic error is balanced by the choice of a suitable NMR standard. The lecture will reflect on the potential of the computational protocol to serve as an alternative to empirical prediction tools in the structure characterization of IDPs by NMR spectroscopy.

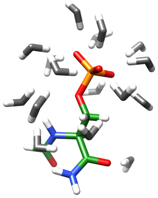

Figure 1: *Phosphorylated serine fragment embedded in the surrounding explicit solvent.*

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I9

Mechanistic insights into *Z*-selectivity in (photo)catalytic retinoid synthesis

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[2]*Gavin Herbert Eye Institute and the Department of Ophthalmology, University of California, Irvine, California, USA 92697*

[3]*Department of Pharmacology, Case Western Reserve University, Cleveland, Ohio, USA 44106*

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Polyene retinoids are an important class of biologically active molecules involved in many facets of human physiology. The geometric configurations of retinoids have enormous impact on their chemical and biological properties. For example the *Z*-isomeric form of retinal plays an important role as a chromophore of rod and cone photoreceptor cells in the visual cycle. Genetic or environmental factors affecting chromophore production can lead to diseases of the retina and eventually blindness. Pharmacological interventions by means of *Z*-isomers of retinal and retinyl acetate are used to maintain vision in inherited retinal degenerative disease [1].

We recently developed three paths to access such biologically relevant 9-*cis* and 13-*cis* retinoid derivatives: (a) palladium-based catalytic approach [2], (b) direct monochromatic photoisomerisation [3] and (c) photocatalytic isomerization using iridium catalyst [3]. The single-step protocols are easily scalable and allows for gram-scale synthesis of the Z-isomers. However, depending on the method and the nature of all-*trans* substrate various distributions of *Z*-isomers were observed.

To understand the distribution of the products we carried out extensive quantum chemical calculations [2,3]. Our multi-level approach include geometry optimizations at the density functional theory (DFT) level, single-point energy rafinements at the local coupled-cluster level and excitation energies calculations at the (simplified) time-dependent DFT level. In the case of catalytic reaction we showed that the active catalyst exists in a dimeric form and the reaction proceeds via six-membered chair-like chloropalladate intermediate. We related the distribution of photochemical products with the relative energy ordering of the intermediates at the excited potential energy surface. In addition, we developed the "local polarization change" (LPC) model that explains photoisomerisation product distribution using only HOMO and LUMO atomic populations.

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I10

Ring Coupled Cluster Doubles at the Multireference Level

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Accurate treatment of molecular systems of inherently multireference (MR) nature routinely involves a correction step incorporating electron correlation based on a multideterminantal initial wavefunction. Correlation correction within the MR coupled cluster (CC) framework put forward by Mukherjee et al.[1] is examined in this work. The corrected wavefunction is parametrized by applying internally connected excitations on the reference. Contractions among cluster operators is avoided by adopting a normal ordered exponential Ansatz. Derivation of the equations is based on generalized normal ordering and applies the corresponding generalized Wick-theorem.

Main challenges of the theoretical approach are presented by redundancy among excited functions and by the myriad of cumulant involving contractions arising from the generalized Wick-theorem. The latter issue is addressed by adopting a generalization of the ring approximation of the CCD equations, that can accommodate cumulant rank of four at maximum. Generalized valence bond type reference function represents an additional benefit, due to the corresponding cumulants possessing a fragment structure. Treatment of linear dependence, ignored in the original formulation[2], is performed akin to frame theory, removing any need for a selection scheme among excited vectors.

The method shows kinship with the MR based extension of the random phase approximation (ERPA), developed by Pernal[3], both featuring 6th order scaling. Numerical comparison is presented for torsional potentials, covalent bond breaking and for weakly interacting closed shell systems.

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Quasistructural molecules

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The notion of molecules and structures is central to our chemical understanding. One seemingly useful definition of molecules is that they correspond to minima on potential energy surfaces (PES) and the local PES must support at least one bound rovibrational state. The structure of a molecule is usually considered to be the geometry corresponding to the minimum. If a molecule exists and has a structure, it is also commonly accepted that its internal motions can be separated into vibrations and rotations, motions which usually have very different time and energy scales.

Nevertheless, there are chemical systems where both the notion of a molecule, that of a structure, as well as the separation of rotational and vibrational motion can be questioned. The lecture is centered around molecular ions and complexes where the concept of a structure and the separation of vibrations and rotations seems to break down, yielding a quasistructural molecular system with associated highly unusual nuclear dynamics [1]. All of the following characteristics should hold, for a smaller or larger extent, for a molecular system to be considered quasistructural (from a high-resolution spectroscopic point of view): (a) the notion of a static equilibrium structure, corresponding to a minimum on the potential energy surface of the molecule, loses its strict meaning, (b) internal nuclear motions (rotations and vibrations) become dominant, resulting in an effective molecular structure often even qualitatively different from the equilibrium one, (c) separation of the internal nuclear motions breaks down, rotational and vibrational degrees of freedom cannot be separated from each other when interpreting even the lowest rovibrational states of the molecule, resulting in effective rotational constants drastically different from the equilibrium ones even for the ground vibrational state, (d) classification of the rovibrational states requires the use of permutation-inversion symmetry and molecular-symmetry groups, and (e) some of the rovibrational eigenenergies assigned to a vibrational parent state exhibit unconventional (in the most striking cases “negative”) rotational contributions.

Sophisticated tools characterizing the fourth age of quantum chemistry [2] are able to yield a quantitative understanding of the energy level structure and the high-resolution spectra of quasistructural molecules but it is certainly of interest to develop new models, also described in the lecture, to aid the qualitative understanding of nuclear motion dynamics of quasistructural molecules.

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Exploring crystal chemistry of silver(II) with DFT modelling

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In this talk I will discuss the contribution that DFT modelling has made in the recent decade to our understanding of inorganic crystals containing divalent silver. Our interest in Ag^{2+} stems from its hidden potential to form extended crystal lattices of strongly covalent character that are intimately linked to rich electronic and magnetic properties of its compounds. Its chemistry has been almost exclusively restricted to fluoroargentates, because fluorine as the most electronegative element in the Periodic Table seems to be the best match for Ag^{2+} in chemical bonding. In our ongoing pursuit for novel compounds with Ag^{2+} we have been exploring various possibilities of fluoroargentates(II) to from extended crystal lattices and have been mapping new grounds for yet novel inorganic compounds beyond fluorides. From the very beginning our quest has been guided by DFT modelling. It has played crucial role in prediction and subsequent identification of newly synthetized phases and reviled to us excitingly rich crystal chemistry of this elusive cation [1–4]. Broadening the crystal chemistry of Ag^{2+} paves the way for diversity of electronic phenomena that has been for a long restricted exclusively to precursors of high-temperature superconducting copper oxides [5].

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Abstracts
Contributed Talks

C1

Studying ultrafast photorelaxation in functional Fe(II) complexes

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The photodynamics of functional complexes of the abundant and environment-friendly iron is nowadays in the forefront of ultrafast science. Spin-transition complexes showing light induced spin-state trapping, such as $[Fe(terpy)_2]^{2+}$ (terpy = 2,2′:6′,2″-terpyridine) with long high-spin state lifetime, are potential candidates for photo-switchable elements[1], while other complexes, such as $[Fe(bmip)_2]^{2+}$ (bmip = 2,6-bis(3-methyl-imidazole-1-ylidene)-pyridine) with long metal-to-ligand charge transfer state lifetime, could be utilized as photosenzitizers.[2] Photorelaxation dynamics of these complexes are studied experimentally among others by transient absorption spectroscopy and time-resolved X-ray scattering. We present results of time-dependent density functional theory computations and determine such observables from quantum wavepacket dynamics simulations via the Multiconfigurational Time-Dependent Hartree method on fitted potential energy surfaces in order to rationalize experimental findings on these species.[3]

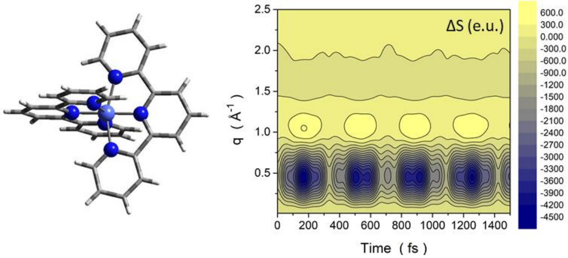

Figure 1: Structure of a photo-switchable $[Fe(terpy)_2]^{2+}$ and computed time-resolved difference X-ray scattering signal for vibrational dynamics in its lowest quintet state initiated where the wavepacket is supposed to enter into the quintet manifold.

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C2

Exploring the mechanism of biomimetic nitrogen fixation and its side reactions

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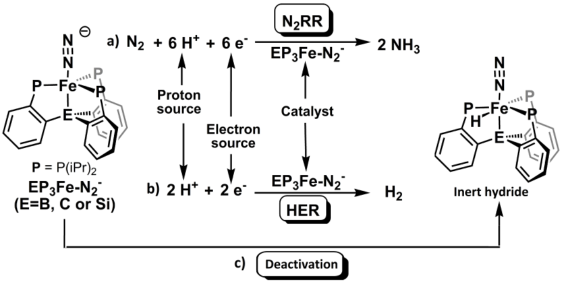
Synthetic iron nitrogenases (Figure 1, left) are promising novel catalysts for ammonia synthesis [1]; these bioinspired single-site metal complexes catalyse the reduction of N_2 (N_2RR; Figure 1a) under atmospheric pressure, which is a significant advantage compared to the traditional Haber-Bosch-process. However, this catalytic system has two major drawbacks which hinders any practical application. Firstly, the catalysts are not selective as they also facilitate the undesired hydrogen evolution reaction (HER; Scheme 1b). Secondly, the catalyst complex deactivates quickly due to the formation of inert hydride side products (Figure 2c).

In order to create an industrially applicable molecular catalyst (which is the long term goal of ongoing researches), the lifetime and N_2RR vs HER selectivity needs to be dramatically increased. This can only be achieved by a rational, theory (QM) based re-design of the ligand scaffold.

Figure 1: Structure and reactivity of biomimetic ammonia synthesis catalysts



In this computational study, we compare the thermodynamics and kinetics of conceivable “on-path” (N_2RR) and “off-path” (deactivation, HER) elementary steps by means of DFT-D calculations. Based on the obtained Gibbs free energy profiles, along with the discussion of the available experimental data, we determine which of the mechanisms can be competent under the reported catalytic conditions.

Our results [2,3] revealed that the most probable HER route involves protonation of iron hydrides, which immediately suggests that preventing Fe-H bond formation (e. g. by additional steric protection of the iron center) can be a successful strategy for enhancing both lifetime and selectivity.

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Ab Initio Description of Heterogeneous Catalysis - Monomolecular Alkane Cracking over H-MFI Zeolite

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The catalytic activity of protonated zeolites is driven by bridging Al-O(H)-Si groups which represent Brønsted acid sites. At low conversions, the alkane cracking over acidic zeolites mainly follows the monomolecular mechanism,[1] where hydrocarbon molecules are protonated and undergo C–C bond scission, yielding shorter alkanes and alkenes. Kinetic experiments provide the so-called “apparent” enthalpy barrier of this process, which consists of the “intrinsic” enthalpy barrier and the enthalpy of alkane adsorption.

The dependence of the intrinsic enthalpy barrier on the alkane chain-length in monomolecular cracking has been debated in the literature. Most researchers conclude that the intrinsic enthalpy barrier is constant for all *n*-alkanes,[2] whereas a recent density functional theory (DFT) study shows that this barrier decreases with increasing number of carbon atoms.[3] *Ab initio* quantum chemistry may explain this ambiguity, but is useful only when energy barriers are predicted with chemical accuracy (4 kJ/mol). This was recently achieved using multi-level CCSD(T):MP2:PBE+D2 calculations for the proton exchange barriers in the presence of n-alkanes in H-MFI zeolite.[4]

We investigate here the monomolecular cracking of n-alkanes (propane, n-butane, n-pentane, and n-hexane) over the zeolite H-MFI, using the multi-level CCSD(T):MP2:PBE+D2 methodology. We calculate intrinsic and apparent enthalpy barriers together with adsorption enthalpies. The adsorption enthalpies of alkanes are calculated using either static approach within harmonic approximation or dynamic hybrid approach, in which enthalpies of alkane adsorption are calculated from molecular dynamics (with the PBE density functional + D2 dispersion) and are refined by MP2 corrections obtained from cluster calculations of selected structures (“frames”) along the simulated trajectories. Our studies show that the intrinsic enthalpy barrier depends strongly on how the adsorption enthalpy is calculated. The static approach provides the intrinsic enthalpy barriers, which are independent of the hydrocarbon chain-length, whereas the dynamic approach results in barriers that decrease with increasing carbon number. This ambiguity originates mainly from the difference in dispersion contributions to the adsorption enthalpy calculated using two alternative approaches.

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C4

Potential energy curves using machine learning configuration interaction

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Machine learning is of rapidly increasing interest in many fields and quantum chemistry is no exception to this. In this context its use has often involved interpolating and extrapolating potential energy surfaces for dynamics calculations. Recently a different approach was proposed [1] where machine learning is used to accelerate the calculation of the wavefunction in a selected configuration interaction computation, rather than estimate points on a potential energy curve. In this machine learning configuration interaction (MLCI) an artificial neural network learns on the fly to predict important configurations in a calculation that iteratively constructs a compact wavefunction. It has been demonstrated, for small molecules and basis sets, that a prototype MLCI is competitive with stochastic or perturbative ways of selecting configurations and can be faster for higher-accuracy calculations [1].

The further development of MLCI has included using the machine learning predictions as a hash function so that it is not limited by the need to store all of the possible single and double substitutions in memory when efficiently removing duplicates. This improved method is discussed then demonstrated to be faster when compared with the original method or random selection of configurations.

By also adapting MLCI to use configuration state functions then pure spin states can be guaranteed. This approach is then used to compute challenging potential energy curves and the transferability of the artificial neural networks is investigated. Results for N_2 when using the cc-pVDZ basis are displayed in Figure 1 where we find that a curve of essentially full configuration interaction (FCI) quality can be calculated in three hours on one processor.

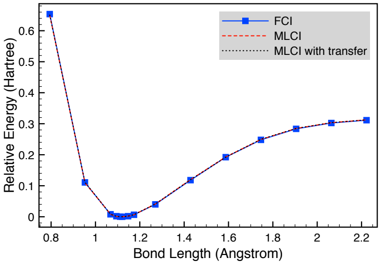

Figure 1: *Potential energy curve for N_2 when setting all minima to zero.*

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Machine Learning for Excited State Dynamics: Fitting Multi-Dimensional Potentials for Energies, Forces, and Couplings

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Providing high accuracy at low computational costs is one of the main and long-lasting goals of many new ab-initio methods. Recently, machine learning algorithms have been increasingly used to address this problem and predict energies as well as forces with quantum chemical precision within milliseconds. However, excited state ab-initio molecular dynamics simulations still face another problem due to the fact that not only one potential energy surface has to be treated, but several electronic states including the couplings between them. Therefore long dynamics simulations with high accuracy were out of reach. In this work, we avoid the bottleneck of costly ab-initio calculations and train machine learning models on the potential energy surfaces of excited states, corresponding forces and couplings to enable long time scale simulations. As an example we show the surface hopping molecular dynamics simulations of the methylenimmonium cation executed with the program suite SHARC (Surface Hopping including ARbitrary Couplings) [1] for 1 ns, for which the quantum chemical simulation would have taken an estimated ~19 years. [2] We provide a framework on how to generate the training set [3] and encode the electronic state to increase the accuracy of a many-state machine learning potential for energies. As machine learning models, we use multi-layered feed-forward neural networks [2,4] and kernel ridge regression [4,5], which show the scopes and different possibilities of machine learning models for the treatment of excited state potential energy surfaces and their corresponding properties.

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C6

Towards ab-initio surface-hopping dynamics with a density matrix renormalization group self-consistent field approach

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Nonadiabatic surface-hopping dynamics[1, 2, 3] is an established method of studying photophysical and photochemical processes in medium to large molecules. Its accuracy depends on the reliability of the underlying electronic structure method, and often, multiconfigurational electronic structure methods will be required, especially if the processes in question involve relaxation to the ground state.[4] Traditionally and most commonly, the state-average complete active space self-consistent field method (SA-CASSCF) is used (see, for instance, Ref. 5), whose exponential scaling with the number of active orbitals greatly limits the size of the molecules that can be studied. However, the density matrix renormalization group (DMRG) is now an established remedy for the exponential scaling problem of multiconfigurational methods, and the DMRG-SCF method has been successfully employed for active orbital spaces beyond the reach of CASSCF.[6, 7]

In this contribution, we present an efficient implementation of analytic state-average gradients and interstate non-adiabatic coupling vectors for state-average DMRG-SCF wavefunctions, paving the way to nonadiabatic surface-hopping dynamics with DMRG-SCF.[8]

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C7

Prediction of excited state properties for sizable molecular systems including spin-orbit effects

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We will present our efforts to expand the usability of the quasirelativistic two-component (2c) hybrid time-dependent (TD)-DFT method and the GW method in combination with the correlation-augmented Bethe-Salpeter equation (GW/cBSE) to calculate properties of large molecules containing heavy elements [1,2]. For the properties of these compounds spin-orbit effects can often not be neglected if a quantitative description is sought for. To allow for calculations of 2c quasirelativistic excitation energies of molecules with hundreds of atoms the resolution-of-the-identity algorithm (RI-K) and seminumerical algorithms for the complex exchange were implemented. Further the 2c extension of the current-dependent metaGGA response [3] formalism was implemented. This is crucial for a quantitative description of antiferromagnetic coupled systems or current-carrying states, where the current is induced by spin-orbit coupling itself or external fields, e.g. magnetic fields. Finally, a tool converting theoretical and experimental spectra to common variables known by workers in both fields (e.g. RGB colour codes) was developed within the TURBOMOLE program package to allow for a rapid comparison between experimental and theoretical data. The presentation will aim at describing the formalism of the implemented methods and approximations described above as well as comparing the obtained results to high-level ab-initio data (e.g. 2c coupled-cluster schemes) and experimental results.

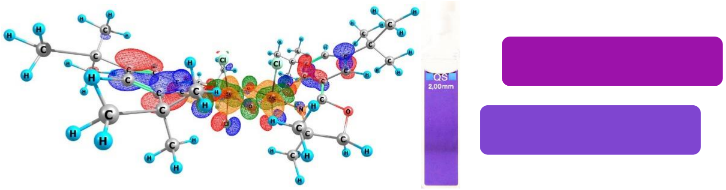

Figure 1: *Figure 1: left: trial molecule, middle: picture of measured sample, upper right: calculated color (2c GW/cBSE@PBE0) from a possible trial compound, lower right: measured color from sample compound.*

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C8

The Förster energy transfer in metal organic frameworks

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Metal organic frameworks are promising materials with many applications in photoelectronics, sensoring and other fields. The benefit of these materials is the well-known 3D structure, which provids control of distance and relative orientation of the optically active linker molecules. Recently, Haldar et al. [1] showed experimentally an efficient anisotropic energy transfer in Zn-SURMOF2 with different lifetimes explained as monomer-based and exciton-based processes, respectively.

This presentation tries to provide a deeper, theoretical understanding of the excited state formation and the Förster energy transfer in Zn-SURMOF2 containing anthracene-dibenzoic acid as organic linkers. We will show that the anthracene unit of the organic linker and its orientation play a key role in the energy transfer.

In our work, a combined periodic and molecular oligomer approach is chosen to describe the MOF by selecting suitable linker-node units for which quantum chemical simulations of the ground and first excited state are performed. The Coulombic coupling as a measure of the energy transfer rate is then obtained applying the Transition-Density-Cube (TDC) method, as presented by Krueger et al. [2] For two different phases of the SURMOF2, we studied the electronic coupling along several hopping routes with specific focus on the anthracene moiety orientation. Regarding the exciton localization in dependence of the direction, we analysed the electron-hole correlation of several oligomers.

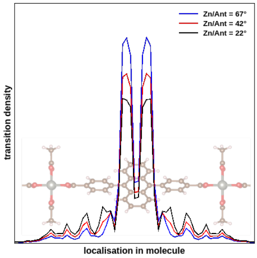

Figure 1: Tilt-angle dependency of the transition density

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C9

A Song of Light and Life. From Molecular Modeling to *in silico* Photobiology

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The interaction between light and different biological systems represents a crucial phenomenon in biology and is notably responsible of many fundamental outcomes related to signaling as well as energy conversion and storage. Light is indeed essential to assure life as we know it. On the other hand light may also represent an external stress producing harmful effects related most notably to cancer development.

In this talk we will, through a series of examples mostly related to DNA photolesions induction and repair, illustrate the crucial role played by molecular modeling and simulation in elucidating such processes. We will also illustrate the crucial need of tackling multiscale phenomena taking into account at the same time complex electronic structures and their interplay with dynamical sampling and time evolution in complicated biological macrostructures.

By using appropriate and high level molecular modeling and simulation strategies we will prove that the scientific field is nowadays ready to provide answers to, and hence rationalize, biological questions related most notably to mutation, DNA replication, and cell resistance to stress.

Hence, we will prove that we are clearly leaving the age of the simulation in model systems to enter into the age of a veritable *in silico* photobiology.

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C10

Calculating ionization energy in condensed phase using a QM:QM method

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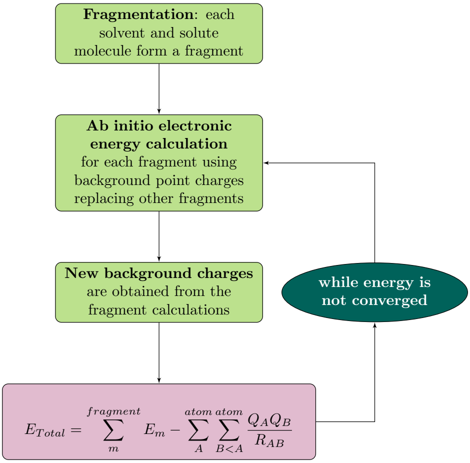
We aim to reliably describe singly and doubly ionized states in the condensed phase. The final goal is to model Auger decay and related processes such as Intermolecular Coulomb Decay (ICD). Standard ab initio calculations are not feasible due to the unfavorable scaling of the computational cost with the size of the system. Applicability of dielectric models is limited for highly charged systems. Another alternative is to use QM/MM approaches which however typically do not explicitly account for electronic polarization.

To calculate vertical ionization energies we propose a simple energy based fragmentation method where each fragment is treated separately and self-consistence is achieved within Coulombic interaction. The scheme is shown on the figure below.



We have tested the approach both for single and double ionization. We started with a simple case of nucleic acid bases ionized in water environment. We show the conceptual advantage of the QM:QM approach over both large scale DFT calculations and electrostatic embedding QM:MM calculations. Next, we will discuss different doubly charged states of LiCl water solution. This study is motivated by recent experimental observation of non-local Auger processes in this system upon the ionization of lithium 1s electron[1].

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C11

Photochemistry in Helium Droplets: State-Dependent Solvation Effects in $Cs_2He_n^+$

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Helium is used as a convenient tag molecule in ion spectroscopy. Despite their low adsorption energy, helium atoms might considerably influence electronically excited states or induce isomeric broadening.[1] Here, we present an experimental-theoretical study of helium-solvated cesium dimer cation. We observe unexpectedly high excitation energy shifts induced by helium atoms and show that these shifts can be used to analyze solvation patterns as well as the excited state character.

Three absorption bands are observed in Cs_2^+ within 3 eV, see Figure 1a. Position and shape of the bands are quantitatively reproduced using both single-reference and multi-reference methods and spin-orbit calculations (Figure 1b), employing reflection principle for spectrum modeling. Upon solvation, the excitation energy into $1^2\Sigma_u^+$ and $2^2\Pi_u$ states increases considerably, with a shift of more than 0.1 eV already for $Cs_2He_{10}^+$, while the $1^2\Pi_u$ state is only mildly affected. This can be rationalized by calculated solvation patterns: Cs_2^+ is preferentially solvated by helium on its ends, and diffuse target orbitals of $1^2\Sigma_u^+$ and $2^2\Pi_u$ states are deeply affected. In the $1^2\Pi_u$ state, its π-like orbital is perpendicular to the Cs-Cs axis and is not considerably altered by adsorbed He atoms.

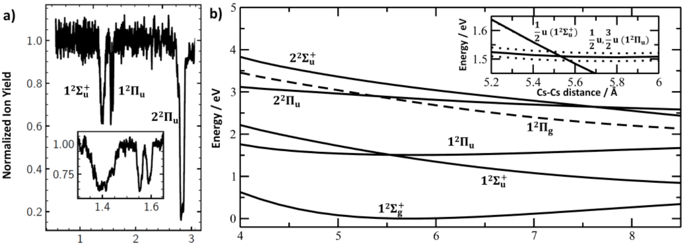

Figure 1: a) Experimental spectrum of Cs_2He^+. Note spin-orbit coupling splitting of the $1^2\Pi_u$ state in the inset. b) Potential energy curves of selected states in Cs_2^+ calculated at the EOM-CCSD/def2QZVPPD level. In the inset, spin-orbit coupling of the $1^2\Pi_u$ state is shown (dotted lines, calculated at the MRCI(1,5)/ECP46MDF level of theory).

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Tunnelling splittings in water clusters using instantons

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Ring-polymer instanton (RPI) method [1] can be used to calculate tunneling splittings between symmetric wells in high-dimensional molecular systems. It approximates the tunnelling dynamics using an optimal tunnelling path along which the quantum process predominantly takes place. The method has been generalized to treat systems with multiple wells [2]. This enabled the calculation of tunnelling splitting patterns in water clusters in full dimensionality and their interpretation through the rearrangement motions in the cluster.

The RPI method consists of three time-consuming steps: locating of the minimum action path (MAP) in full dimensionality, the calculation of hessians along the path and the calculation of the so-called fluctuation prefactor. We present our numerical methods to reduce the computational effort involved in each of the above steps.

We developed the string method [3] for locating instantons (MAPs) in order to reduce the number of path discretization points. In the quadratic string method [4], we optimize the path in local quadratic estimates of the potential energy surface (PES) to reduce the number of iterations. We also extend the Mil'nikov-Nakamura original multidimensional formulation of the instanton method [5] to treat the asymmetric paths, which regularly appear in the studies of water clusters, to avoid the matrix diagonalization in the prefactor calculation, and apply it in Cartesian coordinates, to retain the simplicity of the RPI method.

Finally, we calculate ground-state tunnelling splitting patterns in water dimer, trimer and pentamer using our methods and identify the important rearrangement motions that appear in the spectrum.

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C13

Diastereoselective Synthesis of New Isoxazoles and Pyrazoles. Experimental and theoretical study.

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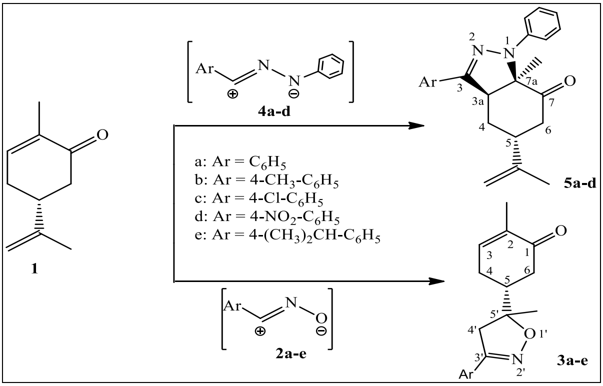
New series of chiral isoxazoles and pyrazoles with monoterpenic skeleton, have been efficiently synthesized from naturally occurring (R)-Carvone, using 1,3-dipolar cycloaddition reaction with arylonitrile oxides and diarylnitrilimines. The reaction showed high peri-, and regioselectivity. In the case of diarylnitrilimines, the reaction revealed to be highly diastereoselective. The structure of the newly synthesized adducts were fully established via spectroscopic analysis and X-ray crystallography. The theoretical study used to explain the diastereoselectivity experimentally observed fully rationalizes the experimental observations at structural, energetic and mechanistic point of view.



C14

Intruder-free Fock space multireference coupled cluster method in the molecular studies

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In this work we focus on the Fock space (FS) realization of the multireference coupled cluster (MR-CC) theory and its application in the studies of the electronic structure. The key point is the Intermediate Hamiltonian (IH) formulation which offers an easy way to replace the iterative solution of the standard Bloch equation by the direct diagonalization of the properly constructed matrix ('dressed' $\bar{H}$ called IH) with the help of the equation-of-motion CC (EOM-CC) strategy. Thanks to this we can omit all problems with the so-called intruder states which for years have blocked the wider application of this method. Majority of the results are connected with the solution of the FS problem in the two-valence sectors, e.g. (1,1) (EE - excitation energy) or (2,0) (DEA - double electron affinity). Having access to various realizations of the FS-CC approaches (EE, IP, EA, DIP, DEA, etc.) we propose a new computational strategy to calculate excited states of systems (AB), i.e. we adopt as the reference that form of the uncharged or charged analogues (AB, AB^+, AB^-, AB^{2+}, AB^{2-}, etc.) as a reference, which form a closed-shell system, avoiding the UHF (Unrestricted Hartree-Fock) reference. This strategy offers a very simple route for the calculations of excitation energies for open-shell systems, In particular the introduction of the full triples both into expansion of the T and S operators in the (1,1) sector resulted in the significant improvement of the agreement of excitation energies with the experiment for series of molecules. On the other hand, encouraging results are obtained in the studies of the dissociation of a single bond with solution based on the (2,0) sector as an indirect application of the DEA calculations.

C15

Half-projection applied to the strongly orthogonal geminal product wavefunction

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Proper description of electron correlation is a central problem of quantum chemistry. Geminal-based wavefunctions form a family of multireference functions in which the wavefunction is built from two-electron blocks. These wavefunctions possess properties that make them good reference functions for multireference correction schemes, and a lot of these frameworks have the further advantage of being cost effective. Generalized valence bond perfect pairing (GVB-PP) is one of the simplest models where all two-electron units are singlet and obey the so-called strong orthogonality condition. Unfortunately, the GVB-PP model fails to properly describe elongation of multiple covalent bonds.

To resolve this problem, triplet geminals may be incorporated in the Ansatz. Allowing singlet-triplet mixing within the geminals while keeping the strongly orthogonal framework forms a model which will be termed strictly localized geminals (SLG) here. The SLG wavefunction is in general spin contaminated, which is an undesirable feature of a reference function. Spin purity can be restored by projection to the subspace spanned by the spin eigenstates corresponding to the desired spin quantum number. Projection-after-variation often yields non-analytic, and sometimes discontinuous potential curves, and while variation-after-projection cures this problem, the method violates size consistency[1].

Since both spin contamination and lack of size consistency are unwanted for a good reference function, we seek a compromise by applying the half-projection operator[2]

$$\mathcal{A}^S = \frac{1}{\sqrt{2}}\left(1 + f\hat{\mathcal{P}}\right),$$

to the SLG function, and thus obtaining the half-projected SLG (HPSLG) wavefunction. Here S denotes the desired spin quantum number, $f = (-1)^S$ and $\hat{\mathcal{P}}$ is the spin-flip operator which exchanges the spatial parts of the alpha and beta spinorbitals. By requiring the energy of the HPSLG function to be stationary with respect to the geminal coefficients, the resulting equations can be recast as eigenvalue equations which may be solved in an iterative fashion. The properties of the HPSLG wavefunction and its applications will be discussed.

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C16

Dispersion Energy of Symmetry-Adapted Perturbation Theory from the Explicitly Correlated F12 Approach

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Methods of the explicitly correlated F12 approach are applied to the problem of calculating the uncoupled second-order dispersion energy, $E^{(20)}_{\mathrm{disp}}$, in symmetry-adapted perturbation theory (SAPT). The accuracy of the new method is tested for noncovalently bound complexes from the A24 data set [1] using standard orbital basis sets aug-cc-pVXZ supplemented with auxiliary aug-cc-pVXZ_OPTRI sets [2]. For near equilibrium geometries, it is possible to recover the dispersion energy with average relative errors consistently smaller than 0.1% (with respect to the CBS extrapolated limit estimated from regular orbital calculations). This level of accuracy is achieved already in the basis set of a triple-ζ quality, when a Slater-type [3] correlation factor $\exp(-0.9r_{12})$ is combined with variant C of the F12 approach. The explicitly correlated approach clearly outperforms regular orbital calculations in the basis set of quintuple-ζ quality (average relative errors of 1%).

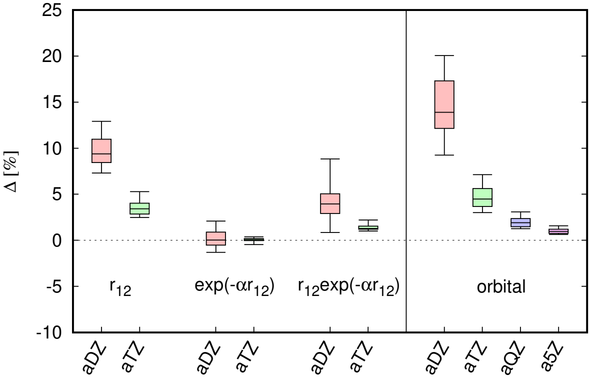

Figure 1: *Relative percent errors of the $E^{(20)}_{\mathrm{disp}}$ energy calculated for dimers from the A24 data set*

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C17

The concept of error in computational spectroscopy

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The concept of error is often neglected in *ab initio* based theory; we have got used to providing numbers without indication of the associated uncertainty. In my contribution, I will focus on error estimation in computational spectroscopy in the electronic domain.

I will start with a discussion of statistical error in the simulated spectra within the so-called reflection principle (or alternatively nuclear ensemble method). Having the error measure, I will present different strategies to accelerate the convergence of calculated spectra.[1] Next, I will discuss the systematic error stemming from the approximate treatment of the nuclear motion within the nuclear ensemble method. Some error measures will be proposed and discussed. The discussion will be based on some recent examples from our laboratory.[2,3]

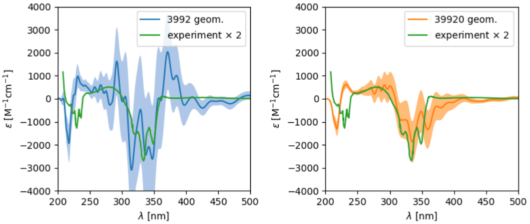

Figure 1: Temperature derivative of UV absorption spectrum of azobenzene together with error bars [3]

Finally, I will briefly discuss the systematic error related to the *ab initio* level of theory. Here, the estimate is notoriously difficult unless we use stochastic methods to solve the electronic Schrödinger equation – then the systematic error transfers into the statistical one. I will discuss the possible role of statistical techniques in error estimation.

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Microhydration of HOIO: structural and thermochemical properties of HOIO + n H2O (n =1 -4)

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Iodine oxides have drawn the attention of atmospheric chemists because of the possible implications in the destruction of the stratospheric ozone layer. Moreover, iodine oxides are also relevant for nuclear safety, because they can be found inside the containment of the pressurized water reactor in the hypothetical case of a core melt accident. Despite the importance of iodous acid (HOIO) in atmospheric and nuclear chemistry, computational studies on HOIO species are scarce and only recently the experimental evidence of iodous acid in the gas phase has been reported [1]. Sipilä and co-workers detected HIO_2 at Mace Head in Ireland, with a lower concentration limit estimated to be 2×10^6 molecules cm^{-3}.

The goal of our study is to provide reliable thermodynamic properties of microhydrates of iodous acid HOIO. Systematic theoretical study has been carried out on the effect of sequential addition of water molecules to neutral iodous acid HOIO. The HOIO + n H_2O (n = 1 - 4) molecular complexes have been theoretically investigated using the ωB97XD DFT method along with aug-cc-pVTZ basis set. Single-point energies were calculated at the ωB97XD/aug-cc-pVQZ and DK-CCSD(T)-cf/ANO-RCC-VQZP levels of theory. The thermochemical properties ΔH, ΔS, and ΔG for the hydration of HOIO have been reported for all molecular complexes over the temperature range 200-400 K. The results of the hydration reactions indicate that the hydrated complexes are possible, and the lowest free energy of the formation of $HOIO.nH_2O$ had the minimum (-13.8 kJ mol^{-1}) at n = 2 when the temperature was 298 K.

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C19

Restricting Solvation to Two Dimensions: Soft Landing of Microsolvated Ions on Inert Surfaces

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Understanding the impact of surfaces on the H-bond topology of neat [1] and doped [2] water clusters remains a challenge. In order to decipher such dimensional restriction effects, we introduce and study a well-controlled model system that decouples the intricate chemical interaction phenomena from those physical effects that emerge solely from restricting the spatial dimensions from three to two [3]. With the aim to stimulate future experimental investigations, this is accomplished by simulating the deposition of doped water clusters, being microsolvated Na^+ and Cl^- ions, on an epitaxial xenon surface grown on a copper support using ab initio molecular dynamics. By comparing deposited doped clusters to their gas-phase references, we have found remarkable changes for Na^+ solvatomers, while the microsolvated Cl^- clusters remained intact on the surface. Energy correlation analyses have shown that the microsolvation shell of the cationic clusters imprints arrangements of water molecules that are unfavorable for H-bonding, thus readily leading to large-amplitude "plastic deformations" of the H-bonding network after deposition, up to imprinting networks that are unfavorable in the gas phase. In stark contrast, the anionic clusters are characterized by strongly attractive water-water interactions, which allow only for insignificant "elastic deformations" upon soft-landing. Given its fundamental nature, the discovered phenomenon is expected to be general rather than specific to the particular system classes investigated.

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C20

A novel, thermodynamics-based objective function for the parameterization of molecular mechanics force fields

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Conventional force fields (FFs) are sum of potential energy terms that are usually parameterized based on quantum chemical calculations of optimized geometries, relative energies, vibrational normal modes and frequencies of conformers. FF parameters can be either energetic ones or geometric ones (i.e. force constants, position of well minima), which, however, have to be determined simultaneously, as geometric parameters don't exclusively determine the equilibrium geometry, and normal modes and frequencies also depend on the geometric parameters. Furthermore, harmonic vibrational analysis even of a single conformer provides more information than the number of parameters, thus either a single, but usually ad hoc, objective function incorporating different types of information is defined and minimized [1][2], or a multi-objective optimization procedure is employed [3] to provide solutions to the overdetermined problem.

We propose a single, physically established objective function that uses the temperature range of the planned application to incorporate geometries, relative energies, normal modes and harmonic frequencies of the conformers in a thermodynamically balanced manner, and it even eliminates the need for normal mode matching (see e.g. [1][3]). The objective function is also generalized to saddle points in order to derive transition state FFs [2]. Examples of various applications are presented.

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C21

The rigorous local field approach for the effective calculation of linear and nonlinear optical properties of solvated systems

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Solute-solvent interactions can have a significant impact on the molecular properties of the solute. In particular, nonlinear optical (NLO) responses of molecules have been shown to be highly sensitive to the solvent effects. Consequently, various solvation models describing these interactions have been purposed. In general, these models can be categorized based on whether they treat solvent molecules as discrete units (explicit models) or not (implicit models). While the former allow for more rigorous treatment of intermolecular interactions and solvation shell structure effects, they are computationally and methodologically more complex than the implicit solvation models.

In our study we focused on the study of higher order NLO properties of *para*-nitroaniline (*p*NA) in the presence of solvents with different multipolar character using an explicit solvation model, the rigorous local field (RLF) approach [1]. The computational structure of the RLF model allowed us to account for and critically assess different methodological aspects that come into play during the calculation of NLO properties both at the microscopic (solute hyperpolarizibilities) and macroscopic (susceptibilities) levels.

Firstly, we assessed the sensitivity of our model to the method applied to generate representative solute-solvent structures employing molecular dynamics (MD) with different (non)polarizable force fields and QM/MM models. Secondly, we combined the local field calculations based on the RLF model with the NLO property interpolation schemes, which allowed us to process large amount of structures (5000 per MD trajectory). In this way, we calculated up to the second dipole hyperpolarizabilities considering both electronic and vibrational (nuclear relaxation and ZPVA) contributions, as well as frequency-dispersion corrections. Finally the electric field-induced second harmonic generation (EFISH) susceptibility of *p*NA was calculated and compared with the experimental data.

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Abstracts
Posters

PS I - P1

SAM radical decay in solution vs. in PFL-AE/LAM enzymatic environment

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S-Adenosyl-L-methionine (SAM) molecule is present in many enzymatic reactions, acting as a cellular methyl donor [1], producing the 2-aminobutyrate radical to generate diphtamide [2], and being the central cofactor in the radical SAM enzyme family [3]. This superfamily (formed by more than 100,000 enzymes) is known to catalyse a plethora of biochemical processes (more than 70 reactions). All these enzymes are thought to be activated for catalysis through homolytic cleavage of the S-$C_{5'}$ bond in the SAM forming the 5'-deoxyadenosyl radical (dADO·, Figure 1) [3]. Remarkably, the ribosyl ring of the free form of the dADO$^{\cdot}$ radical is unstable and can easily undergo a self-decay, which is unwanted pathway in radical SAM enzymes. Here, we aim at understanding the key factors stabilizing the generated dADO· radical in the enzymatic environment as compared to solution. For this purpose, we investigate two radical SAM enzymes: pyruvate formate lyase activating enzyme (PFL-AE) and lysine 2,3-aminomutase (LAM) [4,5] using standard quantum-chemical methods.

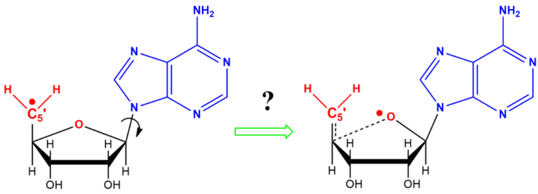

Figure 1: Schematic representation of the decay process of the dADO· radical (left). The curve arrow represents a rotational dihedral angle.

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PS I - P2

The peculiar case of oxo-Mn(Salen)

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The oxo-Mn(Salen) molecule has been a subject of numerous computational studies motivated by its role in catalysis of the enantioselective epoxidation of unfunctional olefins. Its closely lying singlet and triplet states pose a considerable challenge due to its multireference character, which is the reason why the system has been used repeatedly to assess the performance of methods designed for treatment of strongly correlated systems. One of the frequently applied methods is density matrix renormalization group (DMRG), especially combined with the CASSCF approach [1, 2, 3, 4]. More recently, even the effects of dynamic correlation has been examined [3, 4], however, the underlying problem remains – the varying reports of different ground states at the DMRG-CASSCF level for calculations performed using active spaces of similar size and in the identical basis sets.

Our aim was to contribute to these efforts by exploring the impact the active space composition and basis set has on the character of the ground state. For this purpose, we selected two active spaces consisting of 22 and 27 orbitals for DMRG-CASSCF calculations. Afterwards, we studied the effect of dynamic correlation using our implementation of the DMRG-based tailored coupled clusters (DMRG-TCCSD) method [3], which newly employs the local pair natural orbital approach (LPNO). With the LPNO implementation we were able to investigate the effect of dynamic correlation up to the quadruple-ζ basis set, which amounts to 1178 basis functions.

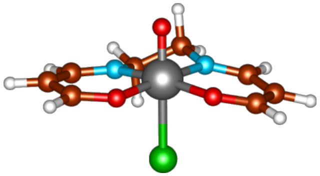

Figure 1: *A molecule of oxo-Mn(Salen)*

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PS I - P3

NMR shielding in transition metal complexes and nuclear magnetic dipole moments of stable transition metal nuclei

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Accurate calculations of NMR shielding constants opened possibility to correct systematic error in nuclear magnetic dipole moments [1, 2, 3]. We present NMR shielding calculations for series of transition metal complexes based on coupled cluster theory and four-component relativistic DFT. Solvent effects were modeled using implicit and explicit models. NMR shielding constants were combined with experimental NMR frequencies to re-derive nuclear magnetic moments of all NMR active stable transition metal nuclei. Extraordinary large corrections were found in this data set.

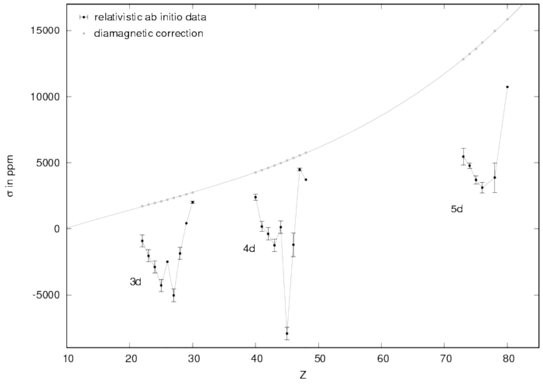

Figure 1: *Large difference between diamagnetic correction and ab initio NMR shieldings for transition metal complexes is the origin of large systematic errors in tabulated nuclear magnetic moments [4]*

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PS I - P4

Molecular Crystals of Tetra-Ethenyl-group(XIV) Compounds

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Congested molecules in the solid state are always in a competition of their intra- and intermolecular interactions. Nowadays, the former interactions are well understood by quantum mechanical calculations for the gas phase, whereas for the latter, being responsible for the solid state of matter in general, there is a lack of suitable computational methods. Both, the variety and the amount of the mostly weak intermolecular interactions hamper the theoretical approaches. They come to be less complicated if crystalline material is considered. Here, in an almost infinite three-dimensional arrangement we have mostly the same conditions for each molecule.

Therefore, when scrutinizing the important intermolecular interactions we need suitable model systems with known crystal structures. The most appropriate candidates are apparently series of molecules with central atoms in the same three-dimensional coordination sphere. The simplest is the tetrahedral geometry as existing for group-14 elements with four equal ligands.

Hence, tetra-ethenyl-group (XIV) compounds are studied with various density functionals including dispersion corrections and compared to experiment. Here, the C analogue was found to have two polymorphs, Si and Ge one polymorph of the two former, and Sn and Pb exhibiting a third polymorph. This thus entails three different polymorphs possible for these species, with their relative stabilities investigated. Finally, we disentangle the interactions of these species and the cause of the stability of these different polymorphs when moving down the group XIV.

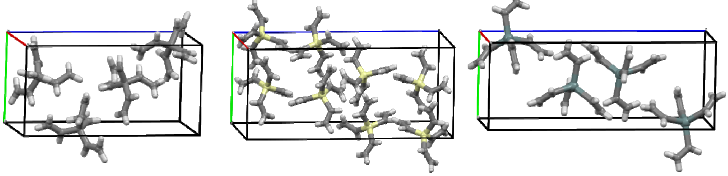

Figure 1: The crystal structures of tetra-ethenyl-methane (left, space group $P2_12_12_1$), tetra-ethenyl-silane (middle, space group *Pbca*), and tetra-ethenyl-stannane (right, space group $P2_1/c$).

PS I - P5

Relativistic coupled clusters externally corrected by four-component DMRG

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There are three essential problems in computational relativistic chemistry: electrons moving at relativistic speeds, degenerate energy levels and dynamical correlation. Currently available quantum-chemical methods are capable of solving systems with one or two of these issues. However, there is a significant class of molecules, in which all the three effects are present. These are the heavier transition metal compounds, lanthanides and actinides with open d or f shells. In this project, we propose to combine two numerical methods in order to address this challenging class of molecules. These are the relativistic versions of coupled clusters method and density matrix renormalization group (DMRG) method. According to our best knowledge, this is the first relativistic implementation of the coupled cluster method externally corrected by DMRG [1].

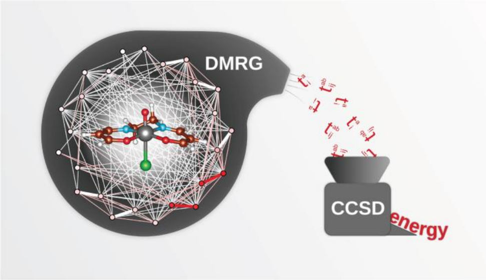

Figure 1: Graphical scheme of coupled clusters externally corrected by DMRG [3].

In the externally corrected approach, first a DMRG calculation is done on the most important part of the active space, keeping the rest of the system fixed. This accounts for the static correlation. Then a CC calculation is performed on the rest of the system, keeping in turn the DMRG part fixed. This captures the dynamical correlation. Already the simplest version thereof, the tailored CCSD [2], yields very promising results [3].

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On shape dependence of rutile nanoparticles toxicity

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Using B3LYP/6-311G* treatment, the nearly spherical structures of $[Ti_7O_{28}H_{26}]^{2-}$, the rod-like structures of $[Ti_2O_{10}H_{10}]^{2-}$ and $[Ti_7O_{30}H_{10}]^{2-}$ chains and the structures of their neutral complexes with Cu^{2+} coordinated at various terminal or bridging oxygen sites in the lowest spin states were optimized in order to assess the toxicity of rutile nanoparticles. Cu – ligand interaction energy parameters and Cu charges were evaluated. Spherical structures are more reactive than the rod-like chains of the (nearly) same size. The reverse relation holds for the degree of their toxicity as indicated by the extent of the electron density transfer to the Cu^{2+} probe. The experimentally observed higher cytotoxicity of rod-like nanoparticles in comparison with the spherical ones might be explained by the higher electron density transfer to the interacting animal cells.

PS I - P7

How to teach a non-relativistic wavefunction relativity

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Herein, we will use the X-ray Constrained Wavefunction (XCW) method [1] to test the possibility of adapting a non-relativistic wavefunction to relativistic effects (we have chosen the HgH_2 molecule) [2,3], see Figure 1. The XCW method combines the minimization of energy and the minimization of the difference between a reference (F^*) and the XCW (F) structure factors within a single Lagrange functional [1]:

$$L(\boldsymbol{c},\boldsymbol{\epsilon},\lambda)=L(\boldsymbol{c},\boldsymbol{\epsilon})-\lambda[\chi^2(\boldsymbol{c})-\Delta] \quad .$$

Δ is the desired precision, λ is the fitting parameter and the agreement statistics reads:

$$\chi^2=\frac{1}{N_r-N_p}\sum_{\boldsymbol{h}}^{N_r}\frac{[F(\boldsymbol{h})-F^*(\boldsymbol{h})]^2}{\sigma^2(\boldsymbol{h})} \quad .$$

N_r is the number of structure factors and N_p is the number of adjustable fitting parameters used in the model, which in our case is 1, σ is the standard deviation of the reference structure factors F^*. A structure factor is the Fourier transform of periodic/crystal electron density [1]:

$$F(\boldsymbol{h})=\int_{cell}\rho(\boldsymbol{r})\exp(2\pi i\,\boldsymbol{r}\cdot\boldsymbol{Bh})\,d\boldsymbol{r} \quad ,$$

where $\boldsymbol{B}$ is the reciprocal-lattice matrix, depending only on the shape of the crystal unit cell and $\boldsymbol{h} = [h_1h_2h_3]$ are integers called the Miller indices which describe the direction of the scattered X-ray beam.

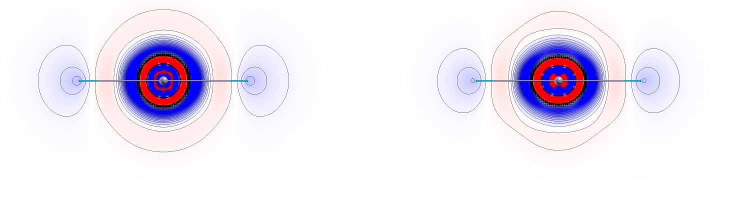

Figure 1: Net relativistic effects (left) and $XCW_{\lambda=60}$ relativistic effects (right) in HgH_2

Acknowledgements: VEGA 1/0598/16

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New Generations of Sunflower Molecules: Theoretical Study of Electronic Structure and Charge Transport Characteristics

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Generally, the circulenes are the macrocyclic compounds containing central [n]-sided polygon which is surrounded by [n] fused benzene rings [1]. Series of novel hetero-[n]circulenes of the first, second and the third generation including S and Se heteroatoms for n = 6, 7, 8 and 9 were theoretically designed. Their chemical and electronic structures were investigated using the DFT computational method on B3LYP level with SVP basis set. The shapes of frontier molecular orbitals were discussed. In the next step, interaction energies and charge transfer characteristics including electric drift mobilities were evaluated for model parallel-stacked and parallel-shifted dimer configurations at the room temperature using the Marcus theory and the Einstein relation [2,3].

Based on the calculated properties, the second and the third generation of sunflower molecules containing the six-membered central ring and heterorings with sulphur and selenium are suggested to be perspective candidates for the construction of organic p- and n-type semiconductors, respectively. Obtained theoretical results were compared with available experimental data for selected studied and reference α-sexithiophene, [6]circulene (coronene) and octathio[8]circulene (sulflower) molecules.

I would like to thank for financial contribution from the STU Grant scheme for Support of Young Researchers (1619).

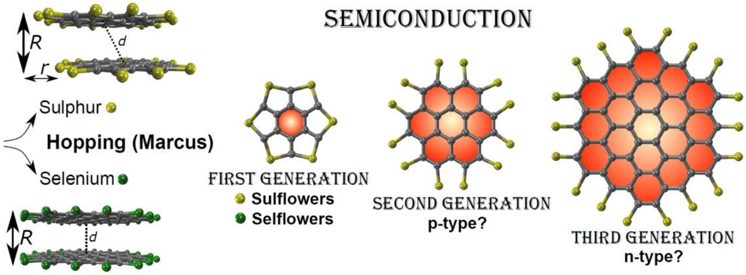

Figure 1: Chemical structure of new generations of sunflower molecules

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PS I - P9

Prospects of using mixed Gaussian and plane wave basis sets and graphics processing units in mainstream quantum chemistry

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The aim of this poster is to show what we learned from our activities in an off-mainstream field of quantum chemistry, namely from calculations on vibrational excitation of polyatomic molecules by electron impact. An illustrative example is shown in Fig.1.

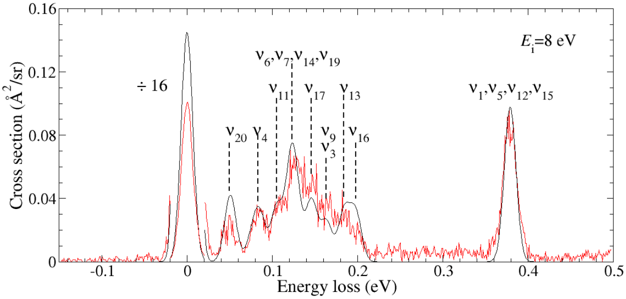

Figure 1. Experimental (in red) and calculated (in black) electron energy loss spectrum of benzene[1].

The most time consuming step in these electron scattering calculations is the evaluation of exchange integrals of the type (gk|gk), where g's are gaussians and k's are plane-wave functions. In quantum chemistry the use of mixed Gaussian and plane-wave basis sets proved profitable in evaluation of Coulomb parts of DFT[2] potentials and Hartree-Fock energies. [3] We show how they can be also applied efficiently to evaluation of exchange integrals, in particular when use is also made of graphics processing units.

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Calculations of the Photoabsorption Spectra of Small Charged Helium Clusters

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We present the calculated photoabsorption spectra for He_N^+ where $N = 5, \ldots, 9$. These cluster sizes complement our previous work [1] on $N = 3, 4, 10$ for which the experimental data exist [2]. Our aim is to study changes in the photoabsorption spectra of different cluster sizes – in our previous work, the differences in the photoabsorption spectra of He_3^+ and He_4^+ have been very small, while the photoabsorption spectrum of He_{10}^+, on the other hand, has been significantly lower.

Our recent calculations show that the photoabsorption spectra of clusters up to size $N = 8$ share similar height and shape, while the photoabsorption spectrum of He_9^+ is, similarly to that of He_{10}^+, significantly lower. The comparison of all the photoabsorption spectra is depicted in Figure 1

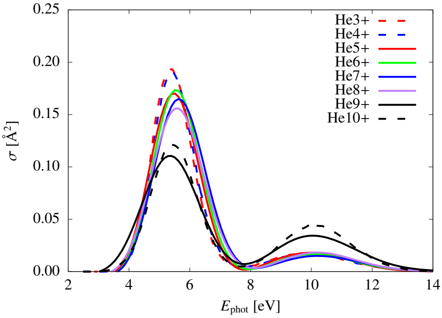

Figure 1: Comparison of the photoabsorption spectra of He_N^+, $N = 3, \ldots, 10$.

Our assumption is, that the inner structure of the cluster may play a role. All the clusters up to size $N = 8$ have a trimer-like ionic core. The two larger clusters ($N = 9, 10$) have the dimer-like ionic core. The clusters with the same ionic core structures exhibit similar photoabsorption spectra which supports our assumption.

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PS I - P11

Laplace MP2 method with mixed Gaussian / Plane wave Density Fitting

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In this poster we report development of Laplace MP2 method based on a compact, sparse, mixed plane-wave / Gaussian density fitting representation of Coulomb integrals. Coulomb integrals are partitioned into short- and long-range contribution using a modified Ewald summation. The short range contribution is calculated in Gaussian basis set using density fitting techniques, while the long range part is treated in the plane wave basis. The method is implemented in the PySCF package. Sparse matrix algebra is used throughout the code.

PS I - P12

On the Synergy of Matrix-Isolation Infrared Spectroscopy and Vibrational Configuration Interaction Computations

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[2] Institute of Material Chemistry, TU Vienna, Austria
[3] Institute of Physical Chemistry, LFU Innsbruck, Austria

Numerous developments in quantum chemistry promise an economic and flexible, yet, accurate access to Potential Energy Surfaces (PESs) of polyatomic molecular systems, where the design of global PESs is cumbersome and expensive. A prominent field where accurate PESs are needed is Vibrational Structure Theory, *e.g.*, for the calculation of vibrational states of molecular systems by variational methods for solving the time-independent nuclear Schrödinger equation, i.e., Vibrational Self Consistent Field (VSCF) and Vibrational Configuration Interaction (VCI). Within a variety of authors working in this field, we find the most versatile implementations in the MOLPRO software package [1] with the PES generator and VSCF/VCI algorithms by Rauhut et al. [2,3]. In this work, we recorded high-resolution spectra by Argon and Neon Matrix-Isolation Infrared (MI-IR) Spectroscopy, a technique that suppresses molecular rotation to access pure vibrational spectra. We perform VSCF/VCI computations on *ab initio* multi-mode PESs to support assignment of the MI-IR spectra, which, *vice versa*, validate the accuracy of the computations. With this iterative spectroscopic characterization (Fig. 1), we are able to solve some inconsistencies in the well-studied spectrum of the water monomer [4] and to confirm the experimentally implied molecular picture by quantum chemical calculations. We extend this combined experimental and computational approach to compounds, where a precise characterization is highly relevant, *e.g.*, key components in the activation of carbon dioxide or volatile organic compounds found in the atmosphere.

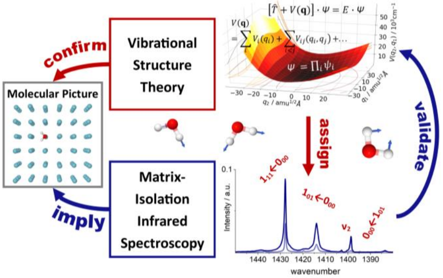

Figure 1: Schematic illustration of the iteration between theory and experiment in the course of molecular characterization by IR spectroscopy.

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Improving the benchmark data for the lattice volumes and energies of X23 molecular crystals

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Ab initio calculations of the main properties of molecular crystals are of high importance not only for the predictive purposes (*e.g.*, the crystal structure prediction of various polymorphs [1]) but also to validate particular computational methods in terms of their accuracy. For the latter, a consistent set of reference lattice volumes and energies of these systems is needed.

The most widely used X23 reference set [2] of molecular crystals was originally derived through the back-correction of standard sublimation enthalpies to 0 K by vibrational energy contributions, for which experimental heat capacities were used for some molecular crystals. However, the role of thermal expansion on the cell volumes was not explicitly considered in Ref. [2].

A consistent strategy of deriving X23 cell volumes and lattice energies will be presented. For this purpose, we rely on the quasi-harmonic approximation for the description of thermal expansion and take phonon dispersion into account. The respective vibrational free energy contributions are calculated utilizing dispersion-corrected density-functional theory (with three functionals: PBE-D3, BLYP-D3, and RPBE-D3). Reference cell volumes at a particular temperature were modelled through structure and lattice relaxations and averaged over the three density functionals. New reference lattice energies have been obtained from experimental standard sublimation enthalpies to 0 K and including all necessary vibrational contributions obtained with the three aforementioned density functionals. The quality of these newly derived reference values for the X23 molecular crystals will be discussed.

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Toward Accurate Noncovalent Interactions by Scalable Quantum Monte Carlo

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Single-determinant (SD) fixed-node diffusion Monte Carlo (FNDMC) attracts increasingly more popularity as a benchmark method scalable to large noncovalent systems. Its limits are however still unknown. It is therefore timely to explore and delineate its limitations. We focused on set of different weakly noncovalently bound dimers to explore how accurate SD-FNDMC can be and if it is able to achieve benchmark accuracy for selected systems where conventional approaches do not reach reference accuracy (say up to 2% of relative error). We demonstrate that substantial accuracy improvements may be reached, still within SD framework, with rather simple computation SD-FNDMC protocol adjustments involving PBE0 orbitals instead of more traditional B3LYP ones, and, in combination with innovative Jastrow term design [1].

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PS I - P15

The influence of the metal-ligand charge transfer effects on the structural stability and the strength of the spin-orbit coupling in Ni(II)-based metal-ligand complexes

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The structural stability, charge transfer effects and the strength of the spin-orbit couplings in different Ni(II)-ligand complexes with square-pyramidal and octahedral coordination have been studied at M06/def2-TZVP level of theory. Accordingly, two different, porphyrin- and diketo-pyrphyrin-based four-coordination macrocycles as planar ligands as well as pyridine, pyrrole and mesylate anion molecular groups as vertical ligands were considered in order to build the square-pyramidal and octahedral coordination configurations. For each molecular system the identification of equilibrium geometries and the intersystem crossing (the minimum energy crossing point) between the potential energy surfaces of the singlet and triplet spin states is followed by computing the spin-orbit couplings between the two spin states. Structures, based on the diketo-pyrphyrin macrocycle as planar ligand, show stronger five- and six-coordination organometallic complexes due to the extra electrostatic interaction between the positively charged central metal cation and the negatively charged vertical ligands (See at Figure 1 the electrostatic potential map of the two macrocycles). The results also show that the magnitude of the spin-orbit coupling is strongly influenced by the atomic positions of deprotonations of the ligands and implicitly the direction of the charge transfer between the ligand and the central metal ion.

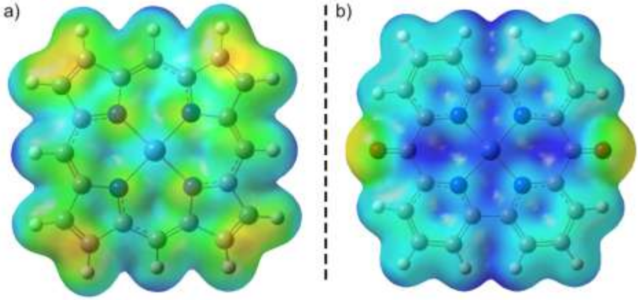

Figure 1. The two maps of the electrostatic potential ($e_{min}=0.1e$ and $e_{max}=0.3e$) for the

Ni(II)$^{2+}$–porphyrin^{2-} (*a*) and of Ni(II)$^{2+}$–diketo-pyrphyrin (*b*) complexes.

PS I - P16

Density Embedding for Organic Molecules on Surfaces

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Organic/metal interfaces are interesting systems, both, for potential applications as well as from a fundamental point of view. Theoretically, a common way to approach such extended two dimensional systems is via density functional theory (DFT). Often hybrid functionals for treating exchange-corrrelation effects are necessary to accurately describe the interaction and a possible charge transfer between metal and molecule. However, the computational cost for such large systems may present a severe bottleneck when employing hybrid functionals. An upcoming approach to this problem is the application of embedded (DFT in DFT) methods, which allows one to use the more accurate functional, the so-called high-level functional, for a smaller region of the system and the so-called low-level functional (e.g. LDA etc) for the remaining system. We have performed such embedding calculations with a modified VASP (Vienna Ab Initio Simulation Package) code [1]. This modified VASP code can also be used for CW (Correlated Wavefunction) in DFT embedding which opens up the possibilities of excited state calculations on surfaces. The CW method is carried out with MOLPRO. So far small systems including H_2, H_2 *on Cu*(110) and *Benzene on Pd*(110) have been tested.

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PS I - P17

Estrogen-quinone-induced DNA modifications: A computational study

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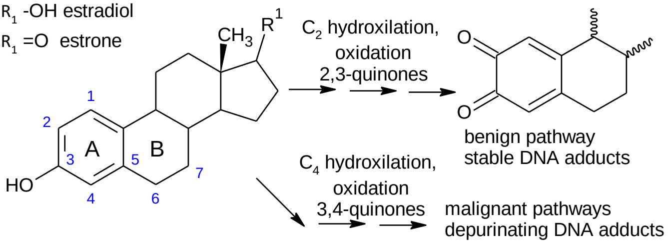
Long-term exposure to estrogens, and hormone replacement therapies (HRT) significantly increase the probability of breast and endometrium cancer [1]. Several mechanisms were suggested to contribute to estrogen-induced carcinogenesis. Here, we focus on the interaction of estrogen-quinones with DNA. The reaction of 2,3-quinones leads to stable DNA adducts (which can be repaired by the DNA repair enzymes), but 3,4-quinones form depurinating adducts which are likely to cause mutations, which can, in turn, lead to the initiation of cancer [2].

The aim of our work was to investigate the factors that influence the reaction of estrogen-quinones (estrone, equilin and equilenin which differ in the saturation of ring B) with purine nucleobases at the molecular level. Using DFT calculations we studied the reaction mechanism of 2,3- and 3,4-estrogen-quinone addition to adenine and guanine. The reaction in case of 3,4 quinone starts with a Michael addition: the C_1 of the quinone can be either the N_7 of guanine or of the N_4 of adenine. From the adducts several reaction routes are conceivable. Either rearomatization of the quinone ring (i.e. forming a cathecol) occurs coupled to the loss of the catalytic proton on C_1, followed by the depurination step (i.e. breakage of the C-N glycosidic bond and loss of the sugar ring from the nucleotide) or these two steps might happen in reverse order.

In case of 2,3-quinones an acid catalyzed tautomerization takes place first leading to a quinone-methide (a double bond is formed between C_5-C_6). Afterwards, C_6 of the quinone methide carries out an electrophilic attack on the exocyclic amin of the nitrogen base leading to the stable adduct.

Our calculations show that there is no notable difference between guanine and adenine in these reactions. Thermodynamic data suggests that in the case of estrone and equilin the rearomatization step foregoes the depurination, while in case of equilenin the opposite is likely.



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PS I - P18

A new adiabatic method of averaging intermolecular interaction energy over vibrations of the monomers.

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An interaction energy of the weakly-bound molecular complexes is represented by interaction energy surfaces, that in principle depend on all degrees of freedom of the complex. However, such surfaces are very expensive to calculate and their application in calculations of properties may be very difficult, sometimes not feasible. This is the reason why usually the surfaces of reduced dimensionality, depending only on the intermolecular degrees of freedom, are constructed. The simplest way to obtain such surface is to employ the rigid-monomer approximation, i.e., assume the monomers to be rigid. However, it has been shown that surfaces obtain within this approximation are not reliable enough in calculations of some properties [1]. A significant progress can be observed if one uses the surface which is averaged over vibrations of the interacting molecules [2, 3, 4]. In the applications performed so far, the averaging is performed over the vibrations of the free molecules, whereas in the real world they vibrate in the field of the interacting partner. In the present work we propose a new adiabatic procedure of averaging the interaction energy over the vibrations of the monomers in the complex. One can expect that the effects taken into account in this approximation and not present in the previous ones, can be particularly large for complexes with relatively strong interaction energy and significant anisotropy. Thus, we present preliminary results for the N_2-HF complex. The results are obtained for a few vibrational states of the interacting molecules.

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The extrapolation Atomic Natural Orbitals of basis set to complete basis set (CBS) limit

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The van der Waals complexes bonded by weak interaction play crucial role in many chemical systems or processes. The correct description of these noncovalent complexes requires the use of the most sophisticated computational methods:

- First, only methods including electron correlation effects such as MP2 or CCSD(T) approaches can be used.
- The second important factor in an accurate calculations of noncovalent complexes is the quality of basis sets which have to contain polarization and diffusion functions.

The binding energies calculated with finite basis sets were extrapolated to complete basis set limit by using standard extrapolation techniques [1, 2]. The relativistic ANO-RCC-VXZP and aug-cc-pVXZ-DK (X = D, T, Q) basis sets were used for calculations with finite basis sets. Results estimated from ANO-RCC calculations were in quantitative agreement with the benchmark data obtained by standard aug-cc-pVXZ-DK (X = D, T, Q) basis sets considering chemical accuracy of ±1 kcal/mol [3].

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PS I - P20

High-accurate Geometries and Intermolecular Interaction Energies of small Systems

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As hydrogen-bonded systems are highly important in biological and chemical systems, there is a huge interest in describing the underlying intermolecular interactions, especially energies, very accurate. Therefore, several benchmark sets have been created containing intermolecular interaction energies calculated with one of the most accurate and affordable method, the so-called gold-standard in quantum chemistry: coupled-cluster with single, double and pertubative triple excitations, CCSD(T). Additionally, the basis set need to carefully chosen or even extrapolation schemes need to be used to minimize the errors.

In this work, we present revised geometries and intermolecular interaction energies for the HB49 benchmark set, containing 49 small systems with two molecules interacting by hydrogen bonds.[1] In addition, we obtain relaxed potential curves by varying the intermolecular distance. CCSD(T) basis set extrapolations were used for all geometry optimizations and single-point calculations (see Figure 1).[2]

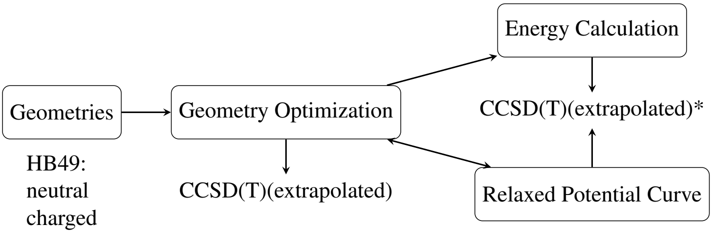

Figure 1: *Steps for highly accurate geometries and CCSD(T) interaction energies; the star indicates a larger basis set for the single-point calculations.*

The potential curves indicate the importance of the relaxation energies, especially for the stronger bound species.

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PS I - P21

Accuracy of Density-Functional Approximations and QM:QM Embedding Methods for Molecular Crystals

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The accurate modeling of structures and stabilities of molecular crystals is crucial for the field of organic crystal structure prediction since the relative stabilities of polymorphs often differ only by very few kJ/mol [1]. In Ref. [2] we have presented revised benchmark values for the often used X23 set of molecular crystals. For the benchmark of unit-cell volumes, we have back-corrected experimental results for thermal and zero-point-energy effects, allowing a direct comparison with lattice relaxations based on electronic energies. For benchmarking lattice energies, experimental sublimation enthalpies were back-corrected for vibrational contributions taking into account the effect of thermal expansion.

Herein, we discuss the accuracy of several dispersion-inclusive density functional approximations compared to the revised X23 benchmark data. A promising approach to reduce the computation time for molecular crystals is the embedding of a quantum-mechanical model into another, which enables the usage of hybrid functionals for larger systems. Therefore, we also evaluate the performance of combining PBE0:PBE+D3, PBE0:PBE+MBD, and B3LYP:BLYP+D3[3], as well as BLYP:DFTB3+D3[4]. In addition, we also present and discuss an additional benchmark set focusing on polymorphic molecular crystals in order to evaluate the quality of relative energies.

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Electronic structure, bonding and volatility of carbonyl compounds of Tc, Re, and Bh

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Molecular properties of $M(CO)_5$ and $MH(CO)_5$, where M = Tc, Re, and Bh, and of the products of their decomposition, $M(CO)_4$ and $MH(CO)_4$, were calculated using Density Functional Theory and Coupled-Cluster methods implemented in the relativistic quantum chemistry program suits such as ADF, DIRAC and ReSpect [1].

The predicted first M-CO bond dissociation energies (FBDE) of $M(CO)_5$ and $MH(CO)_5$ turned out to be significantly weaker than those of the corresponding Re homologs. The reason for that is the relativistic destabilization and expansion of the 6d AOs, responsible for weaker σ-forth and π-back donations in the Bh compounds. The relativistic FBDEs of $M(CO)_5$ have, therefore, a Λ-shape behavior in the row Tc-Re-Bh, while the non-relativistic values increase towards Bh.

Using results of the molecular calculations and a molecule-slab interaction model, adsorption enthalpies, ΔH_{ads}, of group-7 carbonyl closed-shell hydrides on quartz and Teflon were estimated for future gas-phase chromatography experiments. It was found out that $BhH(CO)_5$ should be almost as volatile as the homologs, however, its interaction with the surfaces should be somewhat stronger than that of $MH(CO)_5$ (M = Tc and Re), while the $M(CO)_4$ (M = Tc, Re, and Bh) molecules should be non-volatile. It will, therefore, be difficult to distinguish between group-7 $MH(CO)_5$ species by measuring their ΔH_{ads} on surfaces of Teflon and quartz with an error bar of ± 4 kJ/mol.

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PS I - P23

Electronic excited states of AuSi

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The results of theoretical calculations for the ground state and thirteen excited states of AuSi molecule are presented [1-2]. Calculations were carried out with the spin-free relativistic the infinite order two-component method and high-level correlated methods. The spin-orbit coupling is introduced via the restricted active space state interaction (RASSI) method with the use of the atomic mean-field SO integrals (AMFI). The results are compared with the available experimental and theoretical results. The spectroscopic parameters are presented and the full and exact potential energy curves. The calculated excited states seems to be very stable. The results obtained suggest that the experimental data should be reconsidered.

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PS I - P24

Spectroscopic properties of diatomic molecules CdI and CsCd

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Spectroscopic properties of diatomic molecules CdI and CsCd were calculated by *ab initio* methods. The main aim, from the enviromental perspective, is to determine molecular data for both molecules, which can be plugged-in to the software package ASTEC [1], that is used to simulate various possible accidents and/or critical situations in the fission reactor of PWR type.

State-averaged Complete Active Space SCF (SA-CASSCF) combined with the multi-state perturbation theory to the second order (MS-CASPT2) [2-4] was used for the calculation of the potential energy curves of the ground state and low-lying excited states. Spin-orbital interactions within RASSI approach with active space using SA-CASSCF wavefunctions and MS-CASPT2 energies (CASPT2/RASSI method) [5], were also calculated. From the known potential, we have determined the following spectroscopic properties of these diatomic molecules: equilibrium distance R_e, rotational constant B_e, harmonic frequency ω_e, constant of anharmonicity $\omega_e x_e$, excitation energy T_e and dissociation energy D_e. Dunham analysis [6] and numerical solution of vibrational Schrödinger equation (module *vibrot* from MOLCAS software [7]) were used for the spectroscopy analysis. The results for CsCd are the first molecular data produced so far.

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PS I - P25

Benchmark calculations with Coupled Cluster methods on Charge Transfer states

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There are numerous publications on benchmarking quantum chemistry methods for excited states. These studies rarely include Charge Transfer (CT) states although many interesting phenomena in e.g. biochemistry and material physics involve transfer of electron between fragments of the system. Therefore, it is time to test the accuracy of quantum chemical methods for CT states, as well. Since only special DFT functionals are capable of describing CT states, coupled-cluster type methods play an important role in this field. In this presentation we first suggest a set benchmark systems consisting of dimers having low-energy CT states. On this set, the calculation of excitation energy has been performed with coupled cluster methods including triple excitations (CC3, CCSDT-3, CCSD(T)(a)*), as well as with methods including full or approximate doubles (CCSD, CC2, EOM-CCSD(2), STEOM-CCSD). The results show that the popular CC2 method is much more inaccurate for CT states than for valence states. CCSD seems to have the same systematic overestimation of the excitation energies as for both valence and CT states. On the other hand, the new CCSD(T)(a)* method including non-iterative triple excitations preforms very well for all type of states, delivering essentially CCSDT quality results.

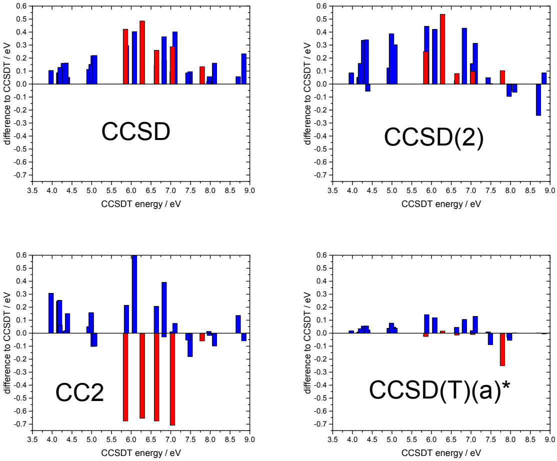

Figure 1: Error of the excitation energy for valence (blue bars) and CT (red bars) states obtained by different couple cluster methods.

PS I - P26

Electronic Structure Informatics for Exploring Efficient CO_2 Adsorbents

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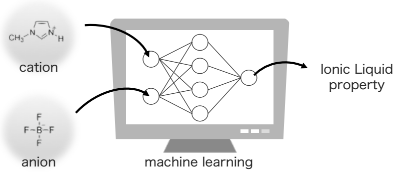
Ionic liquids are non-volatile and highly stable solvents, which consisted only pair of cations (mostly organic) and organic/inorganic anions. Due to the unique liquid properties of ionic liquids, they have used to a wide range of applications such as cellulose dissolution, energy storage, electrolytic solution, and so on. Since Blanchard found that ionic liquids have CO_2 absorption abilities, large amounts of theoretical studies based on electronic structure calculations and molecular dynamics simulations have been reported for exploring novel ionic liquids with better CO_2 absorption abilities. However, due to the high computational costs of quantum chemical calculations, it has been considered difficult to predict such a novel ionic liquids only with the quantum chemistry based methods. In this study, using an interdisciplinary approach of quantum chemistry and information science, we will introduce a new prediction scheme for designing ionic liquids with higher CO_2 absorption abilities. We will present the method how to describe ionic properties as much compact as possible toward inverse design of ionic liquids.



Acknowledgments

Some of the presented calculations were performed at the Research Center for Computational Science (RCCS), the Okazaki Research Facilities, and the National Institutes of Natural Sciences (NINS). This study was supported in part by the Advanced Information and Communication Technology for Innovation (ACT-I; Grant number: JPMJPR16UB) Precursory Research for Embryonic Science and Technology programs (PRESTO; Grant number: JPMJPR16NC) from the Japan Science and Technology (JST) Agency.

PS I - P27

Implementation of the full CCSDT method with tensor decompositions

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We report a complete implementation of the coupled-cluster method with single, double, and triple excitations (CCSDT) [1, 2] where tensor decompositions are used to reduce the computational costs. For the two-electron integrals the standard density fitting [3] or Cholesky decomposition [4] are used. For the coupled-cluster triple amplitudes tensor we employ the Tucker-3 compression [5] format

$$t_{ijk}^{abc} = \sum_{XYZ} t_{XYZ}\, U_{ai}^{X}\, U_{bj}^{Y}\, U_{ck}^{Z}, \tag{1}$$

where the quantities U_{ai}^{X} are obtained from singular value decomposition (SVD) of an approximate triple amplitudes tensor, as introduced in our previous work [6]. The central tensor t_{XYZ} is obtained as a result of the coupled-cluster iterations. The efficiency of the method relies on the fact that the optimal size of the SVD subspace (the length of the summation over X, Y, Z) sufficient to obtain a constant relative accuracy in the correlation energy scales linearly with the size of the system. Combined with proper factorization of the coupled-cluster equations this leads to N^6 scaling of the computational costs of the SVD-CCSDT method, compared with the N^8 scaling for the conventional (uncompressed) CCSDT.

The accuracy and efficiency of the method is demonstrated by benchmark calculations of total energies and interaction energies for several model systems. The method is chemically accurate and even more demanding levels of accuracy, such as 0.1 kJ/mol, can be obtained with a reasonable size of the SVD subspace.

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PS I - P28

Comparison of Ultrafast Intersystem Crossing in Iron(II) and Rhenium(I) Complexes

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Intersystem crossing (ISC) in transition metal complexes (TMCs) is very different from ISC in typical organic molecules, due to the high density of excited electronic states and very large spin–orbit couplings in these TMCs. Here, we compare the ultrafast ISC mechanism of two prototypical TMCs, the third-row complex $[Fe(CN)_4(2,2'\text{-bipyridine})]^{2-}$ and the fifth-row complex $[Re(CO)_3(\text{imidazole})(\text{phenanthroline})]^+$. Both complexes have been assigned spectroscopically ISC on a 100 fs time scale in aqueous solution.[1, 2] However, considering the nuclear charge of the two metals, the Re complex should exhibit significantly faster ISC than the Fe complex. By extensive simulations using the Surface Hopping including Arbitrary Couplings (SHARC) [3] method, we show that the ISC mechanisms of these two complexes are different. Most prominently, we provide evidence that ISC in the Re complex can be clearly separated into electronic ISC and nuclear-relaxation-driven ISC, whereas in the Fe complex this is not the case.

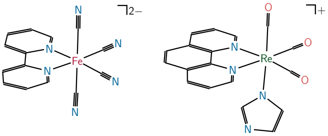

Figure 1: *Chemical structures of the investigated complexes.*

[1] W. Zhang, K. S. Kjær, R. Alonso-Mori, U. Bergmann, M. Chollet, L. A. Fredin, R. G. Hadt, R. W. Hartsock, T. Harlang, T. Kroll, K. Kubiček, H. T. Lemke, H. W. Liang, Y. Liu, M. M. Nielsen, P. Persson, J. S. Robinson, E. I. Solomon, Z. Sun, D. Sokaras, T. B. van Driel, T.-C. Weng, D. Zhu, K. Wärnmark, V. Sundström, K. J. Gaffney: Manipulating charge transfer excited state relaxation and spin crossover in iron coordination complexes with ligand substitution, *Chem. Sci.*, **8**, 515 (2017).

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Binuclear Cu-Cu/Cr-Cr paddle wheel complexes: Theoretical study

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Geometry, energetics, electronic structure and the topology of electron density of di-copper and di-chromium acetate diaqua complexes are presented at the DFT as well as at the multi determinant *ab initio* (MP2, CAS, NEVPT2) levels of theory. Experimentally determined X-ray structure and derived charge densities are taken from the work of Herich *et al.*[1] Metal-metal (Cu-Cu and/or Cr-Cr) interactions are characterized by means of Quantum Theory of Atoms in Molecules (QTAIM)[2] and *via* electron localization function (ELF)[3] visualization. The comparison of metal-metal interactions shows on a small value of the physical bond order in di-copper and a moderate value in the case of di-chromium complex.

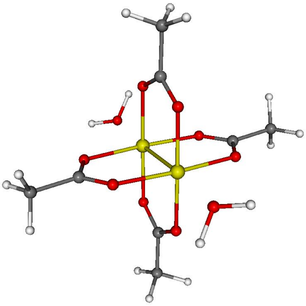

Figure 1: Structure of studied binuclear Cu-Cu complex

In addition, a NEVPT2 potential energy surface (PES) scan with respect to change of the metal-metal distance (with water molecules in a constant position with respect to the metal atom) is presented.

We are grateful to the Slovak Grant Agencies APVV (contract No. APVV-15-0079 and APVV-15-0053), VEGA (contracts No. 1/0598/16, 1/0718/19 and 1/0466/18) and SIVVP project(ITMS code 26230120002).

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PS I - P30

Application of the GVB-rCCD method to simple molecular systems

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Using Multi-Reference (MR) wave functions is necessary to describe several molecular processes where Hartree-Fock based methods fail, such as bond dissociation. GVB (Generalized Valence Bond) is a particularly simple MR wave function whose building blocks are electron pairs (geminals). The electron correlation within geminals is obtained exactly, which is often sufficient for a qualitatively correct description of the potential energy surface. For more accurate results correction methods are needed to obtain the intergeminal part of the correlation.

Motivated by the GVB based extended RPA (GVB-ERPA) of Pernal[1], we have recently generalized the rCCD (ring Coupled Cluster Doubles) method for MR functions[2] to provide a companion theory. Derived with the help of the Generalized Wick Theorem[3], the rCCD equations are given as an expansion in terms of density cumulants. Applying the rCCD correction to the GVB wave function leads to a fairly accurate method with low computational cost.

In my poster I show the advantages and disadvantages of GVB-rCCD on various examples, such as the double bond dissociation of H_2O, the deprotonation of CH_3OH, the umbrella inversion of NH_3 and the interaction of a He_2 dimer. I compare GVB-rCCD to GVB-ERPA and also to benchmark results obtained from either Full-CI or CCSD(T) calculations. I also demonstrate the importance of higher rank cumulants in obtaining accurate GVB-rCCD results.

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PS I - P31

Machine learning for dynamics simulations

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Different applications and developments of machine learning potentials will be presented, aiming at fast and accurate molecular dynamics simulations. As a first example, the simulation of infrared spectra computed including anharmonic effects is chosen [1,2]. Here, high-dimensional neural networks exploit chemical locality [3,4] and predict accurate potentials from only a few training points chosen with an adaptive sampling scheme [1,5]. Emphasis is put on the intrinsic charge model derived from molecular dipole moments [1,2]. Furthermore, weighted atom-centered symmetry functions (wACSFs) are discussed as descriptors [6]. Finally, machine learning potentials are used to carry out excited-state molecular dynamics and open up the possibility to reach time scales in the nanosecond regime [7].

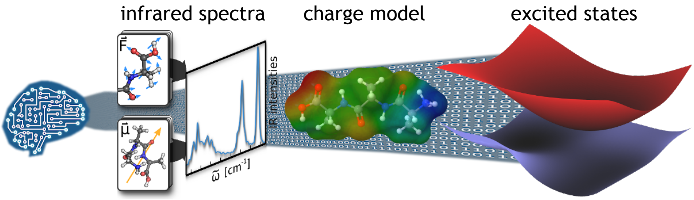

Figure 1: Machine learning enables a) the simulation of infrared spectra including anharmonic effects for large molecules, b) the prediction of charges with an intrinisic partitioning scheme, and c) the simulation of nanosecond excited-state dynamics.

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PS I - P32

Lowest Spin States Energetics in Fe(II)-Porphyrin Model

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Metal-porphyrins play a crucial role in many biological processes. Fe(II)-porphyrins with a d^6 Fe configuration exhibit nearly degenerate lowest lying electronic states of different spin symmetry whose relative energy and order depends on many factors, e.g. the coordination environment or geometry. This is also the reason for their wide biochemical versatility.
In our work we study the electronic structure of the Fe(II)-porphyrin model introduced by Li Manni and Alavi [1] by means of the recently developed tailored coupled cluster methods [2]. For 3 slightly different geometries and several complete active spaces (CASs), we have performed CASSCF and DMRG-CASSCF orbital optimizations with subsequent TCCSD [2] or (D)LPNO-TCCSD [3, 4] dynamic correlation treatment. Our results are in agreement with the recent experimental studies [5] and unlike [1] predict $^5A_{1g}$ to be the ground state.

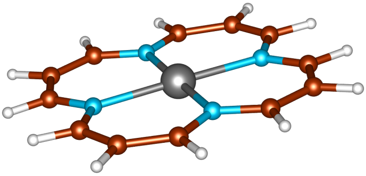

Figure 1: *The porphyrin model of Li Manni and Alavi [1] used in our work*

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The ups and downs of DFT in high-order electric property calculations for hydrogen-bonded systems

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The performance of a wide palette of density functional theory (DFT) methods in predicting high-order electric properties of a series of linear hydrogen-bonded (HB) complexes was assessed. In particular, the electronic and vibrational contributions to the electric polarizability and the first and second hyperpolarizabilities were computed using the CCSD(T)/*aug*-cc-pVTZ level of theory as reference.[1] The high-order properties of HB complexes were found to be significantly enhanced compared to the isolated subsystems indicating a strong influence of intermolecular interactions on the properties. In addition, our analysis revealed that vibrational contributions represent a dominant counterpart of the excess high-order properties and anharmonicity needs to be taken into account to acquire a physically correct picture. As the evaluation of high-order molecular properties requires also correct consideration of electron correlation effects, the hyperpolarizabilities of weakly bound systems appear to be a challenging target for computational chemistry. Following our studies [1,2] focused on the understanding of physical origins of the electronic and vibrational excess (hyper)polarizabilities using the MP2 and CCSD(T) methods, we tested the capability of various DFT approaches to predict the high-order electric properties of the same series of HB complexes.[3]

For all the studied properties, the mean absolute deviation below 20% was achieved using the CAM-B3LYP functional, while LC-BLYP and MN15 were shown to be only slightly less accurate. On the other hand, we report huge errors by ωB97X, M06 and M06-2X functionals. Based on the explicit evaluation of anharmonic terms, this failure was traced down to a poor determination of higher-order energy derivatives with respect to normal modes. These results reveal serious flaws of some DFT approximations and suggest caution in selecting the appropriate functional to calculate also other molecular properties that contain vibrational anharmonic contributions.

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PS II - P34

Vibronic and spin-orbit coupling in the $X\ ^2\Pi_u$ state of SCCS⁻: An *ab initio* approach

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The goal of this study was to investigate the vibronic and spin-orbit coupling in the ground state $^2\Pi_u$ of SCCS⁻ by *ab initio* methods. Two reasons motivated us to carry this study, first one was the importance of SCCS⁻ radical from the astrochemical point of view and its possible detection in space, and the second one was Renner-Teller effect which molecule exhibits in the ground and the first excited electronic state.

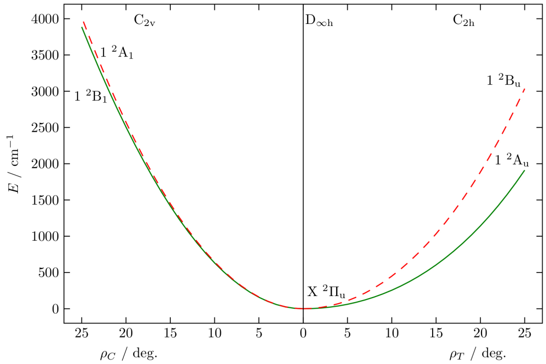

Figure 1: *The potential energy curves of the ground* $X\ ^2\Pi_u$ *state along the cis- and trans-bending coordinates.*

The vibronic levels in the ground electronic state of SCCS⁻ anion are calculated by means of the model for the treatment of the Renner-Teller effect in any-atomic linear species developed by M. Perić and coworkers in its variational form [1], where potential energy curves in the Born-Oppenheimer approximation were obtained by *ab initio* multi-reference configuration interaction calculations, Figure 1. Effect of the spin-orbit coupling in the ground state was studied taking into the account interaction with the first excited state. Based on the present results, we propose several assignments of unidentified bands reported by Nakajima *et al.* who studied the spectrum of SCCS⁻ by laser-induced fluorescence spectroscopy. [2]

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Random phase approximation for many body noncovalent systems

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The problem of many-body noncovalent interactions appears to be insurmountable for the first four rungs of DFT. The three-body energy requires full exact exchange, which in turn requires a nonlocal correlation energy formulated in terms of virtual orbitals. The direct random-phase approximation, thought of as a fifth rung DFT approximation, solves the qualitative issues that DFT has with many-body systems.

Tests on noble gases, methane clathrate, and others demonstrate the role of a proper choice of the Kohn-Sham determinant. Provided a judicious choice of orbitals, RPA is an excellent method for modeling the nonadditive energies of hydrogen-bonded and mixed-interaction systems. It overcomes the well-known issues of lower-rung DFT with the description of the exchange nonadditivity of three-body noncovalent systems. Moreover, RPA based on SCAN or SCAN0 achieves accuracy similar to MP2.5 for the treatment of nonadditive interactions around equilibrium. In contrast to MP2.5, it has a much more affordable computational cost and can be readily applied to condensed phases. For trimers where the intermolecular distances are beyond equilibrium and which are important in condensed phases, the neon and argon data show that the RPA asymptote follows the CCSD(T) reference.

Acknowledgments: This work was supported by the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement No 759721).

PS II - P36

Ultrafast Quantum Chemical Screening of Azeotropic Mixture

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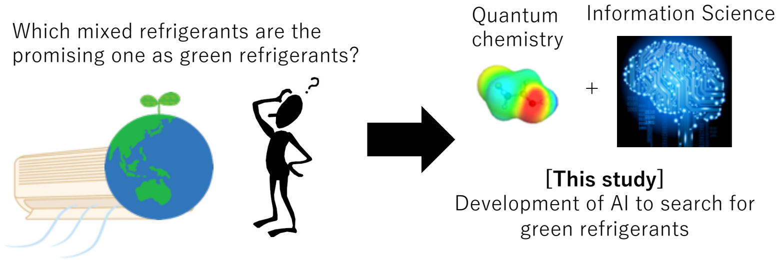
Refrigerants are substances that can be used in the refrigeration cycle of air conditioning and refrigeration equipment because of their thermodynamic properties. Among various chemical compounds, chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) had been utilized as refrigerants since their cooling efficiency are very high. However, as is well known, usage of these compounds is being phased out under the Montreal Protocol, an international agreement to protect the ozone layer. To develop substituent materials with high cooling efficiency and low environmental loads, many researchers and engineers have been working very hard to search for such materials. However, no better materials than those currently used have not been found. One of the most effective strategy to search for novel green refrigerants is using mixed refrigerants. In mixed materials, however, intermolecular interactions among different species cause non-linear thermodynamic property change to molar fraction. It had been considered difficult to predict candidate mixed green solvent prior to performing a number of experiments, which are expensive and time consuming.

With the above backgrounds, we have tried to develop a novel database that combine theoretical and experimental thermodynamic data for applying artificial intelligence in the field of refrigerants development. In this poster, a novel approach to find out green solvent materials which is based on quantum chemical calculations and information science will be introduced.



Acknowledgments

Some of the presented calculations were performed at the Research Center for Computational Science (RCCS), the Okazaki Research Facilities, and the National Institutes of Natural Sciences (NINS). This study was supported in part by the Precursory Research for Embryonic Science and Technology programs (PRESTO; Grant number: JPMJPR16NC) from the Japan Science and Technology (JST) Agency.

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PS II - P37

An Optimization Approach to Solving the Kohn-Sham Equation

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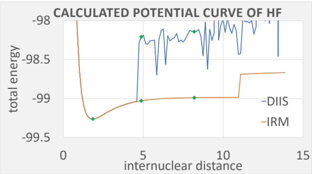
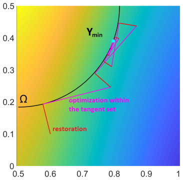
An optimization approach inspired by the Inexact Restoration Method (IRM) [1] is presented as an alternative to standard eigenvalue approaches to solving the Kohn-Sham (KS) Equation. Our motivation to consider such approach lies in the observation that an iteration of a Self-Consistent Field (even together with stabilization techniques, such as DIIS [2]) does not always converge. In the original paper, IRM has been tested for solving the Hartree-Fock (HF) Equation. A preliminary study of the modified algorithm to be suitable for the KS Equation has been done in [3] also at the level of the HF Equation. Here, we present the KS Equation results (with Local Density Approximation of the exchange-correlation term).



(a) Calculated potential curve of HF molecule showing the convergence issues



(b) Illustration of the iterative process

As a simple test case we have chosen the potential curve of the Hydrogen Fluoride molecule. Algorithms have been tested for several internuclear distances. We have been interested in the stability of the convergence, in the correctness of the result and also in the number of required iterations. The optimization algorithm has proven its reliability in situations, where DIIS has not converged. The results of the tests also pointed to its limitations and helped to find a direction of further development.

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Exploring Hydrogen Amplification Reaction and Deactivation Mechanism of Biomimetic Fe-nitrogenases

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Biomimetic nitrogenases that mimic the active site of the nitrogenase enzyme are attractive alternatives for ammonia production under ambient conditions instead of the energy-intensive Haber–Bosch synthesis. However, the turnover number of these recently synthetized artificial nitrogenases is still low due to fast catalyst degradation and competing side reactions.

In order to facilitate the design of new, more efficient catalysts, we use quantum chemical calculations. [1][2] In our present study we examine all possible reaction routes resulting in catalytically inactive hydride species and H_2-generating cycles (Figure 1.) starting from iron hydrides.

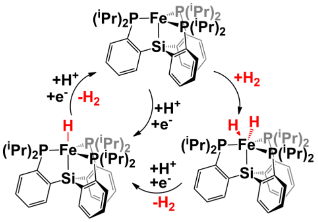

Figure 1: Conceivable reaction pathway of hydrogen evolution

We calculate the Gibbs free energy of all conceivable intermediates and transition states of the deactivation and hydrogen evolution reaction pathways and draw the reaction network of the feasible reactions. We identify the critical reaction steps that may be responsible for the low catalytic efficiency of the catalysts. We are also planning to perform microkinetic modelling and compare our theoretical results with the experimental data to validate our hypothesis for the deactivation and HER mechanism.

In future studies we suggest modifications in the tetradentate EPPP ligand to increase the efficiency of artificial nitrogenases and contribute to the development of atmospheric pressure ammonia synthesis.

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PS II - P39

Investigation of electronic spin states in substituted $[Fe(terpy)_2]^{2+}$ functional molecules

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Iron(II)-complexes are potential candidates for effective functional molecules, due to their capability of light induced spin-transition. $[Fe(terpy)_2]^{2+}$ (terpy = 2,2′:6′,2″-terpyridine) is one of the most heavily investigated systems, due to its long –lived quintet state. [1] Modification of the photochemical and -chemical properties of the complex can be achieved via modification of the ligand. Ligand substitution can help us to tune the lifetime of the quintet state by increasing/decreasing the potential energy barrier between the singlet and the quintet state. [2]

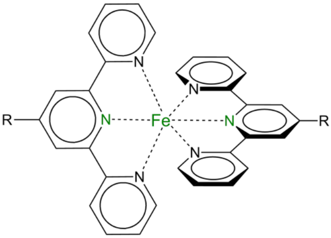

Figure 1: Structure of the $[Fe(4'\text{-}R\text{-}terpy)_2]^{2+}$ complexes [2]

In my talk I will present the results of density functional theory and time-dependent density functional theory computations of the modified $[Fe(terpy)_2]^{2+}$ complexes an how the substitution of electron donating and withdrawing groups affect the lifetime of the quintet state.

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[2] D. SÁROSINÉ SZEMES, T. KESZTHELYI, M. PAPP, L. VARGA, GY. VANKÓ, Quantum-chemistry-aided Ligand Engineering for Potential Molecular Switches: Tuning the High Spin to Low Spin Energy Barrier in Photoexcited $[Fe(terpy)_2]^{2+}$-based Molecules, *in preparation*

PS II - P40

Bullvalene, a molecular shape shifter

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Bullvalene ($C_{10}H_{10}$) rapidly rearranges its structure between 1.2 million isomers. In an unsubstituted state, these are fully degenerate. Upon substitution, the degenracy is lifted, but the fluxional behavior remains. It allows the substituents to almost freely float on the surface of the bullvalene cage and thus access all isomers. In our communication [1], we analyse the rearrangement networks using automated quantum chemical calculations. These start with the generation of the rearrangement network graph utilizing the symmetries of the bullvalene and the rearrangement transition state, followed by the structure optimizations and energy calculations.

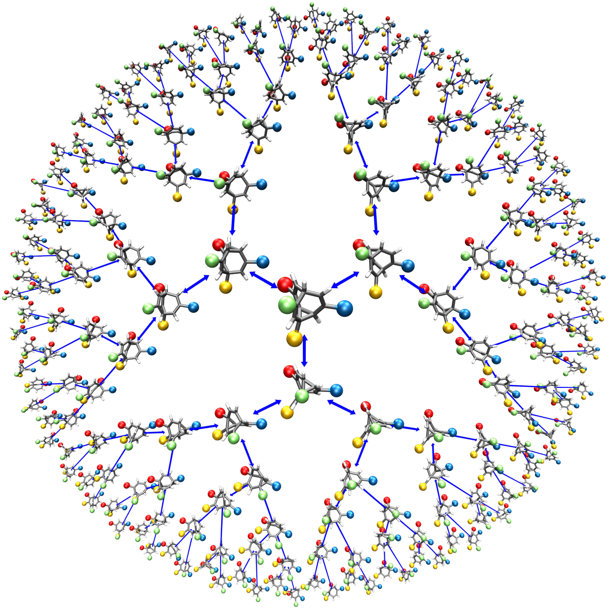

Figure 1: *Schematic representation of bullvalene fluxionality: A section of the rearrangement network of a tetrasubstituted bullvalene including all isomers up to 6 rearrangements away from the central structure.*

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PS II - P41

Anti-Kasha nitrogen photoelimination from diazoalkanes

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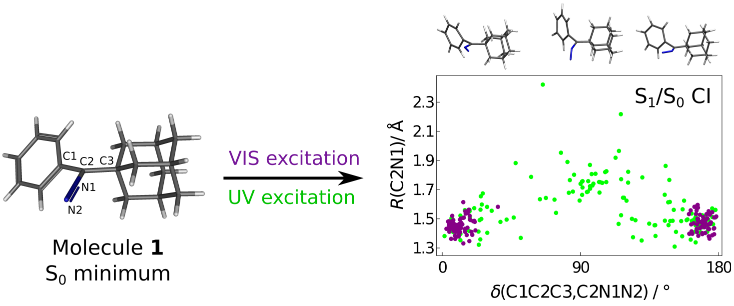
Nitrogen elimination from diazoalkanes is a well known reaction, which can easily be induced both thermally and photochemically [1-2]. In this work we present a photochemical study of diazo compound **1**. Experimentally, it was observed to have a pronounced anti-Kasha photochemistry, as it gives greater yield of nitrogen elimination after UV excitation than after VIS excitation. Also, an anti-Kasha fluorescence was observed.

Nonadiabatic surface hopping dynamics was used to elucidate the photochemical behaviour of **1**. To simulatie VIS and UV excitations, the dynamics was initiated in corresponding energy windows, i.e. in the S_1 and S_2/S_3 states respectively. In both types of simulations the S_1/S_0 CI was easily reached by elongation of the CN bond. We identified the anti-Kasha pathway of nitrogen elimination in around 30 % of trajectories initiated by UV excitation. The source of anti-Kasha fluorescence was also identified in around 4 % of UV-initiated trajectories and confirmed by excited-state optimization.



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PS II - P42

Determination of dynamic higher-order electric response properties. Mixed analytical/numerical approach

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Accurate theoretical determination of higher-order electric properties of relevance for the nonlinear optics (NLO) processes [1] is still a great challenge. Analytical computation of these properties based mostly on the response theory formalism has been implemented at various levels of theory, including accurate Coupled Cluster methods (CCSD and CC2 models) and a variety of DFT functionals. However, analytical determination of the second hyperpolarizability tensor γ is a serious computational task. In this study we employed a mixed approach, introduced by Jaszuński [2], of numerical differentiation of the analytically obtained dynamic response tensor components, with respect to the static electric field. The computational procedure is illustrated by the scheme below:

$$\alpha_{zz}(-\omega;\omega) \xrightarrow{dF_z} \beta_{zzz}(-\omega;\omega,0) \xrightarrow{dF_z} \gamma_{zzzz}(-\omega;\omega,0,0)$$

Differentiation twice of the zz component of polarizability α yields the zzzz component of the electro-optical Kerr effect (EOKE) tensor $\gamma(-\omega;\omega,0,0)$ [3]. By choosing different dynamic β tensors we obtained second hyperpolarizability tensors $\gamma(-2\omega;\omega,\omega,0)$ and $\gamma(0;\omega,-\omega,0)$ corresponding to Electric Field Induced Second Harmonic Generation (EFISHG) and Electric Field Induced Optical Rectification (EFIOR) processes, respectively.

For our test case the pyridine molecule was chosen. We used CAM-B3LYP functional and the Pol basis set of Sadlej [4]. All our analytical frequency-dependent calculations were carried out using the Dalton package [5]. We analyzed the overall accuracy of the approach, numerical stability of numerical differentiation, the range of applicability. The mixed procedure, if applied correctly, is superior to computational intensive analytical calculations.

The support of the WCSS centre in Wrocław (grant 222) is acknowledged. Part of the calculations were performed at the PAAD platform in Katowice.

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Multi-slit-type interference in C 2s photoionization of polyatomic molecules

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In the present work, we enlighten the first evidence of the multi-slit-type interferences in the C 2s photoionization of several polyatomic molecules: propane, n-butane, isobutane and methyl peroxide. We extend a previous study on the inner-valence MOs of a series of simple hydrocarbons with two centers [1]. This type of interference is related to both electronic and geometrical structure.

A more complex pattern is observed due to molecular orbital delocalization, blurring the distinction between interference and diffraction. The potential to extract geometrical information is emphasized, as a more powerful extension of the EXAFS technique.

We demonstrate that from the multi-slit interference patterns quantitative conformational analysis, generally outside the capability of photoionization studies, can be addressed, namely the determination of the relative weight of conformers in long-chain hydrocarbons and in a heterosystem (dimethylperoxide).

The experimental results are compared with the theoretical predictions by density functional theory (DFT) calculations. Cross-section calculations have been performed with the linear combination of atomic orbitals (LCAO) B-spline code [2], which provides an accurate solution of the DFT (Kohn-Sham) Hamiltonian for bound and continuum states.

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PS II - P44

The electronic structure of the transition metal complexes

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In our study were investigated the interactions between transition metal complexes and small molecules like for example O_2, CO_2. Standard B3LYP/6-311G* geometry optimization in various charge and spin states was performed using the Gaussian09 [1] program package. Solvent effect of dichloromethane was approximated by the Integral Equation Formalism Polarizable Continuum Model as implemented in Gaussian09. The stability of the optimized structures was confirmed by vibrational analysis (no imaginary vibrations). To elucidate the affinity towards CO_2 the obtained results were compared with the study of Froehlich and Kubiak [2].

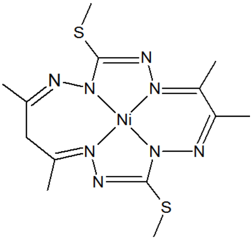

Figure 1: Structure of the Ni(II) macrocyclic complex under study from [3]

Acknowledgements
We thank the Slovak Grant Agencies APVV (contract No. APVV-15-0053), VEGA (contract No. 1/0598/16) and SIVVP (project ITMS 26230120002).

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MAPPING PATHWAYS OF DIATOMIC LIGAND MIGRATION INTO H-NOX DOMAINS AS A MODEL OF SGC ACTIVATION

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Keywords: H-NOX domain, molecular dynamics simulation, sGC, diffusion

Diatomic gas molecules are the ligands of numerous proteins, enabling them to perform their functions. Especially nitric oxide (NO), O_2 and CO contribute significantly to gas sensing in living organisms by binding to heme proteins. Heterodimeric heme protein αβ soluble guanylyl cyclase (sGC) is the unique receptor for nitric oxide (NO) in man which regulates various physiological processes through the NO (H-NOX domain)/cGMP (cyclase domain) signaling pathway. Dysfunctioning of this signaling network has been linked to cardiovascular, neurodegenerative and inflammatory diseases making sGC an intereting target for the pharmaceutical industry (with only a single drug presently on market which still need more advanced development for its performance). Therefore, deep mining in the knowledge of sGC would be critical for designing a potent drug.

In the present work, we tackle the gas-binding mechanism to H-NOX domain which leads to sGC activation. Two starting structures of homologous H-NOX proteins were selected, from the facultative anaerobe *Nostoc* genus and obligate anaerobe *Thermoanaerobacter tengcongensis,* as there is lack of the crystal structure of sGC. We studied the diffusion of NO, O_2 and CO using 600 ns long molecular dynamic simulations on these two proteins following a protocol previously published in our preceding work.[1] Cluster analysis of obtained trajectories in conjunction with visual inspection allowed us to explore the most likely pathways of gas migration throughout the protein body to distal heme pocket. Quantitative assessment of ligand diffusion through the trajectories enabled us to obtain rate constants for migration, which indicate that ligand diffusion in these proteins is similarly fast as in myoglobin for which experimental data also exists. Finally, we describe a few factors contributing to the differential activity of the diatomic ligands on the studied proteins.

Acknowledgements: The financial support of a Stipendium Hungaricum Fellowship, the Egyptian Government, NKFIH Grants 115503 and 116305, and of the Protein Science and its Applications National Programme (HunProtEx, 2018-1.2.1-NKP-2018-00005) is thankfully acknowledged. MD simulations were carried out at the facilities of the Hungarian NIIF Institute. Also, financial support.

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Catalytic properties of vanadium centers introduced into BEA zeolite

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Vanadium-based systems are used as catalysts for numerous oxidation processes, including oxidative dehydrogenation (ODH) of light alkanes. In this process alkanes are transformed into olefins, which are considered valuable substrates for the production of fuels and chemicals. It is believed that the activity of vanadium systems is directly linked to the properties of vanadium-oxygen species present on the catalyst surface.

The aim of the present studies is to gain deeper insight into the nature of the V species, which may be active in the ODH reaction. In our studies we focus on systems in which vanadium active phase is introduced into Beta (BEA) zeolite and compare the obtained results with those for V_2O_5.

The theoretical investigations were performed within Density Functional Theory (DFT) within cluster and periodic approaches with Perdew-Burke-Ernzerhof (PBE) functional. Cluster calculations were done with Turbomole program, using def2-TZVP basis set and resolution-of-identity (RI) procedure. Periodic calculations were done with VASP program, using PAW pseudopotentials, energy cutoff of 500 eV, and 1x1x k-point grid.

The exact structure and framework location of vanadium ions are not well defined based on the experimental evidence. It is postulated that vanadium may be present as V^V=O, V^V-OH, or HO-V^V=O centres. Therefore, these forms placed in nine non-equivalent crystallographic positions as well as in the ion exchange position are considered in the system under study. The performed calculations indicate that vanadium is present primarily in the V^V=O form. It can also be present as V^V-OH, but mainly in T2 and T6 BEA framework positions. The catalytic activity of the V species is due mostly to the properties of oxygen atoms linked to vanadium. DOS plots points also to the importance of the silanol OH groups present in the vanadium vicinity as possible active sites.

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PS II - P47

An Extension of the Charge and Energy Decomposition Scheme (ETS-NOCV) – On the Importance of Kinetic and Potential Energy Contributions in Chemical Bonding

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A chemical bond being "…of the fundamental territories of chemistry…" [1] is not an observable quantity in a quantum mechanical sense; accordingly, several quantum methods and models [1], which are suitable for descriptions of chemical bonds exist. Although these approaches apply various criteria leading to the division of electron density into atoms and bonds, [2] unarguably the two fundamental quantities used in quantum chemistry and often discussed in the context of chemical bonding are the kinetic and potential energy terms.

Accordingly, in this work we have further extended our charge and energy decomposition scheme ETS-NOCV [3] by decomposition of the orbital interaction energy term (associated with electron density reorganization due to formation of a chemical bond) into kinetic and potential energy contributions. It provides for the first time direct relation between the NOCV-based deformation density components $\Delta\rho_i$ (e.g. σ, π, etc.) and the corresponding changes in kinetic and potential energy terms ΔT_i and ΔV_i.

It has been found [4] that interfragment dative and covalent-type electron charge reorganizations upon formation of a series of strong and weak bonds employing main-group elements are due to lowering of the negative kinetic energy contributions, as opposed to the intrafragment polarizations (e.g., hyperconjugations in ethane), which are, in contrary, driven by the potential energy (electrostatic) component. Moreover, a ligand to metal donation and metal → ligand back-donation known universally from a Dewar-Chatt-Duncanson model, have been found to be driven by the opposite $\Delta T_i/\Delta V_i$ mechanisms.

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PS II - P48

Structure and electronic properties of clean and wet Cs(001)

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Cesiated molybdenum surface is a principle construction material of the H^- sources that are being developed for the needs of the future nuclear fusion devices [1]. The role of cesium is to decrease the work function, which is important for efficiency of the electron extraction [2]. Periodic density-functional theory (DFT) as implemented in the VASP [3, 4] has been employed to investigate the zero and the finite temperature structure of the Cs(001) and the effect of T on the work function. As these properties are primarily governed by the Cs-Cs interactions, we used a clean Cs surface as a simple model representing multiple layers deposited on a Mo surface. Two different simulation temperatures have been considered in our ab-initio molecular dynamics simulations: T_1=223 K is below and T_2=423 K is above the melting temperature. The radial distribution function computed for the uppermost layers at T_1 shows that the Cs atoms behave in the same way as in the crystalline material, while they behave like a molten Cs at the higher temperature considered in this work. Surprisingly, the finite temperature work function turns out to be nearly independent of these significant structural changes and the values computed for T_1 and T_2 are almost identical. By means of the zero temperature calculations we have also investigated the effect of the water deposition on the work function of Cs(001), which is the process that necessarily occurs at the operating conditions of the device [2]. Three different adsorption scenarios describing the deposition of a water molecule on Cs(001) have been investigated: i) physisorption, ii) partial dissociation to OH^- and H^+, and iii) a full dissociation to O^{2-} and 2 H^+. According to our simulations, the scenario ii) represents the most likely faith of H_2O adsorbed on the external Cs surface. Although such a process leads to a rather modest decrease of the work function with respect to the clean surface, our calculations clearly show that this effect is cumulative and hence the water adsorption represents an important factor that must be taken into account when analyzing the performance of the present generation of the H^- sources.

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Wave function overlap based assignment of UV absorption spectra and state specific analysis of solvation effects

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Overlaps between many-electron wave functions play an important role in photochemical studies as they offer an intuitive and straightforward way to track the electronic character of the states along different nuclear geometries without the need for complex diabatization procedures [1]. One example of a problem where tracking the electronic character of many states is required is the theoretical assignment of electronic spectra of polyatomic molecules.

In this contribution, we propose a procedure based on the computation of electronic wave function overlaps for automatically determining the character of electronic transitions and apply it to the study of UV spectra of DNA bases in the gas phase and in the aqueous environment. Spectra are generated using the nuclear ensemble method in the gas phase and in solution and the electronic states at all nuclear geometries are assigned based on overlaps with a set of reference states defined at the ground state minimum geometry. This allows a state specific analysis of solvation effects. Solvent-solute electrostatic interactions are state specific and strongly destabilize nRyd states, and to lesser extent nπ* and πRyd states while ππ* states are slightly stabilized.

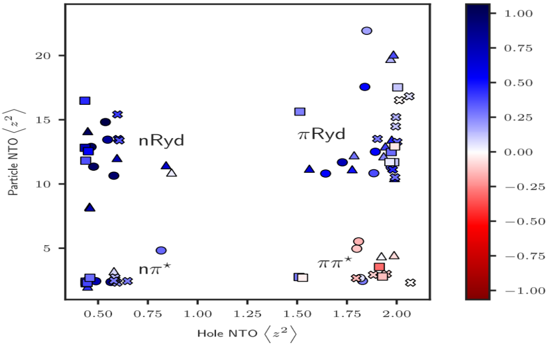

Figure 1: Solvent induced shifts for different types of electronic transitions present in the spectra of DNA bases.

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Shine a Light on Me:
Simulating the Reactivity of a Water Oxidation Catalyst

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Water splitting is carried out by photosystem II as part of photosynthesis to fuel cell growth and produce the oxygen we breathe. For decades, researchers have been attempting to harness this process to produce hydrogen gas for use as fuel. Recently, Schwarz et al. [1] have synthesized a molecular Mn-V oxide catalyst capable of promoting efficient light-induced water oxidation. To enable the design of improved catalysts with greater activity and stability on the basis of the Mn-V oxide catalyst, a deeper mechanistic understanding of this catalyst's reactivity is required. To this end, our research has followed a two-pronged approach: to establish the role of the Mn-V oxide catalyst in the water oxidation reaction, we have used DFT and TD-DFT to characterize a variety of possible intermediary catalyst-substrate assemblies. These intermediates will serve as starting points for further investigation of the water oxidation reaction mechanism. Furthermore, we employed the *ab initio* Nanoreactor [2], a discovery tool for reactive molecular dynamics pathways, to uncover previously unknown degradation products of the Mn-V oxide catalyst. Through these theoretical studies, we are working toward unraveling the reactivity of the Mn-V oxide catalyst, uncovering both the water oxidation reaction mechanism as well as new catalyst degradation pathways and enabling the design of improved water oxidation catalysts.

This research project is carried out at Institute for Theoretical Chemistry of the University of Vienna as part of the Transregional Collaborative Research Center TRR234 CataLight: Light-driven Molecular Catalysts in Hierarchically Structured Materials, coordinated by Ulm University.

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PS II - P51

Reaction Energetics & Diels-Alder Reaction Profiles for Enediones and Decalines by Means of DFT

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The original goal of our study was an energy comparison between isomers of several forskolin derivatives. Relative stabilities of decalines and related enediones were assesed with respect to cis/trans isomerism at the ring junction as well as with respect to axial/equatorial position of tert-butylsilyloxy substituent.

A comparison with experiment motivated us to perform a reaction path analysis for enedione synthesis from cis-(*tert*-butyldimethylsilyloxy)buta-1,3-diene with *p*-benzoquinone, which has been substitued by methyl and phenyl/naphthyl groups in the positions 2 and 5, respectively. Our results demonstrate that all energy barriers are quite close to each other (it is about 19–23 kcal mol^{-1}). The mechanism of the substituted *p*-benzoquinone addition to butadiene appears to be a non-concerted one.

All calculations were performed by means of density functional theory (DFT) employing the B3LYP/6–31G* implementation along with the SMD implicit solvation model of toluene and tetrahydrofuran.

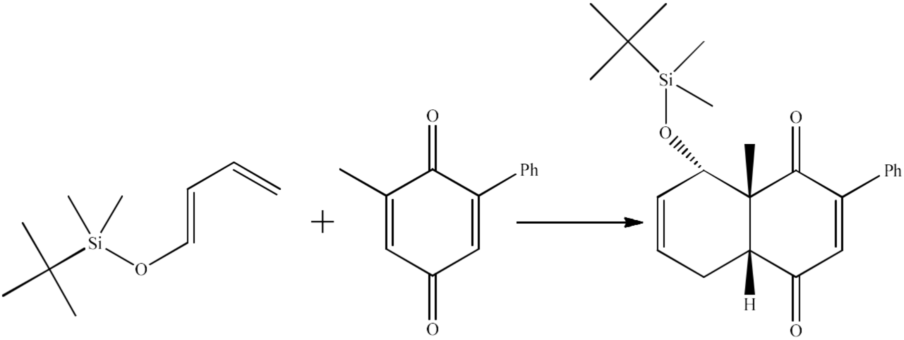

Figure 1: Example of the synthesis within Diels-Alder reaction.

PS II - P52

The kinetic energy potential from Kohn-Sham non-interacting kinetic energy expression.

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[2]*Institute for Microelectronics and Microsystems (CNR-IMM), Via Monteroni, Campus Unisalento, 73100 Lecce, Italy and Center for Biomolecular Nanotechnologies @UNILE, Istituto Italiano di Tecnologia (IIT), Via Barsanti, 73010 Arnesano (LE), Italy*

One of the most challenging aspects found in orbital-free density functional theory OF-DFT is to find a sufficiently accurate form of the so-called kinetic energy (KE) functional and potential. The KE functional is usually separated into two main contributions, namely Weizscker and Pauli term. The former has simple semi-local expression written throughout the electron density and its gradient. The Pauli term, however, can not be written in such a simple semi-local form which is the true bottleneck of this theory.

In order to understand better the spatial behavior the Pauli potential term in OF-DFT, one usually utilize Bartolotti-Acharya formula [1]. We have developed the new tool [2] to study the features of Pauli term. The new method employs the Optimized Effective Potential (OEP) method to calculate the KE potential corresponding to the Kohn-Sham non-interacting KE expression. The methodology and preliminary results will be presented during the poster session.

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PS II - P53

Electric properties of carbazole and its derivatives

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Dipole polarizability and higher-order electric properties are fundamental quantities in many areas of physics/chemistry, such as understanding of non-linear optics (NLO) processes [1]. Modern computational chemistry has the resources to properly determine these properties at different levels of theory, such as various Coupled Cluster (CC) methods or numerous Density Functional Theory (DFT) functionals. Unfortunately, for large, polyatomic molecules, the accurate determination of these quantities is still a challenging task. In our study we calculated electric dipole moments (μ), dipole polarizabilities (α), first-order (β), and second-order hyperpolarizabilities (γ) of carbazole and its derivatives. These molecules are very promising candidates for NLO applications, and some of their electric properties have already been calculated, e.g. [2].

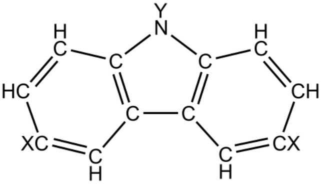

Figure 1: Studied molecules. X = H, F, Cl or Br; Y = H, CH_3 or CH_2CH_3.

We used SCF, CAM-B3LYP density functional [3], CC2, and CCSD methods with two basis sets: Sadlej Pol [4] and its reduced version Z3Pol [5]. All calculations were performed using the Dalton suit of program [6]. Our main goal was to verify the reliability of the CAM-B3LYP/Z3Pol results for the higher-order properties. The support of the WCSS centre in Wrocław (grant 222) is acknowledged. Part of the calculations were performed at the PAAD platform in Katowice.

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PS II - P54

Simulation of organic solvents and their effect on *Candida antarctica* lipase B

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The tremendous potential of enzymes can be further enhanced by using them in organic solvents rather than their natural aqueous reaction media. [1] Computer simulations with atomistic resolution are powerful tool for providing suggestions for improving and tuning enzymatic function. In order to ensure correct description of the organic phase *in silico*, we start with investigation of the structure and dynamics of acetonitrile and its binary mixtures with toluene and water in the whole composition range by molecular dynamics simulations with several combinations of empirical non-polarizable force fields. The acetonitrile and toluene system has been theoretically studied for the first time. [2] For static properties, it is possible to get nearly quantitative agreement with experimental data for both kinds of mixtures. The right trends for dynamical properties are also captured. Molecular insight to the systems, provided by radial and combined distribution functions, shows antiparallel arrangement of the closest acetonitrile molecules in the neat liquid. The addition of toluene causes structuring of acetonitrile and enhances the preference of antiparallel arrangement. Water has a smaller effect on the acetonitrile radial distribution functions, but it affects the preferences for individual arrangements.

With such a description in hands, we can examine the effect of organic solvents on the behaviour of Candida antarctica lipase B (CALB) - one of the most technologically used lipases. In general, lipases exhibit interfacial activation, i.e., an increase of activity at the lipid-water interface. This is caused by movement of a protein domain (lid) located near the active site which then makes it more accessible for the substrate. The size of the lid of CALB as well as the mechanism of its opening in contact with the less polar phase is not clear and, therefore, still debated and investigated. [3, 4] We use classical molecular dynamics simulations combined with enhanced sampling techniques to systematically study the effect of mutations in the lid domain and the role of the reaction medium on the lid motions.

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PS II - P55

Electronic spectra beyond the nuclear ensemble method

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We discuss possible limitations and improvements of the reflection principle (in the simulation community often called the nuclear ensemble method) as a method for electronic spectra modelling.[1] It is a semiclassical method which surpasses the harmonic approximation and it can easily cover the non-Condon effects, i.e. the dependence of the transition dipole moment on the vector of nuclear coordinates. It therefore describes forbidden transitions and temperature effects. On the other hand, it does not cover vibrational structures or interference effects in general.

We show that the statistical aspect is very important as we need thousands of excited state calculation in order to obtain converged spectra. Therefore, we want to: a) use efficient data processing with the best possible signal-to-noise ratio,[2] b) estimate the statistical error of not fully converged spectra, and c) use advanced statistical techniques such as machine learning to reduce the number of *ab initio* calculations. We show the applications of the aforementioned approaches to absorption spectra modelling of some important species.

The second part of this work is focused the so-called dephasing representation which is a natural extension of the reflection principle.[3] It is based on phase averaging of semiclassical trajectories and it covers also interference effects and vibrational structures, but it is very computationally demanding. We discuss again the limitations of this approach and we illustrate them on one-dimensional cases. We also present data for few molecular systems.

Financial support by Czech Science Foundation (project number 18-16577S) is gratefully acknowledged. Financial support from specific university research (MSMT No 21-SVV/2019).

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PS II - P56

Quantum chemical study of *ortho*-quinones toxicity through their copper(II) coordination ability

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Quinones are organic compounds formed by oxidation of aromatic molecules, most commonly phenols. While most phenols and their derivatives have beneficial effects, mono-substituted phenols can be toxic and carcinogenic [1]. This toxicity can be attributed to the formation of phenoxy radicals as well as *ortho*-quinones (1,2-benzoquinone) [2]. Benzoquinones cause cell damage through their ability to bind to thiol groups present in proteins as well as to DNA [3]. Furthermore, the quinone radical system reduces oxygen to the superoxide radical anion that can dismutate into hydrogen peroxide [2]. Therefore, the phenol toxicity could be partially explained by the toxicity of *ortho*-quinones.

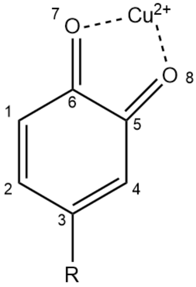

Fig. 1 – Structure and atom numbering of studied ^{2}[p-X-Q…Cu]$^{2+}$ complexes.

The toxicity of *ortho*-quinones was examined using the method of copper (II) probe, which had been previously used to explain antioxidant activity of various antioxidants [3]. The geometries of 27 neutral *para*-substituted *ortho*-quinones p-X-Q and their copper(II) complexes ^{2}[p-X-Q…Cu]$^{2+}$ (Fig. 1) were optimized at B3LYP/6-311G* level of theory [4]. Electron density distribution was evaluated in terms of Quantum Theory of Atoms-in-Molecules (QTAIM) topological analysis [5]. The toxicity, expressed in terms of Log(1/IC$_{50}$) of phenols in mouse lymphocyte leukemia cells (L1210) [2], was correlated with the electron density transfer between copper ion and coordinating oxygen atoms and similar parameters. Found correlations indicate that *ortho*-quinones contribute to the overall toxicity of phenols.

This work was supported by the Slovak Grant Agency VEGA (contract no. 1/0598/16) and by the Slovak Science and Technology Assistance Agency (contract no. APVV-15-0079).

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PS II - P57

Fragmentation of NOON-based measures for assessing the expected bias cancellation in SD FNDMC.

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Fixed-node diffusion Monte Carlo (FNDMC) calculations of large noncovalent systems rely on compact yet effective trial wave function Ψ_T, very often composed of single Slater determinant (SD), the nonequivalence of which may lead to innacurate FNDMC energy differences. Recently, Dubecký [1] introduced a measure of SD nonequivalence, δ, based on the Euclidean distance between the natural orbital occupation number (NOON) vector of the SD and the exact solution in the NOON vector space, evaluated at CCSD/aug-VDZ level. For truly large systems, its estimation, however, becomes intractable. In this study, by performing the many-body decomposition of δ in a number of noncovalent complexes, we show that δ can be decomposed and approximated by $\tilde{\delta}$ from fragment calculations. It turned out, that $\tilde{\delta}^2$ (including all two-body fragment interactions) may serve as the upper limit estimate of the overall δ.

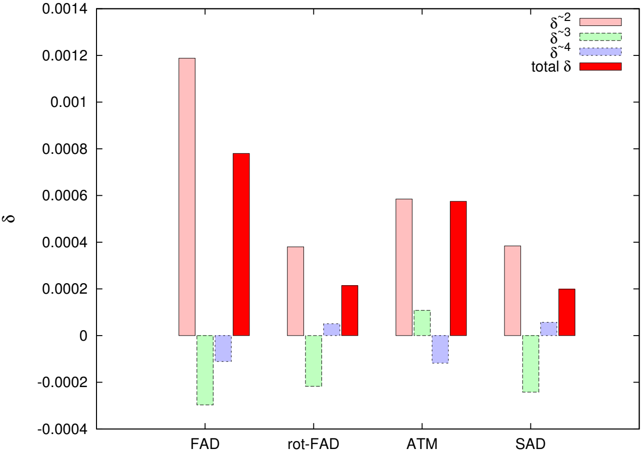

Figure 1: *Many-body decomposition of δ*

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Lifetimes of alkaline earth atoms computed within the Hermitian formulation of the coupled cluster response theory

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In this work we present a scheme for the computation of lifetimes of electronic states of atoms and molecules. We are focused on the cases where the matrix elements for dipole, quadrupole and spin-orbit operators all play important roles.

The theory presented in this work is based on the Hermitian formulation of the coupled cluster response theory [1,2]. In our previous work, we proposed a method for the computation of the transition moments between the excited states [3], as well as the transition moments from the ground state [4]. In this work we complement the theory with the derivation and implementation of the spin-orbit coupling matrix elements within the CCSD and CC3 approximations for the coupled cluster amplitudes.

The results are obtained with Gaussian and Slater basis sets. We present numerical results for lifetimes of selected electronic states in Ca, Sr, and Ba atoms and in Sr dimer.

Acknowledgments: This work was supported by the Polish National Science Centre within the grant No. UMO-2017/25/B/ST4/02698

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PS II - P59

The effect of Spin-Component-Scaling on excited state CC2 and ADC(2) potential energy surfaces

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Benchmark calculations with the regular and spin-component-scaled variants of the CC2[1] and ADC(2)[2] methods are presented for the electronically excited valence and Rydberg states of small and medium-sized molecules. Besides the vertical excitation energies and excited state gradients, the potential energy surfaces are also investigated via scans following the forces that act in the Franck-Condon region. The results are compared to higher level methods CCSD, CCSD(T)(a)* and CCSDT. It is found that certain serious discrepancies discovered earlier[3] for the regular CC2 are also present for ADC(2), but a large fraction of these flaws disappear if spin-component-scaling is employed. This makes these variants attractive alternatives of CC2 and ADC(2), offering more reliable potential energy surfaces and a low-power scaling computational cost with the system size.

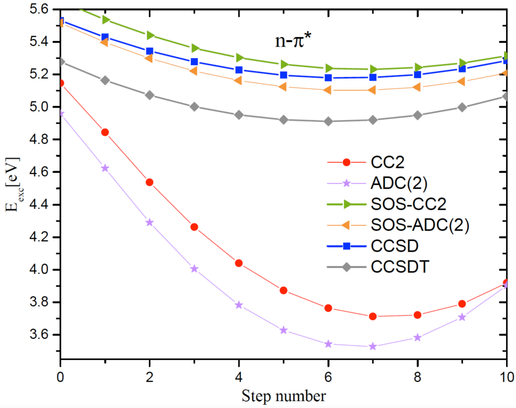

Figure 1: : Illustrative potential energy surface scan for cytosine.

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PS II - P60

CCSD(T) benchmark calculations and DFT modeling of polyethylene crosslinked by metallic atoms

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In our recent paper [1] we have analysed the concerted action of gold atoms and dispersion interactions in the DFT modelling of crosslinked polyethylene. In our model we used two oligomer chains (PEX) with 7 - 23 carbon atoms in each oligomer cross linked with one to three Au atoms through C-Au-C bonds (inset in Figure 1). Binding energies (BEs) with respect to two oligomer doublet fragments and Au are as high as 327 to 385 kJ/mol depending on the length of the oligomer chain. With three C-Au-C bonds is BE as high as 966 kJ/mol. Dispersion interactions in two PEX chains (with no Au atoms) lead to BE 25 - 90 kJ/mol (X = 7 - 23). Gold atoms used as crosslinking elements enhance BEs of PEX chains considerably. Dispersion contribution is lower, depends on the number of C atoms in PEX and keeps well organized parallel structure of PEX chains.

Next, in top to Au we used a series of other atoms, including all three coinage metals acting as a crosslinking element. Figure 1 shows that nearly linear dependence on number of C atoms in PEX holds for all six tested M elements. BE energy with Au is the highest, followed by Cu. BE with Ag is much lower; quite high is BE with zinc. Balanced account of C-M-C bonds with various M atoms and correct description of dispersion interactions needs highly accurate methods. For small PEX-M-PEX species we have performed CCSD(T) and local pair natural orbitals DLPNO CCSD(T) calculations serving as a benchmark for selection of suitable DFT functionals applicable for large systems.

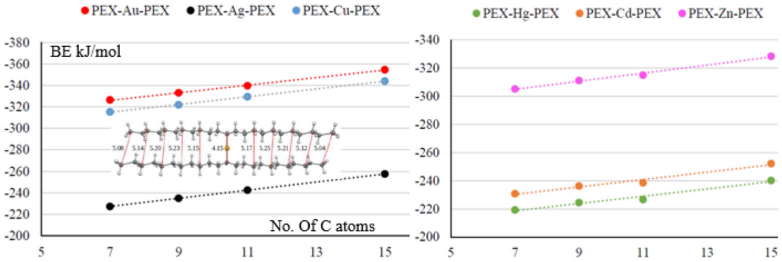

Figure 1: Crosslinking of PEX oligomers by selected metallic elements. X represent No. of C atoms in the oligomer. DFT PBE0+D3 binding energies with respect to two PE radicals (doublets) and the M atom.*

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Study of electronic structure and CO_2 affinity of complexes of transition metals

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The investigated complexes of transition metals (see Figure 1) have been studied in respect of electronic structure - CO_2 affinity relation [1]. Geometry optimization in various charge and spin states has been performed at B3LYP/6-311G* level of theory. The atomic d-population on the central atoms has been evaluated in terms of Mulliken population analysis. Atomic spin populations and charges were evaluated via the Quantum Theory of Atoms in Molecules (QTAIM) [2]. Solvent effects in N,N-dimethylformamide (DMF) were approximated by the Integral Equation Formalism Polarizable Continuum Model as implemented in Gaussian09. To elucidate the affinity towards CO_2 the obtained results were compared with the study of Froehlich and Kubiak on the affinity of [Ni(cyclam)]2+ towards CO_2 [3].

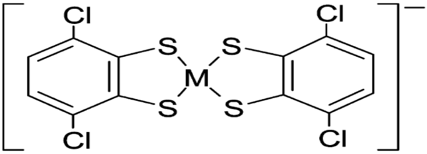

Figure 1: Structure of the investigated complexes

Acknowledgement

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Theoretical investigation of effect of alkylation and bromination on spin-orbit couplings in BODIPY based photosensitizers

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Halogenated and alkylated BODIPY derivatives are emerging as important photosensitizers for their use in photodynamic therapy of cancer cells due to their high triplet quantum yield [1]. Spin-orbit couplings (SOCs) inducing intersystem crossing in these molecules is evaluated with an effective one-electron spin–orbit Hamiltonian. Matrix elements of an effective one-electron spin–orbit Hamiltonian between singlet and triplet configuration interaction singles (CIS) auxiliary wave functions are calculated using a new code capable of dealing with singlets and both restricted and unrestricted triplets built up from up to three different and independent sets of (singlet, alpha and beta) molecular orbitals [2].

BODIPY's with halogen atoms are found to have SOCs significantly greater than BODIPY's possessing just alkyl moieties. Excited state dynamics of brominated-BODIPY was further explored with TD-DFT surface hopping molecular dynamics on potential energy surfaces resulting from the eigenstates of the total electronic Hamiltonian including the spin-orbit (SO) coupling. For the surface hopping trajectories, an accelerated MD approach was used, in which the SO couplings are scaled up, to make the calculations computationally feasible and the life times are extrapolated back to unscaled SO couplings. The life time of the first excited singlet state estimated by semi-classical surface hopping simulations is 180±75 ps [3].

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Searching for Optimal Arrangements of Perylene Pairs in Singlet Fission

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A multiple exciton generation, such as singlet fission (SF), in which one singlet exciton splits into two triplets could be utilized in organic photovoltaic materials to surpass the Schockley-Queisser limit.[1] The rate of SF depends not only on the excited states of a single molecule but also its packing arrangement. The rate of SF in the crystal structure of perylene diimide (PDI) has been investigated by time-resolved spectroscopy,[2] but the mechanism still keeps unrevealed. Understanding the relationship between its packing arrangement and SF process plays an important role in tuning favorable molecular pairs. A simple model described by the diabatic frontier orbitals is applied in searching for the local maximum rate of SF.[3] First, we examined the value of the square of the electronic matrix element in a six-dimensional space. Then, the SF rates in the local maxima of molecular pairs were obtained with the approximation of the Marcus theory. A few molecular pairs of PDI and terylene diimide (TDI) have been found with fast SF rates to compare with their parental pairs in our model.[4] These optimized geometries would provide a guideline for crystal engineering or covalent dimer synthesis in SF materials.

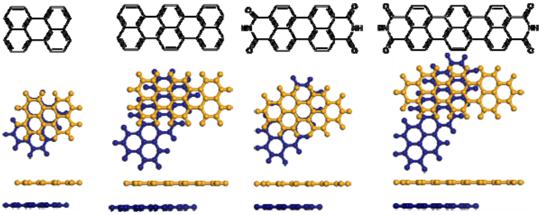

Figure 1: Optimal arrangements of molecular pairs for singlet fission

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