

CESTC 2018

16th Central European Symposium on Theoretical Chemistry

9–12th September

Srní, Czech Republic

Book of Abstracts

Talks

Tailored Coupled Cluster approaches to model strong correlation across the periodic table

Katharina Boguslawski^{1,2}

¹*Faculty of Chemistry, Nicolaus Copernicus University in Torun, Gagarina 7, 87-100 Torun, Poland*

²*Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Torun, Grudziadzka 5, 87-100 Torun, Poland*

The correlation energy is a central quantity in quantum chemistry. It is usually defined as the error in the electronic energy calculated within the independent-particle model of Hartree-Fock theory with respect to the exact solution of the electronic Schrödinger equation. Although there exists no rigorous distinction between different types of electron correlation effects, the correlation energy is typically divided into two categories: static/nondynamic and dynamic. While dynamic electron correlation effects can be accurately described by standard, well-established methods, like Møller-Plesset perturbation theory or single-reference coupled cluster theory, present-day quantum chemistry lacks simple, robust, and efficient algorithms for a qualitatively correct description of strongly-correlated many-body problems. We present a conceptually different approach that is well suited for strongly correlated electrons, but does not use the orbital model. Our method exploits the feature that electron correlation effects can be built into the many-electron wavefunction using two-electron functions, also called geminals. One of the simplest practical geminal approaches is the antisymmetric product of 1-reference-orbital geminals (AP1roG) [1, 2, 3], which is equivalent to the pair-Coupled-Cluster Doubles model.

In this work, we discuss the performance of AP1roG-based methods [3, 4] in modeling electronic structures for molecules containing light and heavy elements, including actinides [1-4]. We will present different excited state models [5, 6, 7] that allow us to target singly- and doubly-excited states with electron-pair theories. Our study indicates that geminal-based approaches provide a cheap, robust, and accurate alternative for the description of electron correlation effects in both ground and excited states.

- [1] K. Boguslawski, P. Tecmer, P.W. Ayers, P. Bultinck, S. De Baerdemacker, D. Van Neck, *Phys. Rev. B* **89** (2014) 201106(R).
- [2] K. Boguslawski, P. Tecmer, P. W. Ayers, P. Bultinck, S. De Baerdemacker, D. Van Neck, *J. Chem. Theory Comput.* **10** (2014) 4873.
- [3] K. Boguslawski, P. W. Ayers, *J. Chem. Theory Comput.* **11**, (2015) 5252.
- [4] K. Boguslawski, P. Tecmer, *J. Chem. Theory Comput.* **113** (2017), 5966.
- [5] K. Boguslawski, *J. Chem. Phys.* **145** (2017), 234105.
- [6] K. Boguslawski, *J. Chem. Phys.* **147** (2017), 139901.
- [7] K. Boguslawski, *in preparation* (2018).

Excited state properties as a key to understand molecular probes

Šimon Budzák¹, Denis Jacquemin², Miroslav Medved¹

¹Department of Chemistry, Matej Bel University, Tajovského 40, 97401 Banská Bystrica, Slovakia

²CNRS UMR 6230, CEISAM, Rue Houssiniere 2, 44322 Nantes, France

The environment-sensitive molecular probes are powerful tools for studying biomolecular structures, distribution of different targets in the cells and new solvents. In this contribution we will first discuss so called solvent probes. Typically, shifts of the absorption spectrum as a function of the solvent properties are observed. Betaine 30 is known for the extraordinary solvatochromism of its visible absorption band that goes from $\lambda=882$ nm in tetrachloromethane to $\lambda=453$ nm in water. This large blueshift partly originates from a dramatic decrease of the dipole moment upon excitation. Another interesting probe is 4-nitropyridine N-oxide which absorbs in UV region. Herein, we will present an analysis of the solvatochromic effects using a series of complementary approaches, including high-level calculation of the excited-state dipole and polarizability in the gas phase, several flavors of the polarizable continuum model, as well as molecular dynamics using an effective fragment potential (EFP) description of the solvent molecules. We will show that only such a ladder of approaches allows for a complete characterization of the electrostatics, hydrogen bond and dispersion contributions to the total solvent shifts.¹

A different type of molecular probes includes fluorescent sensors of metal ions. We will show how the fluorescence of a model Schiff base can be “turned on” in the presence of specific cation while non-radiative deactivation takes place in its absence.²

An important step towards reliable theoretical modelling of fluorescence is the optimization of excited state (ES) geometry. Thanks to advances in methodology and hardware, methods such as CC2, EOM-CCSD are nowadays applicable for the ES optimizations of larger molecules. Although these methods are considered reliable (and often used as a benchmark for cheaper approaches such as TD-DFT), their critical assessment in the context of ES geometries is still highly topical. We will discuss results of our investigation of the excited-state structural parameters determined for a large set of small compounds with the dual goals of defining reference values for further works and assessing the quality of the geometries obtained with relatively cheap computational approaches. We will present a comparison the excited-state geometries obtained with ADC(2), CC2, CCSD, CCSDR(3), CC3, and CASPT2 and large atomic basis sets.³

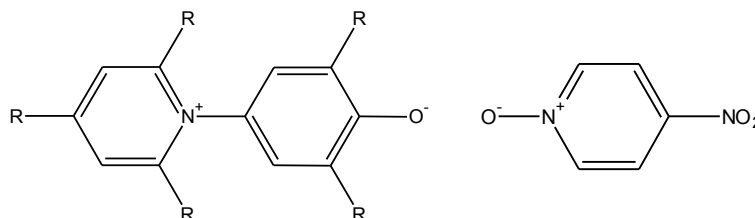


Figure 1: Polarity probes Betaine 30 (left) and 4-Nitropyridine N-oxide (right), R = Phenyl

[1] Budzak S and Jaunet-Lahary T, *et al.*, Chem Eur J **23** (2017) 4108.

[2] McDonald L, Wang J, *et al.*, J Phys Chem B **120** (2016) 766.

[3] Budzak S, Scalmani G, Jacquemin D, J Chem Theor Comput **13** (2017) 6237.

Raman spectroscopic study of polysulfanes in natural fluid inclusions

Vratislav Hurai¹, Ivan Černušák², Kirtikumar Randive³

¹*Institute of Earth Sciences, Slovak Academy of Sciences, Bratislava, Slovakia, e-mail: vratislav.hurai@savba.sk, tel.: 004212/3229 3207*

²*Department of Physical & Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Ilkovičova 6, 84215 Bratislava, Slovakia, e-mail: ivan.cernusak@uniba.sk*

³*Post-Graduate Department of Geology, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur, India, e-mail: randive101@yahoo.co.in*

We describe methane-rich, sulfur-bearing fluid inclusions with up to 68 mol. % H₂S, showing Raman bands at 2488, 2503, 2574, and 2899 cm⁻¹ associated with common ν_1 vibration modes of H₂S and CH₄ at 2609 cm⁻¹ and 2919 cm⁻¹, respectively. In addition, we report on reproducible “phantom” bands within the frequency range of 2579-2660 cm⁻¹. We document that fluid inclusions generate molecular hydrogen and surplus sulfur during irradiation with a 532 nm, 25 mW laser, thus indicating the breakdown of polysulfanes – H₂S_n.

We conducted quantum chemistry modelling based on density functional theory to better understand the origin of unusual Raman bands in the SH-stretching region. We simulated vibrations of simple H₂S, H₂S₂, H₂S₃, H₂S₄, H₂S₅, S₆₋₈ molecules, as well as selected complexes of $n = 1-4$ polysulfanes with the crown-shaped, orthorhombic cycloocta-sulfur identified in investigated fluid inclusions according to intense bands at 150, 219 and 473±1 cm⁻¹. Theoretical calculations suggest that vibrations at 2488, 2503, and 2574 cm⁻¹ most likely reflect symmetric and antisymmetric, H-bonded and non-H-bonded H₂S₂...S₈...H₂S₂, H₂S₂...S₈ and H₂S...S₈...H₂S complexes preserved in recrystallized sulfur melt.

Towards reasonable ab initio sublimation pressures for molecular crystals

Ctirad Červinka¹, Gregory Beran²

¹University of Chemistry and Technology, Prague, Technická 5, 16628, Praha 6, Czechia

²University of California, Riverside, 501 Big Springs Rd, CA 92521, Riverside, USA

Phase behavior of molecular crystals and its first-principles predictions, regarded as hardly feasible for long, have attracted growing interest of theoretical chemists with the advent of the available computational power. Reliable and fast ab initio predictions of stability of crystalline polymorphs or their sublimation pressures might become a game changer in future pharmaceutical research, cosmetic and food industry, exploration of cosmic bodies, epitaxial technologies, environmental modeling, etc.

Diverse quantum levels of theory proved to predict cohesive energies of molecular crystals well within the “chemical accuracy” level. [1] However, it remains extremely challenging to predict and compare the phase stability of various polymorphs [2,3] at finite temperatures and pressures. [4,5] Sublimation pressure exhibits an exponential dependence on temperature meaning that it is extremely sensitive to any uncertainties in Gibbs energy of the given phase. Therefore, a sub-kJ/mol accuracy of the first-principles calculations of cohesive and phonon-based properties for molecular crystals needs to be targeted. In principle, this can be achieved, as illustrated in Figure 1 with the optimistic scenario of calculations of sublimation pressure of solid CO₂.

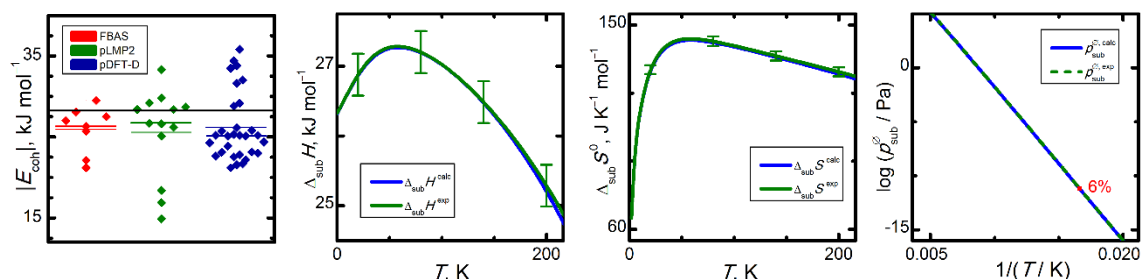


Figure 1: a) Scatter of literature cohesive energies for solid CO₂ calculated from first principles; b) Sublimation enthalpy – an optimistic case; c) Sublimation entropy; d) Sublimation pressure

Realistic scenario of such calculations faces appreciably larger uncertainties in all the computational steps. In this work, four molecular crystals (CO₂, C₂H₆, benzene, and imidazole) are selected to test and develop the methodology for first-principles predictions of sublimation pressures, combining the hybrid many-body interaction model, [3] periodic DFT calculations and ab initio gold, silver and bronze standard methods [6] for evaluation of intermolecular interactions. Taking the extreme sensitivity of sublimation pressures into account, reaching an agreement of theory and experiment within a single order of magnitude over a broad temperature range in a general case would be an appreciable achievement of the computational chemistry.

- [1] C. Červinka, M. Fulem, *J. Chem. Theory Comput.* **13** (2017) 2840-2850.
- [2] C. Červinka, G. Beran, *Chem. Sci.* **9** (2018) 4622-4629.
- [3] Y. Heit, K. D. Nanda, et al., *Chem. Sci.* **7** (2016) 246-255.
- [4] S. Hirata, K. Gilliard, et al., *Acc. Chem Res.* **47** (2014) 2721-2730
- [5] V. L. Deringer, J. George, et al., *Acc. Chem Res.* **50** (2017) 1231-1239.
- [6] L. A. Burns, M. S. Marshall, et al. *J. Chem. Phys.* **141** (2014) 234111.

A new point of view on the van der Waals radius

Dmitry Fedorov¹, Mainak Sadhukhan¹, Martin Stöhr¹, Alexandre Tkatchenko¹

¹*University of Luxembourg, avenue de la Faiëncerie 162a, 1511 Luxembourg, Luxembourg*

The concept of the van der Waals (vdW) radius, as a specific radius describing a distance an atom maintains from other atoms in non-covalent interactions, was introduced by Mack [1] and Magat [2]. Later on, Kitaigorodskii employed it in his theory of close packing of molecules in crystals [3]. Currently, this concept is widely used in the crystal chemistry, molecular physics, and structural biology. However, there is a long-standing problem with determination of the vdW radius considered as a statistical quantity from an experimental point of view.

Generally, one distinguishes between the equilibrium and crystallographic vdW radii [4]. The latter corresponds to the size of peripheral atoms in neighboring molecules packed in crystalline phases. This one is about 10-30% smaller than the equilibrium vdW radius which can be defined as half of the distance between two vdW-bonded atoms of the same chemical element [5]. Based on such a definition, we obtain a simple relation between this radius and the atomic dipole polarizability (in atomic units)

$$R_{\text{vdW}}(\alpha) = 2.54 \alpha^{1/7} \text{ a.u.} \quad (1)$$

which serves as a unified definition of the equilibrium vdW radius. The obtained expression, corroborated by our analysis of the experimental data, is surprisingly different from the corresponding classical result $R_{\text{vdW}} \propto \alpha^{1/3}$ commonly assumed in literature and employed in various models.

Remarkably, Eq. (1) can be simply generalized to vdW-bonded heteronuclear dimers. The equilibrium distance between two different atoms A and B obtained by the arithmetic mean for the polarizabilities

$$D_{\text{a}}(\alpha) = 2 \times 2.54 [(\alpha_A + \alpha_B)/2]^{1/7} \text{ a.u.} \quad (2)$$

is in very good agreement with the related literature data for noble gas dimers.

These findings allow to easily parametrize interatomic vdW potentials and improve the efficiency of computational models for intermolecular interactions [6]. Our definition of the equilibrium vdW radius dispenses with the need for its experimental determination. It paves also the way for a more accurate determination of the crystallographic vdW radii. Finally, the remarkable nature of the derived formula unveils a fundamental relationship between the geometric and electronic properties of atoms improving our understanding of the subtle balance between attractive and repulsive forces on the atomistic level.

[1] E. Mack, *J. Amer. Chem. Soc.* **54** (1932) 2141.

[2] M. Magat, *Z. Phys. Chem.* **16** (1932) 1.

[3] A. I. Kitaigorodskii, *Molecular Crystals*, Moscow: Nauka, (1971).

[4] S. S. Batsanov, *Inorganic Materials* **37** (2001) 871.

[5] A. Bondi, *J. Phys. Chem.* **68** 441 (1964).

[6] D. Fedorov, M. Sadhukhan, M. Stöhr, A. Tkatchenko, arXiv:1803.11507.

Excited state dynamics of transition metal complexes

Leticia González

leticia.gonzalez@univie.ac.at

Institute for Theoretical Chemistry, Faculty of Vienna, University of Vienna, Währinger Strasse 17, 1090 Vienna, Austria

In this lecture, current challenges to describe the electronic excited states and corresponding relaxation mechanism after light irradiation in transition metal complexes will be presented. The accurate description of excited states of transition metal complexes and its dynamics is particularly difficult for a number of reasons. These include the typical near-degeneracy of many electronic states of different nature, the presence of vibronic and spin-orbit couplings, the complex interplay of the complexes with the solvent and ultimately the size of the systems. As an example, the ultrafast intersystem crossing dynamics of $[\text{Ru}(\text{bpy})_3]^{2+}$ will be shown^[1] –as obtained from direct trajectory surface hopping simulations using the SHARC^[2] approach. Further, the applicability of electrostatic embedding quantum mechanics/molecular mechanics (QM/MM) dynamics to describe the excited state processes of $[\text{Re}(\text{CO})_3(\text{im})(\text{phen})]^+$ in water will be illustrated, as well as the power of using quantitative wave function analyses to follow the character of the wavefunction on-the-fly.^[3]

References

- [1] A. J. Atkins, L. González, *J. Phys. Chem. Lett.* **2017**, 8, 3840-3845.
- [2] S. Mai, P. Marquetand, L. González, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2018**, (in press), DOI: 10.1002/wcms.1370.
- [3] S. Mai, F. Plasser, J. Dorn, M. Fumanal, C. Daniel, L. González, *Coord. Chem. Rev.* **2018**, 361, 74-97.

Notes

Wave Function Methods for Excited States and Spectroscopic Applications

Róbert Izsák

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm Platz 1, 45470 Mülheim an der Ruhr, Germany

Although the concept of pair natural orbitals has been known for decades, it was only during the last ten years that they have been employed in the design of efficient computational algorithms for the calculation of accurate ground state energies. The domain-based pair natural orbital (DLPNO) approach has been successfully used to accelerate coupled cluster (CC) methods for both closed and open shell ground states.[1] While it is now possible to accurately calculate ground state energies for molecules consisting of several hundred atoms, the application of PNOs for excited states has proved to be a harder problem. While it is possible to combine ground state DLPNO calculations with canonical excited state equation of motion (EOM) CC theory, the resulting methods still retain the prohibitive scaling of canonical CC theory.[2] However, it is possible to reduce the size of the excitation manifold in which the final diagonalization is carried out to include only the singles by a second similarity transformation. The resulting similarity transformed EOM (STEOM) method scales similarly to time dependent density functional theory (TDDFT), although it requires a ground state CC and ionized EOM calculations. Employing the DLPNO scheme to the latter, it is possible to carry out accurate wave function based calculations for excited states of ~100 atom molecules at near TDDFT cost but without neglecting the contributions of higher excitations. The ingredients of this method are currently tested[3], and the final DLPNO-STEOM method will be made available in the ORCA quantum chemistry program package.

- [1] C. Riplinger, P. Pinski, U. Becker, E. F. Valeev and F. Neese, *J. Chem. Phys.* **144** 024109 (2016).
- [2] A. K. Dutta, F. Neese and R. Izsák, *J. Chem. Phys.* **145** 034102 (2016).
- [3] A. K. Dutta, M. Saitow, C. Riplinger, F. Neese and R. Izsák, *J. Chem. Phys.* accepted for publication (2018).

Towards an accurate theoretical description of molecular solids

Jiří Klimeš¹, Jaroslav Hofierka¹

¹*Faculty of Mathematics and Physics, Charles University, Ke Karlovu 3, 121 16 Prague, Czech Republic*

Molecular solids are materials important both in nature and industries. The accurate calculation of their binding energies is difficult as both strong intramolecular and weaker intermolecular forces need to be described reliably. The random phase approximation to the correlation energy (RPA) has emerged as a promising tool for this task. However, a general tendency to underbind has been observed for systems such as molecular dimers or solids. One of the ways that have been proposed to improve the accuracy of RPA are the so-called singles corrections, originally developed by Ren and coworkers [1] and later modified to improve their accuracy for systems with delocalised electrons [2]. Here we give a brief overview of this scheme and show the results for binding energies of molecular solids [3, 4]. However, to obtain reliable results, one needs also to reach high precision, that is, the results need to be converged with the numerical parameters. The basis-set size is a typical parameter, but it's not the only one. For example, when the many-body expansion (MBE) is used to obtain the binding energy, one needs to converge it with the number of molecules in a cluster and with the real-space cut-off distance. To understand the problems related to convergence, we compared binding energies obtained with VASP, which implements periodic boundary conditions, to MBE results done with a gaussian-basis code Molpro for four crystals of small molecules. This allows us to identify general settings required for both approaches to yield identical results. A basic requirement for MBE and periodic calculations to yield identical lattice energies is that both approaches give identical binding energies also for small clusters of the molecules, most notably for dimers. For many methods, sufficient agreement can be reached. However, I'll show examples where a detailed comparison of dimer binding energies from periodic and finite cluster calculations allowed us to identify issues with implementations of exchange-correlation functionals, problems with pseudopotentials, and other.

[1] Ren, Tkatchenko, Rinke, Scheffler, *Phys. Rev. Lett.* **106** (2010) 153003.

[2] Klimes, Kaltak, Maggio, Kresse, *J. Chem. Phys.* **143** (2015) 102816.

[3] Klimes, *J. Chem. Phys.* **145** (2016) 094506.

[4] Zen, Brandenburg, *et al.*, *PNAS* **115** (2018) 1724.

Energy and density partitioning as tools for investigations of intermolecular complexes – several case studies

Tatiana Korona¹, Sirous Yourdkhani², Michał Chojecki¹

¹*Faculty of Chemistry, University of Warsaw, ul. Pasteura 1, PL-02-093 Warsaw, Poland*

²*Department of Chemical Physics and Optics, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 3, CZ-12116 Prague 2, Czech Republic*

An availability of partitioning schemes for molecular energies and properties increases considerably the explanatory and predictive power of computational chemistry. Such schemes, although often not strict, are nevertheless physically convincing and allow in many cases to provide answers to important questions, concerning e.g. the substituent dependence of stability and reactivity. Among such approaches existing in the literature one can name: charge-density analysis via quantum theory of atoms-in-molecules – QTAIM [1], interacting quantum atoms – IQA [2], natural bond orbitals – NBO [3], functional group-symmetry-adapted perturbation theory (F-SAPT) [4], and others. In this contribution we apply some of these methods to study several interesting molecules and intermolecular complexes in an attempt to explain and predict minima stability and variation of molecular properties [5, 6, 7, 8, 9]. We also present a recently developed extension of the IQA model, allowing to separate π and σ IQA contributions of the electron density, and utilize it to challenge the established point of view of the nature of the substituent effect for the interaction of cations with benzene derivatives [10].

Acknowledgement: This research was supported in part by PL-Grid Infrastructure. The support from the National Science Centre of Poland through grant 2015/19/B/ST4/01812 is gratefully acknowledged.

- [1] R.F.W. Bader, *Atoms in Molecules - A Quantum Theory*; Oxford University Press: Oxford, U.K., 1990
- [2] A.M. Pendás, E. Francisco, M.A. Blanco, *J. Comput. Chem.* 26, 344 (2005)
- [3] A.E. Reed, L.A. Curtiss, F. Weinhold, *Chem. Rev.* 88, 899 (1988)
- [4] R.M. Parrish, T.M. Parker, C.D. Sherill, *J. Chem. Theory Comput.* 10, 4417 (2014)
- [5] S. Yourdkhani, T. Korona, N.L. Hadipour, *J. Phys. Chem. A* 119, 6446 (2015)
- [6] S. Yourdkhani, T. Korona, N.L. Hadipour, *J. Comp. Chem* 36, 3412 (2015)
- [7] S. Yourdkhani, M. Chojecki, M. Hapka, T. Korona, *J. Phys. Chem. A* 120, 6287 (2016)
- [8] M. Chojecki, D. Rutkowska-Żbik, T. Korona, in preparation (2018)
- [9] M. Chojecki, S. Yourdkhani, D. Rutkowska-Żbik, T. Korona, *Comp. Theor. Chem.*, 1133, 7 (2018)
- [10] S. Yourdkhani, M. Chojecki, T. Korona, submitted (2018)

Mechanochemical indicators

Martin Krupička¹

¹*Department of Organic Chemistry, University of Chemistry and Technology, Technická 5, 16628 Prague, Czech Republic*

Mechanochemistry is dealing with the application of mechanical force on the molecule, which increases energy of the system, and complements the other typical methods of activation, i.e. heating, irradiation or application of electric current. Within the realm of covalent mechanochemistry, the force can be applied directionally and to specific atoms. Handful of kinetic experiments have been carried in order to elucidate the processes[1].

In order to understand and design usable mechanochemical reactions, it is important to quantify the forces acting in the system. Therefore, the main aim of our work is to design mechanochemical indicators, which will instantly and reversibly change its spectral properties as a function of external force.

Macrocyclic indicator for the IR range containing the carbonyl group has been synthesized in our lab (Fig. 1). Isomerization of the photoswitch induces the strain in the molecule, which should result in shift of absorption band.

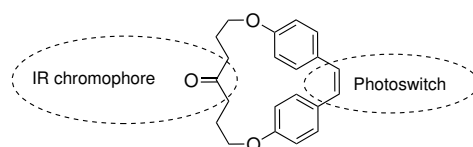


Figure 1: Molecular force probe with carbonyl group for IR spectroscopy

Experimentally more sensitive approach is the application of UV-VIS spectroscopy, either in absorption or fluorescence regime. From the series of fluorophores, tetraphenylethylene (TPE) derivatives were selected as versatile and easily modifiable building blocks. The TPE is designed to be incorporated within a macrocycle or in polymer material.

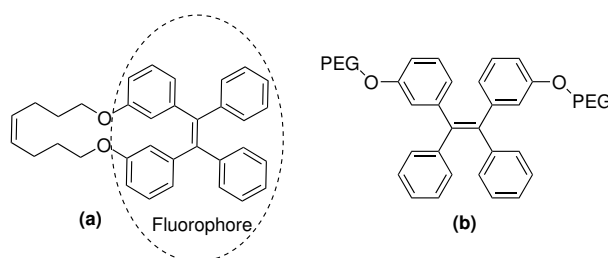


Figure 2: Tetraphenylethylene derivatives as (a) molecular force probe and (b) mechanophore for polymer material

Computational screening has proven to be an important part of the process as the desired compounds are often difficult to synthesize.

- [1] Lenhardt, J. M., Black, A. L. and Craig, S. L. *JACS* **131** (2009) 10818–10819
Wollenhaupt, M., Schran, C., Krupička, M. and Marx, D. *ChemPhysChem* **19** (2018) 837–847.

Coupled-Cluster Method Tailored by Tensor-Network States in Quantum Chemistry

Ö. Legeza¹, L. Veis², A. Antalík², F. Neese³, J. Pittner², K. Gunst⁴, F. Verstraete⁴,
S. Wouters⁴, D. Van Neck⁴, F. M. Faulstich⁵, A. Laestadius⁵, S. Kvaal⁵, R. Schneider⁶

¹*Wigner Research Center for Physics, P.O. Box 49, Budapest, Hungary*

²*J. Heyrovský Institute of Physical Chemistry, 18223 Prague 8, Czech Republic*

³*Max Planck Institut für Chemische Energiekonversion, D-45470 Mülheim an der Ruhr, Germany*

⁴*Center for Molecular Modeling, Ghent University, Technologiepark 903, 9052 Zwijnaarde, Belgium*

⁵*Hylleraas Centre for Quantum Molecular Sciences, Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway*

⁶*Technische Universität Berlin, Straße des 17. Juni 136, 10623 Berlin, Germany*

We present general tensor network state techniques, that can be used for the treatment of strongly correlated molecular systems, and connect them to concepts already used in many-body quantum physics [1]. Recent developments on a new variational tree tensor network state (TTNS) ansatz, the three-legged tree tensor network state (T3NS) will also be discussed [2]. In the T3NS, advantages of the density matrix renormalization group (DMRG) method, in particular a low computational cost and a simple implementation of symmetries, are combined with advantages of TTNS, namely incorporating more entanglement. These methods are very efficient to recover static correlations, however, they require large bond dimension to recover dynamic correlations. Recently, the combination of the DMRG method with coupled cluster (CC) approach resulted in the novel DMRG-TCC method [3], that is the first quasi multi-reference scheme that provides a black-box implementation of the tailored CC (TCC) method up to a numerical threshold [4]. As a result, the DMRG method is responsible for the proper description of non-dynamic correlation, whereas the dynamic correlation is incorporated through the framework of the CC theory. This makes TNS-TCC accessible to a broad class of researchers from various fields of study.

- [1] Sz. Szalay, M. Pfeffer, V. Murg, G. Barcza, F. Verstraete, R. Schneider, and Ö. Legeza, *Int. J. Quant. Chem.* **115**, (2015) 1342.
- [2] K. Gunst, F. Verstraete, S. Wouters, Ö. Legeza, D. Van Neck, *J. Chem. Theor. Comp.* **14** (2018) 2026
- [3] L. Veis, A. Antalík, J. Brabec, F. Neese, Ö. Legeza, J. Pittner, *J. Phys. Chem. Lett.* **7** (2016) 4072.
- [4] F. M. Faulstich, A. Laestadius, S. Kvaal, Ö. Legeza, R. Schneider, arXiv:1802.05699 (2018)

Approximate coupled-cluster schemes with singular-value decomposition of the triple excitations amplitudes

Michał Lesiuk

Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

The CCSD(T) method of Raghavachari *et al.* [1] has established itself as the *gold standard* of quantum chemistry. However, there are many important cases when the CCSD(T) method breaks down and gives even a qualitatively wrong answer. In such cases it would be natural to go to the full CCSDT model [2] or even to some higher-order methods. Unfortunately, the computational costs of the latter two are typically orders of magnitude larger than of CCSD(T) and thus calculations for most molecular systems are out of question.

A promising method to reduce the computational burden related to the T_3 amplitudes is to perform singular-value decomposition (SVD) of some approximate amplitudes and solve coupled-cluster equations in the subspace spanned by only a handful of singular-vectors corresponding to the largest singular values. This approach has been pioneered by Hino *at al.* [3] However, no efficient methods have been known thus far to compute SVD of a given T_3 amplitudes. Brute-force methods applied in Ref. [3] possess a computational cost proportional to \mathcal{N}^8 - the same as the complete CCSDT theory. This eliminates all potential gains from the rank-reduction of the T_3 amplitudes.

We demonstrate a novel technique to obtain SVD of the T_3 amplitudes. The presented method is based on the Golub-Kahan bidiagonalisation strategy [4] and does not require the amplitudes to be stored. The computational cost of the method is comparable to several CCSD iterations. Moreover, the number of singular vectors to be found can be predetermined by the user and only those singular vectors which correspond to the largest singular values are obtained at convergence. We show how the subspace of the most important singular vectors obtained from an approximate triple amplitudes tensor can be used to solve equations of the CC3 method [5] - an approximate variant of the CCSDT theory.

The new method is tested for a set of small and medium-sized molecular systems in basis sets ranging in quality from double- to quintuple-zeta. It is found that to reach the chemical accuracy (≈ 1 kJ/mol) in the total CC3 energies as little as 5 – 15% of SVD vectors are required. This corresponds to the compression of the T_3 amplitudes by a factor of ca. 0.0001 – 0.005. Further benchmarks are performed to check the behaviour of the method in calculation of, e.g. interaction energies or rotational barriers, as well as in bond-breaking processes.

- [1] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).
- [2] J. Noga and R. J. Bartlett, J. Chem. Phys. **86**, 7041 (1987); G. E. Scuseria and H. F. Schaefer, Chem. Phys. Lett. **152**, 382 (1988).
- [3] O. Hino, T. Kinoshita, and R. J. Bartlett, J. Chem. Phys. **121**, 1206 (2004).
- [4] G. H. Golub and W. M. Kahan, SIAM J. Numer. Anal. Ser. B **2**, 205 (1965).
- [5] H. Koch, O. Christiansen, A. M. Sanchez de Merás, and T. Helgaker, J. Chem. Phys. **106**, 1808 (2005).

Fragment-Based DFT methods for Molecular Crystals

Oleksandr A. Loboda^{1,2}, Grygoriy A. Dolgonos¹, A. Daniel Boese¹

¹*Institute of Chemistry, University of Graz, Heinrichstrasse 28/IV, A-8010 Graz, Austria*

²*A. V. Dumansky Institute of Colloid and Water Chemistry, National Academy of Sciences of Ukraine, Vernadsky bld. 42, Kyiv-142, Ukraine*

We developed three fragment-based embedding methods and report their performance for the X23 set of molecular crystals. For each of QM:QM (a quantum mechanical method embedded into another quantum mechanical method) methods aimed to mimic hybrid functionals we present also comparative results obtained with the various density functionals[1]. Our PBE0:PBE+D3, PBE0:PBE+MBD, and B3LYP:BLYP+D3 calculations yield at a reduced computational cost lattice energy errors close to the ones of the parent hybrid density functional method.

Apart of QM:QM methods, we present also an alternative to periodic DFT+D, in which a combination of BLYP embedded into density functional based tight binding (DFTB) is employed. Without any reparametrization the BLYP+D:DFTB+D method essentially yields the same results as periodic BLYP+D calculations for the X23 benchmark set of molecular crystals[2].

[1] O.A. Loboda, G.A. Dolgonos, A.D. Boese, J. Chem. Phys. **XX** (2018) XX.

[2] G.A. Dolgonos, O.A. Loboda, A.D. Boese, J. Phys. Chem. A **122** (2018) 708.

Phonon Superscatterers

Georg K. H. Madsen*

Institute of Materials Chemistry, TU Wien, A-1060 Vienna, Austria

Dopants play an important role in engineering the electronic properties of semiconductor materials. At the same time they can strongly influence the phonon scattering processes and thereby the thermal conductivity. We have recently shown how Boron, when substituted in place of Carbon in 3C-SiC, acts as a super-scatterer and exhibits resonant phonon scattering which is one to two orders of magnitude higher than Nitrogen and other defects.¹ The increased scattering leads to a thermal conductivity that is suppressed by one to two orders of magnitude.

The resonance is caused by a large perturbation in the 2nd order inter-atomic force constants (IFCs). This large IFC perturbation is the result of a small lattice distortion accompanied by a change from tetrahedral to threefold symmetry around the Boron atom. In order to understand the physics behind and the factors causing resonance in semiconductors, we have studied the influence of charge on the defect structure and phonon scattering. We explain the results with the help of a simple 1D mono-atomic linear chain.² We show that small lattice distortions emanating from two or more close energy minima in potential energy surface lead to a very large IFC perturbation. Such a behavior is characterized by a peak in the trace of imaginary part of the T matrix (which is closely related to the scattering rates) and a reflection coefficient approaching unity.

The strong influence of the potential energy surface surrounding the defect atom on the thermal conductivity opens a new path to tailor thermal conductivities where required values range from very low in thermoelectric materials to very high in power electronics applications.

* Electronic address: georg.madsen@tuwien.ac.at

¹ A. Katre, J. Carrete, B. Dongre, G. K. H. Madsen, and N. Mingo, *Phys. Rev. Lett.* **119**, 075902 (2017).

² B. Dongre, J. Carrete, A. Katre, N. Mingo, and G. K. H. Madsen, *J. Mater. Chem. C* **6**, 4691 (2018).

Theoretical study of Ru- and Mn-based coordination compounds with biological activity

Michal Malček¹, Lukáš Bučinský¹, Michal Zalibera¹, Peter Rapta¹, Vladimír B. Arion²

¹*Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinskeho 9, 812 37 Bratislava, Slovak Republic*

²*Institute of Inorganic Chemistry, Faculty of Chemistry, University of Vienna, Währinger Strasse 42, A-1090 Vienna, Austria*

State-of-the-art theoretical approaches are nowadays a valuable tool able to predict the compounds' properties as well as to support (or contradict) the experimentally obtained results in many areas. In this work Density Functional Theory (DFT), Complete Active Space (CAS) and Multi-Reference Configuration Interaction (MRCI) methods have been used to characterize newly synthesized biological active coordination compounds based on Ru or Mn.[1]

Nitric oxide (NO) plays an important role in many different biological processes. [2] The energetics of NO release in Ru-nitrosyl complexes with four equatorially bound indazole ligands has been studied at the DFT level of theory. The obtained reaction enthalpies confirm the release of the NO• followed by binding the Cl⁻ anion (energetic outcome of *ca.* -7 eV). Hyperfine coupling constants of nitrogens and g-tensors of the reduced Ru-complexes were calculated using the unrestricted Kohn-Sham (UKS) formalism.

The new six-coordinate dimanganese(III) complexes with a salen type ligand have been synthesized and characterized. Dimanganese unit is a part of the active site in a series of metalloenzymes, thus the study of Mn-based complexes can shed light on the catalytic activity of these enzymes.[3] Axial and rhombic components of the zero field splitting (ZFS) Hamiltonian as well as the g-tensors were calculated at the DFT, CAS and MRCI level of theory. The inclusion of both spin-orbit and spin-spin coupling has been found crucial for a proper interpretation of the experimentally obtained EPR spectra.

Acknowledgements

We are grateful to the Slovak Grant Agencies APVV (contract No. APVV-15-0079 and APVV-15-0053), VEGA (contracts No. 1/0598/16, 1/0416/17 and 1/0466/18) and SIVVP project(ITMS code 26230120002).

- [1] E. Orlowska, and M. V. Babak, *et al.*, *Inorg. Chem.* (2018) under revision
[2] J. A. McCleverty, *Chem. Rev.* **104** (2004) 403-418.
[3] S. Shova and M. Cazacu, *et al.* *Dalton Trans.* **46** (2017) 11817-11829.

Multiple bond breaking with APSG based correlation methods

Ádám Margócsy¹, Piotr Kowalski², Katarzyna Pernal², Péter Surján¹, Ágnes Szabados¹

¹*Eötvös Loránd University, Institute of Chemistry, H-1518 Budapest, POB 32, Hungary*
²*Lódź University of Technology, Institute of Physics, ul. Wólczańska 219, 90-924, Lódź, Poland*

While quantum chemical methods using only one Slater determinant (single-reference methods) give a qualitatively good description of the ground state of molecules around the equilibrium geometry, they have a tendency to fail for bond dissociation. This problem can be overcome by using multi-reference wavefunctions. Geminal wave functions represent a simple class of the latter, the complete wave function being built from two-electron blocks (geminals). A simple geminal wave function is the APSG (Antisymmetrized Product of Strongly Orthogonal Geminals) using strongly orthogonal and singlet geminals. Since the intrageminal part of the electron correlation is given exactly by APSG, the breaking of a single bond (or multiple isolated bonds) can be described correctly. Breaking of multiple bonds attached to the same atom remains flawed, which can be understood as a consequence of the lack of triplet components[3]. The APSG based correlation methods (aiming to capture the intergeminal part of the correlation) tend to inherit this shortcoming.

A sensitive indicator of the error in the APSG wave function is the so-called local spin obtained by partitioning the total spin squared expectation value into e.g. atomic and diatomic contributions:

$$\langle S^2 \rangle = \sum_A \langle S^2 \rangle_A + \sum_{A \neq B} \langle S^2 \rangle_{AB}$$

This sensitivity qualifies the local spin as a useful quantity when investigating dissociation processes described by APSG.

We present the results of the local spin analysis on simple molecular systems to compare the performance of two APSG based correlation methods on the example of multiple bond breaking. The methods investigated are Linearized Coupled Cluster (APSG-LCC)[1] and Extended Random Phase Approximation (APSG-ERPA)[2]. Based on the numerical results we show that the flaw of the APSG reference function is present in APSG-LCC and APSG-ERPA in different ways. Techniques to overcome the dissociation problems are discussed as well.

[1] Zoboki, Szabados, Surján, *J. Chem. Theory Comput.* **9** (2013) 2602-2608.

[2] Pernal, *J. Chem. Theory Comput.* **10** (2014) 4332-4341.

[3] Surján, Jeszenszki, Szabados, *Mol. Phys.* **113** (2015) 2960-2963.

Excited States of Polyaromatic Hydrocarbons

F. Bettanin¹; L.F.A. Ferrão¹, M. Pinheiro Jr.¹, A.J.A. Aquino^{2,3}, H. Lischka, F.B.C. Machado¹,
Nachtigallova, D.^{4,5}

¹ Departamento de Química, Instituto Tecnológico da Aeronáutica, São José dos Campos, 12228-900, São Paulo, Brazil,

² Department of Chemistry and Biochemistry, Texas Tech University Lubbock, TX 79409-1061, USA

³ School of Pharmaceutical Sciences and Technology, Tianjin University, Tianjin, 300072 P.R.China

⁴ Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nam. 2, CZ-16610 Prague 6, Czech Republic

⁵ Palacky Univ, Reg Ctr Adv Technol & Mat, Dept Phys Chem, Olomouc 77146, Czech Republic

The computational studies of excited states of polyaromatic hydrocarbons were performed by means of the MCSCF and CASPT2 levels to find a methodology suitable and computationally feasible for calculations of the absorption spectra of extended π -systems. The absorption spectra of such systems include the states with multi-configurational character of the wavefunction of both, covalent and ionic character. It is shown that the most important contributions to the excited state wavefunction are present using a reasonable size of the active space in the MCSCF treatment and further correlation contributions are recovered at the CASPT2 level.

Mechanisms and kinetics of charge transfer in aqueous reactions of free radicals with haloorganic substrates

Ivana Nikšić-Franjić

Department of Physical Chemistry, Ruđer Bošković Institute, Zagreb, Croatia, iniksicf@irb.hr

Reactions of α -hydroxyalkyl radicals in aqueous media typically exhibit a rich variety of fundamentally important competitive mechanisms.¹⁻⁴ Of particular interest is proton-coupled electron transfer (PCET), which is a remarkably efficient mechanism of charge transfer vastly important for numerous processes in biology, electrochemistry, industrial catalysis etc. We investigate reactions of the α -hydroxyethyl radical (\bullet EtOH) with four haloacetates, viz. iodoacetate (IAC), bromoacetate (BrAc), chloroacetate (ClAc) and fluoroacetate (FAC), carried out in buffered and non-buffered aqueous solutions. In these conditions, we find that only IAC and BrAc are reduced and consequently dehalogenated by \bullet EtOH whereas ClAc and FAC are resistant to the reductive dehalogenation even at elevated temperatures. The dominant mechanism of the \bullet EtOH induced degradation of IAC and BrAc is the PCET. In contrast to analogous reaction systems and substrates such as alkyl halides, halophenols and halogenated nucleobases, the reduction of IAC and BrAc takes place regardless of the presence of buffers as the external proton acceptors. This implies that the carboxyl group of these two haloacetates can readily accept the transferred proton. The computations show that such a proton transfer most efficiently occurs directly while interposition of one water molecule that acts as a proton relay tends to slow down the PCET. The addition of HCO₃⁻ or HPO₄²⁻ basic buffer anions increases the rate of the PCET owing to larger proton affinities of these anions compared to that of the carboxyl group. The reduction of IAC and BrAc leads to the creation of carboxymethyl radicals whereupon a radical chain reaction is triggered which significantly enhances the Br and I yields. These comparatively simple reaction systems provide valuable insights into PCET processes in which the (halogenated) carboxyl compounds may assume the role of proton and/or electron accepting species.

[1] I. Džeba, M. Bonifačić, I. Nikšić-Franjić, I. Ljubić, *Phys. Chem. Chem. Phys.*, 20, (2018), 19829.

[2] I. Ljubić, B. Matasović, M. Bonifačić, *Phys. Chem. Chem. Phys.* 15, (2013) 18001.

[3] I. Ljubić, A. Sabljic, M. Bonifačić, *J. Phys. Chem. B* 120, (2016) 11810.

[4] G. E. Adams, E. M. Fielden, B. D. Michael, *Fast Processes in Radiation Chemistry and Biology*, John Wiley & Sons, 1973, New York.

Interpreting NMR parameters of metal complexes using relativistic DFT calculations

Jan Novotný¹, Jan Vícha², Pankaj Lochan Bora¹, Stanislav Komorovsky³, Michal Repisky⁴
Michal Straka⁵, Radek Marek¹

¹ CEITEC - Central European Institute of Technology, Masaryk University, Kamenice 5/A4, CZ-62500 Brno, Czech Republic

² Center of Polymer Systems, University Institute, Tomas Bata University in Zlín, Třída T. Bati 5678, CZ-76001, Zlín, Czech Republic

³ Institute of Inorganic Chemistry, Slovak Academy of Science, Dúbravská cesta 9, SK-84536 Bratislava, Slovakia

⁴ Center for Theoretical and Computational Chemistry, Department of Chemistry, UiT – The Arctic University of Norway, N-9037 Tromsø, Norway

⁵ Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Flemingovo nám. 2, CZ-16610, Prague, Czech Republic

In NMR spectroscopy, the heavy atoms strongly influence the nuclear shielding constants of neighbouring light atoms. In this study [1] we analyse paramagnetic contributions to NMR shielding constants and their modulation by relativistic spin-orbit effects in a series of transition-metal complexes of Pt(II), Au(I), Au(III), and Hg(II). We show how the paramagnetic NMR shielding and spin-orbit effects relate to the character of the metal-ligand (M-L) bond. A correlation between the (back)-donation character of the M-L bond in d¹⁰ Au(I) complexes and the propagation of the spin-orbit (SO) effects from M to L through the M-L bond influencing the ligand NMR shielding via the Fermi-contact mechanism is found and rationalized. The SO effects on the ligand NMR shielding are demonstrated to be driven by both the electronic structure of M and the nature of the *trans* ligand, sharing the σ -bonding metal orbital with the NMR spectator atom L. The deshielding paramagnetic contribution is linked to the σ -type M-L bonding orbitals, which are notably affected by the *trans* ligand.

Acknowledgement

This study was supported by the Czech Science Foundation (grant no. 16-05961S and 15-09381S).

[1] Jan Novotný, Jan Vícha, Pankaj Lochan Bora, Stanislav Komorovsky, Michal Repisky, Michal Straka, Radek Marek *J. Chem. Theory Comput.*, **13** (2017), 3586–3601.

Reuniting theory and experiment, the case study on gold

L. F. Pašteka^{1,2}, E. Eliav³, A. Borschevsky⁴, U. Kaldor³, P. Schwerdtfeger²

¹*Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina, 84215 Bratislava, Slovakia*

²*Centre for Theoretical Chemistry and Physics, Massey University, Private Bag 102904, 0745 Auckland, New Zealand*

³*School of Chemistry, Tel Aviv University, 6997801 Tel Aviv, Israel*

⁴*Van Swinderen Institute for Particle Physics and Gravity, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*

The first ionization potential (IP) and electron affinity (EA) of the gold atom have been determined to an unprecedented accuracy using relativistic coupled cluster calculations up to the pentuple excitation level (CCSDTQP) including the Breit and QED contributions. We reach meV accuracy (with respect to the the experimental values) by carefully accounting for all individual contributions beyond the standard relativistic coupled cluster approach. Thus we are able to resolve the long-standing discrepancy between experimental and theoretical IP and EA of gold [1].

[1] L. F. Pašteka, E. Eliav, A. Borschevsky, U. Kaldor, P. Schwerdtfeger, *Phys. Rev. Lett.* **118** (2017) 023002.

Thermodynamics of radical scavenging activity of selected carotenoids

Peter Poliak¹, Peter Škorňa², Erik Klein¹, Vladimír Lukeš¹

¹ *Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic*

² *Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-845 36 Bratislava, Slovak Republic*

Carotenoids are a group of natural plant-produced red, orange and yellow pigments with a highly conjugated π -electron structure. This feature gives these molecules valuable properties with essential importance in nature. They are involved in several biological processes including photosynthesis, photoprotection and cell membrane stabilization. Living organisms benefit mainly from their singlet oxygen quenching properties and free radical scavenging activity [1]. Numerous recent studies have also shown positive effect against neurodegenerative diseases, arterial plague, several types of cancer, cataract or macular degeneration. These effects probably relate to their antioxidant properties [2]. It was also shown that they possess prooxidant properties in certain cases. The fundamental mechanism behind these properties remains unclear.

This contribution proposes a comprehensive theoretical study of the thermodynamics associated with their radical scavenging processes using the density functional theory. In this work, we have investigated the hydrogen atom transfer (HAT) from parent carotenoid, mono-radical species, radical cations and radical anions, as well as electron transfer and proton transfer. To study differences in polar and non-polar environment, an implicit solvation model was employed. Thermodynamically favored reaction sites of the HAT mechanism were identified. Lycopene, β -carotene and zeaxanthin are known for their prooxidative behavior under certain conditions. Their BDE were found to be lower comparing to the strong antioxidants without any prooxidative effect. Carotenoid radicals were found to be even better H atom donors than parent molecules according to their lower BDE value. A decrease in BDE values was similarly observed for carotenoid radical cations. Majority of studied carotenoids showed also lower BDE in the form of radical anions. Contrary to the carotenoid radical cations, the thermodynamically preferred reaction site of the carotenoid radical anions depended on the solvent [3]. Variation of contributions of individual thermodynamic terms to the calculated enthalpies is also discussed. The proposed data represent important building block in assessment of the radical scavenging properties of carotenoids.

[1] Edge R. and Truscott T.G., *Antioxidants* **7** (2018) 5.

[2] Von Lintig J., *The American Journal of Clinical Nutrition* **96** (2012) 1234S.

[3] Poliak P., Škorňa P., Klein E., Lukeš V., *Food Chemistry* **268** (2018) 542.

Acknowledgement

This work was supported by Slovak Grant Agency (project VEGA 1/0594/16). We are grateful to the HPC center at the Slovak University of Technology in Bratislava, which is a part of the Slovak Infrastructure of High Performance Computing (SIVVP project, ITMS code 26230120002, funded by the European Region Development Funds, ERDF) for the computational time and resources made available.

Study of dynamical observables involved in photoionization process

A. Ponzi¹, N. Quadri² and P. Decleva²

¹*Department of Physical Chemistry, Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia*

²*Department of Chemical and Pharmaceutical Sciences, University of Trieste, via L. Giorgieri 1, 34127 Trieste, Italy*

My talk will be focused on the study of dynamical observables which are involved in photoionization process for several systems. In particular, valence photoelectron spectra for a set of isoelectronic diatomic molecules will be taken into account. This study aims to analyze the effect of the electronic structure, with the change of the atomic pair along the row and column of the periodic table and of the bond distance, on the position of the satellite peak as well as on the related dynamical observables profiles. For this investigation, highly correlated calculations have been performed on the primary ionic states and the satellite band for all the molecules considered. Cross sections for the primary ionic states, calculated using Dyson orbitals [1], have been compared with those obtained with Hartree-Fock and Density Functional Theory to probe the impact of the correlation in the bound states on the photoionization observables.

[1] A. Ponzi, C. Angeli, R. Cimiraglia, S. Coriani and P. Decleva, *J. Chem. Phys.*, 140, 2014.

All-electron fully relativistic Kohn–Sham theory for solids based on the Dirac–Coulomb Hamiltonian and Gaussian-type functions

Michal Repisky¹, Marius Kadek¹, Kenneth Ruud¹

¹*Hylleraas Centre for Quantum Molecular Sciences Department of Chemistry, UiT – The Arctic University of Norway, N-9037 Troms, Norway*

First-principle predictions of electronic structure and properties of solid-state materials containing heavy elements pose numerous challenges to computational methods, as variational treatment of relativistic effects is in many cases required and multiple wave-function components coupled by the spin–orbit interaction increase the complexity of the formalism and the computational cost. Here, we present the first full-potential method for solids and surfaces that solves the fully-relativistic four-component Dirac–Kohn–Sham equation within the framework of atom-centered Gaussian-type orbitals (GTOs), providing also a seamless transition to the methodology commonly used in studies of molecules with heavy elements. [1] We provide a detailed description of how key components of such a method are altered in the four-component regime, and show the necessary steps that need to be overcome when employing GTOs on periodic systems. Finally, we demonstrate the validity of the method on 3-dimensional silver halide (AgX) crystals with strong scalar-relativistic effects, and 2-dimensional honeycomb structures (silicene and germanene) exhibiting the quantum spin Hall effect due to a strong spin–orbit coupling.

[1] Marius Kadek, Michal Repisky, Kenneth Ruud, Phys. Rev. X (submitted).

Temperature Dependence of CO Adsorption in H-FER Zeolite: Combined Theoretical and Experimental Investigation

M. Rubeš, M. Trachta, and O. Bludský

Institute of Organic Chemistry and Biochemistry of the CAS, Flemingovo nam. 542/2, Prague 6, 166 10, Czech Republic

The carbon monoxide is a very sensitive IR probe molecule, and thus is quite often used to characterize adsorption sites in various materials.¹ In zeolites, the calculated CO frequency shifts are in good agreement with experimental observations.² However, the CO energetics (e.g. isosteric heats) still presents a challenge for computational chemistry due to the dynamical nature of the adsorption process. Experimentally, we observe about 6-7 kJ/mol difference in isosteric heats at 200 K and 300 K, respectively. This difference cannot be explained by using simple thermodynamics models and molecular dynamics (MD) simulations need to be performed. It is straightforward that the accuracy of the employed potential is of utmost importance. We developed an updated DFT/CC³ methodology to calculate very accurate interaction energies with siliceous framework and Brønsted acid sites. The DFT/CC model was verified with “golden” standard CCSD(T)/CBS on cluster models (up to 4T) and RPA/RSE calculations on several H-FER and siliceous FER structures. The temperature effects were calculated from up to 80 ps MD trajectories for each T-position in H-FER material. Furthermore, the MD simulations indicate significant differences in isosteric heats for different T-positions in H-FER material at 200 K. This effect is partially diminished at 300 K due to the formation of less stable OC-complexes and desorption from the Brønsted site (Fig.1).

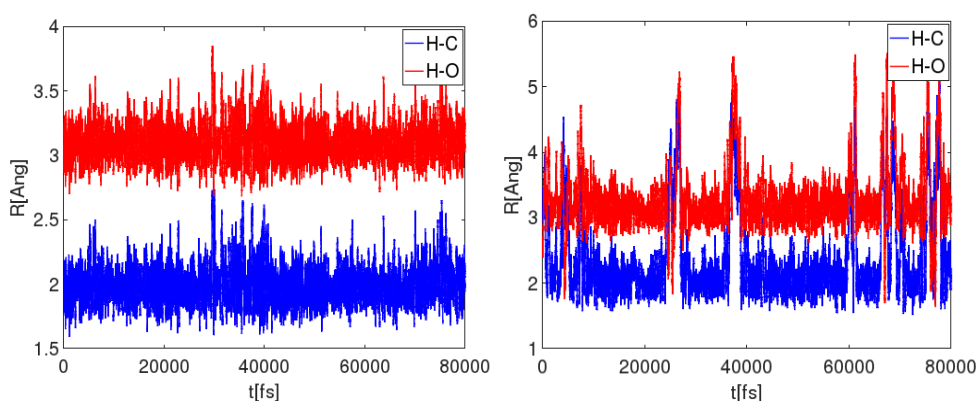


Figure 1: The carbon and oxygen (CO) distances from Brønsted site for (left) 200 K and (right) 300 K.

[1] Nachtigall, P.; Bulánek, R. *Appl. Catal. A* 2006, 307, 118–127.

[2] Bludský, O.; Šilhan, M.; Nachtigallová, D.; Nachtigall, P. *J. Phys. Chem. A* 2003, 107, 10381–10388.

[3] Bludský, O.; Rubeš, M.; Soldán, P.; Nachtigall, P. *J. Chem. Phys.* 2008, 128.

Computation of many-electron wave function overlaps for photochemical studies

Marin Sapunar¹, Davor Davidović¹, Tomislav Piteša¹, Nađa Došlić¹

¹*Ruder Bošković Institute, Bijenička cesta 54, 10 000 Zagreb, Croatia*

Surface hopping calculations account for some of the limitations of classical molecular dynamics by taking into account multiple electronic states and allowing hops between them. In addition to energies and gradients of the electronic states, couplings between the states are required for determining hops between the states. While these can be most directly calculated from nonadiabatic coupling vectors, it is more common to approximate them using overlaps of wave functions at subsequent time steps. This is because analytic nonadiabatic coupling vectors are not implemented in a lot of electronic structure programs, but also because overlaps are used in most algorithms which account for the problem of trivial crossings in surface hopping calculations [1, 2, 3]. While conceptually simple, computing the wave function overlaps quickly becomes expensive as it requires computing all Slater determinant overlaps [4].

In this contribution, we present a highly efficient method for calculating wave function overlaps when the wave functions are expanded in a basis of singly excited determinants. This allows using overlaps with no additional approximations in surface hopping dynamics of medium sized molecules with very little additional cost, despite the $O(n^7)$ scaling for overlap calculations. We also show how overlaps can be used to track electronic states through different geometries, allowing for optimizations of specific diabatic states and exploration of potential energy surfaces.

- [1] Granucci, Persico, *et al.*, J. Chem. Phys. **114** (2001) 10608.
- [2] Meek, Levine, J. Phys. Chem. Lett. **5** (2014) 2351.
- [3] Fernandez-Alberti, Roitberg, *et al.*, J. Chem. Phys. **137** (2012) 014512.
- [4] Plasser, Ruckebauer, *et al.*, J. Chem. Theory. Comput., **12** (2016) 1207.

Approximate solution of Coupled Cluster equations: Application to the Coupled Cluster Doubles method and non-covalent interacting systems.

Szymon Śmiga¹, Eduardo Fabiano^{2,3}

¹*Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland*

²*Institute for Microelectronics and Microsystems (CNR-IMM), Via Monteroni, Campus Unisalento, 73100 Lecce, Italy*

³*Center for Biomolecular Nanotechnologies @UNILE, Istituto Italiano di Tecnologia, Via Barsanti, I-73010 Arnesano, Italy*

We have developed a simplified coupled cluster (SCC) methodology, using the basic idea of scaled MP2 methods [1]. The scheme has been applied to the coupled cluster double equations and implemented in few different non-iterative variants. This new method (especially the SCCD[3] variant, which utilizes a spin-resolved formalism) has been found to be very efficient and to yield an accurate approximation of the reference CCD results for both total and interaction energies of different atoms and molecules. Furthermore, we demonstrate that the equations determining the scaling coefficients for the SCCD[3] approach can generate non-empirical SCS-MP2 scaling coefficients which are in good agreement with previous theoretical investigations.

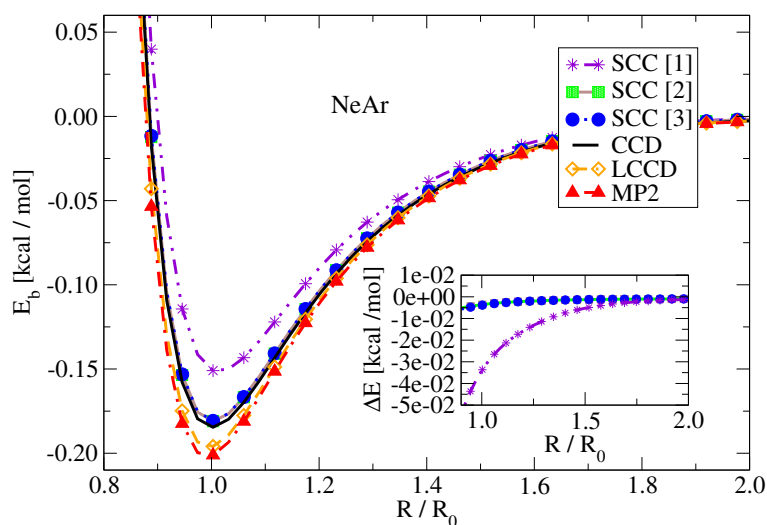


Figure 1: Binding energy curves of NeAr computed using different theoretical methods. In the insets the difference between the variants of SCCD and CCD binding energies are reported.

[1] S. Śmiga, E. Fabiano, *Phys. Chem. Chem. Phys.* 19, 30249 (2017)

Geminal PT based on the UHF wavefunction

Á. Szabados, D. Földvári, Zs. Tóth and P. R. Surján

ELTE Eötvös Loránd University, Faculty of Science, Institute of Chemistry, Laboratory of Theoretical Chemistry, POB 32, 1518 Budapest, Hungary

Electronic structure of inherently multireference systems, exhibiting both static and dynamic correlation continues to be problematic to describe by black box strategies. For long symmetry breaking has been advocated as a useful concept for identifying orbitals participating in strong correlation. The Unrestricted Hartree–Fock Natural Orbitals (UNO) based complete active space (CAS) methodology has in fact been found quite successful in estimating exact occupation numbers. At difference with the success of UHF based CAS, UHF based perturbation theory (PT) performs rather poorly in the Møller-Plesset partitioning, especially when spin contamination is significant at the single determinantal level.

In this work an alternative PT methodology is developed, that exploits the geminal structure of the UHF wavefunction. Either performing Löwdin pairing of the orbitals or approaching from the alternant molecular orbitals perspective, a pair (geminal) structure of UHF is revealed, geminals involving both singlet and triplet ($m_s = 0$) parts. This suggests a zero order Hamiltonian of Dyall-type, including explicit two-electron interaction within geminals. Spin contamination is attenuated by relaxing geminal configuration interaction (CI) coefficients at order zero. Orbitals at the same are not optimized, but conserved as UNOs.

Performance of the theory is demonstrated on singlet-triplet gaps and natural occupation numbers of test systems of biradical character.

Rovibronic spectra of light-dressed molecules

Tamás Szidarovszky¹, Gábor J. Halász², Attila G. Császár¹, Lorenz S. Cederbaum³,
Ágnes Vibók⁴

¹Laboratory of Molecular Structure and Dynamics, Eötvös Loránd University and MTA-ELTE Complex Chemical Systems Research Group, Pázmány Péter sétány 1/A, H-1117 Budapest, Hungary

²Department of Information Technology, University of Debrecen, PO Box 400, H-4002 Debrecen, Hungary

³Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, D-69120, Heidelberg, Germany

⁴Department of Theoretical Physics, University of Debrecen, PO Box 400, H-4002 Debrecen, Hungary and ELI-ALPS, ELI-HU Non-Profit Ltd., Dugonics tér 13, H-6720 Szeged, Hungary

When molecules are exposed to laser fields, whose temporal duration is much longer than the characteristic molecular timescales, the system can usually be described by so-called light-dressed states, which are the eigenstates of the “molecule + light field” system [1]. In this work we investigate theoretically the rovibronic spectra of light-dressed molecules, *i.e.*, we consider light-dressed molecular states induced by a medium intensity continuous-wave laser light and compute the transition amplitudes between these light-dressed states with respect to an additional weak probe pulse [2]. The field-dressed spectra feature absorption peaks resembling the field-free spectrum as well as stimulated emission peaks corresponding to transitions not visible in the field-free case, see Figure 1.

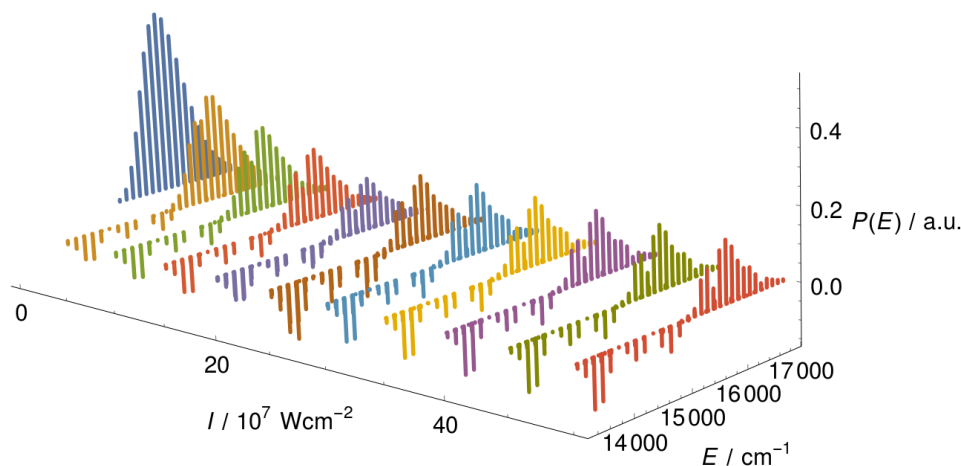


Figure 1: One-photon spectra of field-dressed Na₂ as a function of dressing-light intensity ($\lambda = 658$ nm). Positive and negative transition probabilities stand for absorption and stimulated emission, respectively.

[1] C. Cohen-Tannoudji, J. Dupont-Roc, *Atom-Photon Interactions: Basic Processes and Applications*, Wiley-VCH Verlag GmbH and Co. KGaA, (2004).

[2] T. Szidarovszky, G. J. Halász, *et al.*, *J. Phys. Chem. Lett.* **9** (2018) 2739.

Unconventional Electronic Structure Methods for Actinides

Paweł Tecmer

Institute of Physics, Nicolaus Copernicus University in Toruń, Grudziadzka 5, 87-100 Toruń, Poland

Actinide-containing compounds possess an unusually complex electronic structure, resulting from the large number of low-lying electronic states, spanning many different n and l values. The atomic $7s$, $5f$, and $6d$ orbitals of actinides that participate in bonding are nearly degenerate in energy and partially occupied. This indicates that the (valence) electrons in actinide compounds are strongly correlated. Given the large number of electrons and the importance of relativistic effects in actinide species, reliable theoretical modeling of their electronic structures remains a real challenge for conventional (standard) computational quantum chemistry methods.

These challenges can be overcome using unconventional wavefunction-based methods. Specifically, I will focus on the density matrix renormalization group (DMRG) algorithm and the antisymmetric product of 1-reference orbital geminal ansatz (AP1roG) as well as their advantages over standard electron correlation methods [1,2] and their recent applications to actinide chemistry [3,4].

[1] P. A. Limacher, P. W. Ayers, P. A. Johnson, S. De Baerdemacker, D. Van Neck and P. Bultinck, *J. Chem. Theory Comput.*, **9** (2013) 1394-1401.

[2] K. Boguslawski, P. Tecmer, P. W. Ayers, P. Bultinck, S. De Baerdemacker and D. Van Neck, *Phys. Rev. B*, **89** (2014) 201106(R).

[3] P. Tecmer, K. Boguslawski, O. Legeza and M. Reiher, *Phys. Chem. Chem. Phys.*, **16** (2014) 719-727.

[4] P. Tecmer, K. Boguslawski, and P.W. Ayers, *Phys. Chem. Chem. Phys.*, **17** (2015) 14427-14436.

The Promise and Rise of Machine Learning in Chemistry and Physics

Alexandre Tkatchenko

Faculty of Science, Technology and Communication, University of Luxembourg, Luxembourg

Learning from data has led to paradigm shifts in a multitude of disciplines, including web, text and image search, speech recognition, as well as bioinformatics. Can machine learning enable similar breakthroughs in understanding (quantum) molecules and materials? The main challenge is the disproportionately large size of chemical space, estimated to contain 10^{60} molecules even when only counting small organic drug-like candidates. Aiming towards a unified machine learning (ML) model of quantum interactions, I will discuss the potential and challenges for using ML techniques in chemistry and physics. ML methods can not only accurately estimate molecular properties of large datasets, but they can also lead to new insights into chemical similarity, aromaticity, reactivity, and molecular dynamics. However, to do so one needs to carefully unify spatial and temporal physical symmetries with purpose-designed ML methods. While the potential of machine learning for revealing insights into complex quantum-chemical systems is high, many challenges remain. I will conclude my talk by discussing these challenges.

Infinite lattice sums with Bloch phase factors

Štefan Varga¹

¹ *Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 84536 Bratislava, Slovakia*

In electronic structure calculations of infinite periodic systems the need to include long-range Coulomb interactions leads to the necessity of evaluation of infinite lattice sums of the type

$$\sigma_{lm}(\mathbf{k}) = \sum_{\mathbf{R}} \frac{e^{i\mathbf{k}\cdot\mathbf{R}}}{R^{l+1}} Y_{lm}(\hat{R}) \quad (1)$$

with Y being the spherical harmonic functions. The need for having the sums (1) available for non-zero wave vectors \mathbf{k} is especially pronounced for density fitting calculations in Coulomb metric (case of full exchange and beyond) where reciprocal space treatment cannot be avoided.

While for systems with one-dimensional periodicity analytical formulas for solving (1) can be derived [?] beyond 1D the problem has to be solved numerically. For high values of l one could profit from the fast decay which restricts the summation in (1) to a reasonable size. Nevertheless, for the lowest orders brute force summation would hardly return a sufficiently accurate answer in a reasonable time.

We revisited the renormalization method of Kudin and Scuseria [?] for infinite lattice sums [the $\mathbf{k}=\mathbf{0}$ case of (1)] and have shown that the scheme can be easily generalized to any non-zero wave vector \mathbf{k} with just a minor additional effort [?].

The recurrence formula for fast evaluation of (1) is derived and presented in comparison with the $\mathbf{k}=\mathbf{0}$ case. Our scheme is general and is not limited to any special form of the wave vector. As a by-product we offer a simple novel way of looking at the renormalization scheme. For a general point from inside the Brillouin zone, the number of recurrence steps is typically lower than for the $\mathbf{k}=\mathbf{0}$ case. Compared to the $\mathbf{k}=\mathbf{0}$ case, the method has only modest extra computational expenses.

[1] L. Z. Stolarczyk, M. Jeziorska, H. J. Monkhorst, Phys. Rev. B **37** (1988) 10646

[2] K. N. Kudin, G. E. Scuseria, J. Chem. Phys. **121** (2004) 2886

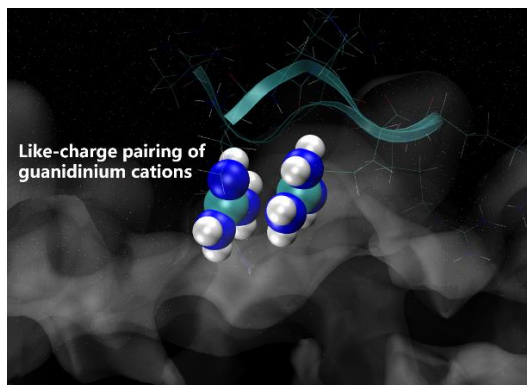
[3] Š. Varga, J. Chem. Phys. **148** (2018) 051102

Arginine “Magic”: Guanidinium Like-Charge Ion Pairing from Aqueous Salts to Cell Penetrating Peptides

Mario Vazdar

¹Rudjer Bošković Institute, Bijenička 54, 10 000 Zagreb, Croatia

It is a textbook knowledge that charges of the same polarity repel each other. For two monovalent ions in the gas phase at a close contact this repulsive interaction amounts to hundreds of kilojoules per mole. In aqueous solutions, however, this Coulomb repulsion is strongly attenuated by a factor equal to the dielectric constant of the medium. The residual repulsion, which now amounts only to units of kJ/mol, may be in principle offset by attractive interactions. Probably the smallest like-charge pair, where a combination of dispersion and cavitation forces overwhelms the Coulomb repulsion, consists of two guanidinium cations in water. Indeed, by a combination of molecular dynamics and electronic structure calculations and electrophoretic as well as spectroscopic experiments we have demonstrated that aqueous guanidinium cations form thermodynamically stable like-charge ion pairs.



The importance of pairing of guanidinium cations in aqueous solutions goes beyond a mere physical curiosity and has significant biochemical implications. For example, arginine-arginine pairing has been frequently found in structural protein databases. In particular, when strengthened by a presence of negatively charged glutamate, aspartate, or C terminal carboxylic groups, this binding motif helps to stabilize peptide or protein dimers and is also found in or near active sites of several enzymes, as suggested by molecular dynamics simulations, SAXS and NMR experiments.

The like-charge pairing of the guanidinium side chain groups may also hold the key to the understanding of the arginine “magic”, i.e., the extraordinary ability of arginine-rich polypeptides to passively penetrate across cellular membranes. Unlike polylysines, which are also highly cationic but lack the ease in crossing membranes, polyarginines do not exhibit mutual repulsion. Instead, they accumulate at the membrane, weaken it, and may eventually cross in a concerted, “train-like” manner. This behavior of arginine-rich cell penetrating peptides can be exploited when devising smart strategies how to deliver in a targeted way molecular cargos into the cell.[1]

[1] Mario Vazdar, Jan Heyda, Philip E. Mason, Giulio Tesei, Christoph Allolio, Mikael Lund, and Pavel Jungwirth, *Acc. Chem. Res.* **51** (2018), 1455–1464.

Nonempirical simulations of two-photon electronic absorption spectra of molecules in solution

Robert Zaleśny, Joanna Bednarska, Wojciech Bartkowiak

Department of Physical and Quantum Chemistry, Wrocław University of Science and Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland

Two-photon absorption process, albeit predicted in 30's of past century, has attracted a significant attention only recently due to several applications, e.g. three-dimensional optical data storage, two-photon polymerization, a recording of high-resolution spectra below the Doppler width or bioimaging. The latter application requires two-photon fluorescent probes characterized by large two-photon absorption cross section and fluorescence quantum yield. The basic characterization of two-photon electronic absorption properties of fluorescent probes is most frequently performed in solution using TPEF or Z-scan techniques and the interpretation of two-photon absorption spectra is by no means a routine task. On the other hand, computer simulations may not only help in unravelling the spectral signatures but may be also useful in the design of new efficient fluorescent probes with tailored optical properties.

This contribution aims at presenting recent advances in the first-principle computer simulations of two-photon electronic absorption spectra of organic fluorescent dyes in solution. A particular emphasis will be put on i/ the nonempirical estimation of inhomogeneous broadening, ii/ the importance of non-Condon effects and iii/ the performance of density functional theory in the prediction of two-photon absorption strengths and vibrational fine structure of absorption bands in electronic two-photon spectra.

Poster Contributions

Local pair natural orbital coupled clusters tailored by matrix product states

Andrej Antalík^{1,2}, Libor Veis¹, Frank Neese³, Örs Legeza⁴, Jiří Pittner¹

¹*J. Heyrovsky Institute of Physical Chemistry, Czech Academy of Sciences, Prague*

²*Faculty of Mathematics and Physics, Charles University, Prague*

³*Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr*

⁴*Wigner Research Centre for Physics, Budapest*

The coupled cluster method (CC) is regarded as the method of choice for the treatment of dynamic correlation in single-reference cases, but fails drastically when strongly correlated systems are involved. One of the possible ways to deal with this issue, is the use of externally corrected CC methods, in which information from an external calculation is introduced in the CC wave function. In particular, the tailored CC ansatz (TCC) proposed by Kinoshita et al. [1] uses the amplitudes for an active space excitations extracted from a small full configuration interaction (FCI) calculation. These amplitudes are kept frozen, while the remaining amplitudes are iterated employing the standard CC framework. However, this approach is limited to small active spaces due to the exponential scaling of the FCI method. The recently developed density matrix renormalization group TCCSD method [2] (DMRG-TCCSD) makes it possible to tackle strongly correlated systems, which require significantly larger active spaces infeasible for standard FCI.

Although DMRG-TCCSD performed well for challenging systems [3], its application to larger molecules might be hindered by the prohibitive scaling of CCSD. In this newly implemented approach, the CCSD part of the method is performed by means of the local pair natural orbital (LPNO) approach [4], in which the imported amplitudes are used to construct pair natural orbitals and to tailor the subsequent CC calculation. Hence, we are able to remove the bottleneck to a certain extent, which opens a way to study medium-sized molecules with strongly correlated electrons, such as enzyme fragments with transition metal cofactors. We examine the properties of the method on tetramethylethane, a disjoint non-Kekul diradical known to require a good treatment of both static and dynamic correlation, and oxo-Mn(salen), whose closely lying triplet and singlet states present a challenge in establishing the ground state.

[1] T. Kinoshita, O. Hino, and R. J. Bartlett, *J. Chem. Phys.* **123** (2005) 074106.

[2] L. Veis, A. Antalík, et al., *J. Phys. Chem. Lett.* **7** (2016) 4072.

[3] L. Veis, A. Antalík, et al., *J. Chem. Theory Comput.* **14** (2018) 2439.

[4] F. Neese, A. Hansen, and D. G. Liakos, *J. Chem. Phys.* **131** (2009) 064103.

Nuclear magnetic dipole moment of ^{209}Bi from new NMR experiments

Andrej Antušek¹, Michal Repisky², Michał Jaszuński³, Karol Jackowski⁴, Włodzimierz Makulski⁴, Maria Misiak⁴

¹*Slovak University of Technology in Bratislava, ATRI, Faculty of Materials Science and Technology in Trnava, J. Bottu 25, 917 24 Trnava, Slovak Republic*

²*Hylleraas Centre for Quantum Molecular Sciences, Department of Chemistry, UiT – The Arctic University of Norway, N-9037 Tromsø, Norway*

³*Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland*

⁴*Laboratory of NMR Spectroscopy, Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*

The presented work is a part of our long term effort for correcting of nuclear magnetic dipole moments [1, 2]. The ^{209}Bi magnetic moment derived from NMR experiment and calculated shielding constants of Bi^{3+} ions in aqueous solutions of $\text{Bi}(\text{NO}_3)_3$ and $\text{Bi}(\text{ClO}_4)_3$ salts is reported [3]. Our values represent an independent confirmation of ^{209}Bi magnetic moment recently determined by Skripnikov et al. [4], which is of utmost importance for the interpretation of Bi^{82+} ion hyperfine splitting experiments. The calculated NMR shielding constants are based on four-component DKS/PBE0 approximation. However this description of the relevant electron correlation effects is inaccurate and this functional underestimates the total shielding. We have corrected this systematic error using different computational protocols. All newly rederived ^{209}Bi magnetic moment values are contained in a narrow interval $3 \times 10^{-3} \mu_N$ and correct long standing systematic error of ^{209}Bi magnetic moment.

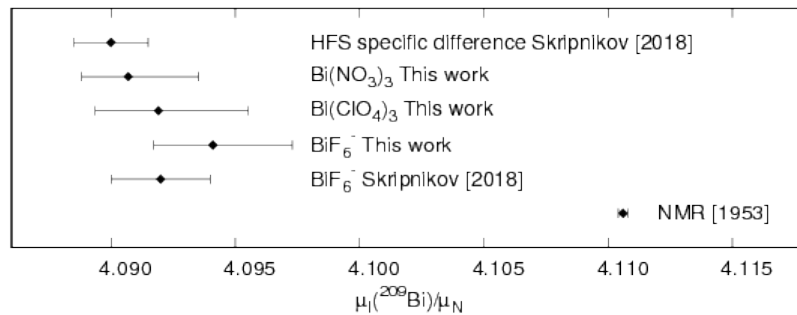


Figure 1: Comparison of ^{209}Bi magnetic moments from various sources.

- [1] A. Antušek, K. Jackowski, M. Jaszuński, W. Makulski, and M. Wilczek, *Chem. Phys. Lett.* **411** (2005), 111.
- [2] M. Jaszuński, A. Antušek, P. Garbacz, K. Jackowski, W. Makulski, and M. Wilczek, *Progr. Nucl. Magn. Reson. Spectrosc.* **67**, (2012), 49
- [3] A. Antušek, M. Repisky, M. Jaszuński, K. Jackowski, W. Makulski, M. Misiak, *Phys. Rev. A*, *submitted*
- [4] L. V. Skripnikov, *et al*, *Phys. Rev. Lett.* **120**, (2018) 093001

Theoretical and Dynamic Study of Malonaldehyde : A comparison with Acetylacetone

T. Ayari^a, M. Sapunar^a and N. Došlić^a

^a Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia,

In this computational study we explore the photodynamics of malonaldehyde and compare it to that of the homologous acetylacetone. Upon photoexcitation to the bright $S_2(\Pi\Pi^*)$ state malonaldehyde relaxes to the $S_1(n\Pi^*)$ state on an ultrashort time scale. Once in the $S_1(n\Pi^*)$ state the population of malonaldehyde splits. Part of the population undergoes internal conversion to the ground state by deplanarization of the H-chelate ring, while the other part crosses to the triplet manifold. The comparison with acetylacetone reveals a substantial increase of the internal conversion pathways, from less than 20% in acetylacetone to 40% in malonaldehyde. We show that the substitution of the aliphatic hydrogens by the methyl groups reduces the accessibility of the S_1/S_0 conical intersection seam in acetylacetone. This leads to crossing to the triplet states and homolytic cleavage of a C-CH₃ bond.

ZMP-SAPT: DFT-SAPT using *ab initio* Densities

A. Daniel Boese¹ and Georg Jansen²

¹ *Department of Chemistry, Physical and Theoretical Chemistry, University of Graz, 8010 Graz, Austria*

² *Faculty of Chemistry, University of Duisburg-Essen, Universitätsstraße 5, 45117 Essen, Germany*

Symmetry Adapted Perturbation Theory (SAPT) has become an important tool when predicting intermolecular interactions. Unfortunately, DFT-SAPT, which uses Density Functional Theory (DFT) for the underlying monomers, has some arbitrariness concerning the exchange-correlation potential and the exchange-correlation kernel involved. By using *ab initio* Brueckner Doubles densities and constructing Kohn-Sham orbitals via the Zhao-Morrison-Parr method, we are able to lift the dependence of DFT-SAPT on DFT in first order. This way, we can compute the monomers at the Coupled-Cluster level of theory and utilize SAPT for the intermolecular interaction energy.

Domain-Based Local Pair Natural Orbital Version of Mukherjee's State-Specific Coupled Cluster Method

Jiri Brabec¹, Jakub Lang^{1,3}, Masaaki Saitow², Jiri Pittner¹, Frank Neese², Ondrej Demel¹

¹*J. Heyrovský Institute of Physical Chemistry, v.v.i., Academy of Sciences of the Czech Republic, Dolejškova 3, 18223 Prague 8, Czech Republic*

²*Max Planck Institute for Chemical Energy Conversion, 45470 Mülheim an der Ruhr, Germany*

³*Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030, 12840 Prague 2, Czech Republic*

We report development of a local variant of Mukherjee's state-specific multireference coupled cluster method based on the domain-based pair natural orbital approach (DLPNO-MkCC). The current implementation is restricted to connected single and double excitations and model space with up to biexcited references. The performance of the DLPNO-MkCCSD was tested on calculations of tetramethylethane. The results show that above 99.9% of the correlation energy was recovered, with respect to the conventional MkCC method. To demonstrate the applicability of the method to large systems, singlet-triplet gaps of triangulene and bis(1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpyrrolidine-2-ylidene)beryllium complex were studied. For the last system (105 atoms), we were able to perform a calculation in cc-pVTZ with 2158 basis functions on a single CPU in less than 9 days.

Hilbert space multireference coupled clusters tailored by matrix product states

Jan Brandejs^{1,2}, Jakub Lang^{1,3}, Jiří Brabec¹, Örs Legeza⁴, Libor Veis¹, and Jiří Pittner¹

¹*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Dolejškova 3, 18223 Prague, Czech Republic*

²*Faculty of Mathematics and Physics, Charles University, Ke Karlovu 2027/3, 12116 Prague, Czech Republic*

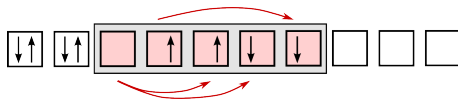
³*Faculty of Science, Charles University, Albertov 2038/6, 12800 Prague, Czech Republic*

⁴*Strongly Correlated Systems “Lendület” Research group, Wigner Research Centre for Physics, H-1525, Budapest, Hungary*

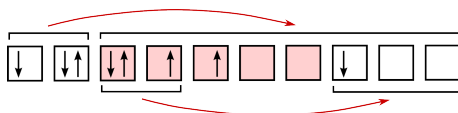
Many compounds, particularly reaction intermediates, feature nearly degenerate energy levels and therefore require multiple Slater determinants for a proper description. This causes the single-reference methods, such as density functional theory (DFT), to break down. Further problems occur when movement of electrons is dynamically correlated. When a combination of these two effects arises, none of the standard methods of quantum chemistry works flawlessly. One prominent approach for dealing with dynamical correlation is the coupled clusters method, whereas for static correlation, one of the strong methods is the density matrix renormalization group (DMRG). We seek to exploit the best of both worlds by performing a multireference coupled clusters calculation on top of DMRG. This approach was originally proposed by Bartlett et al. [1] as the “tailored coupled clusters” method, with the wave function ansatz in the single-reference form of

$$|\Psi_{\text{TCC}}\rangle = e^{\mathcal{T}^{\text{ext}} + \mathcal{T}^{\text{CAS}}} |\Psi_{1 \text{ det}}\rangle.$$

1. Active space DMRG calculation of \mathcal{T}^{CAS} .



2. Coupled clusters calculation of \mathcal{T}^{ext} .



We implemented this method and we demonstrated first successful results in [2]. Hereby, we present the first extension into a multireference version, correcting DMRG externally by Mukharjee’s coupled clusters method. With the new multireference code, we have reached substantial improvement on nearly degenerate systems with variable geometry. The first demonstration was on cyclobutadiene automerization and the second on tetramethyleneethane molecule. In both of these variable-geometry systems, the first excited triplet state approaches the ground state singlet so near, that they can be mistakenly interchanged by quantum-chemical methods.

- [1] Tomoko Kinoshita, Rodney J. Bartlett, *et al.*, The Journal of Chemical Physics **123**, 074106 (2005).
- [2] Libor Veis, Andrej Antalík, Örs Legeza, Ali Alavi, Jiří Pittner, Journal of Chemical Theory and Computation **14**, 5 (2018).

On the Al=Al double bond in the $\text{LiAl}_2\text{H}_4^-$ cluster

Martin Breza

Department of Physical Chemistry STU, Radlinskeho 9, SK-81237 Bratislava, Slovakia

Lundell et al. [1] investigated the $[\text{LiAl}_2\text{H}_4]^-$ cluster via combined photoelectron spectroscopy and ab initio calculations to confirm the formation of a conventional Al=Al double bond in the most stable isomer I of C_2 symmetry (Fig. 1). To find the experimentally observed structure they performed conformational analysis of possible $[\text{LiAl}_2\text{H}_4]^-$ structures in singlet ground spin states at PBE0/6-311++G** level of theory. Adaptive Natural Density Partitioning (AdNDP) analysis indicated that the Al=Al double bond (bond order of 1.76) in the most stable isomer I possesses one σ and one π bond.

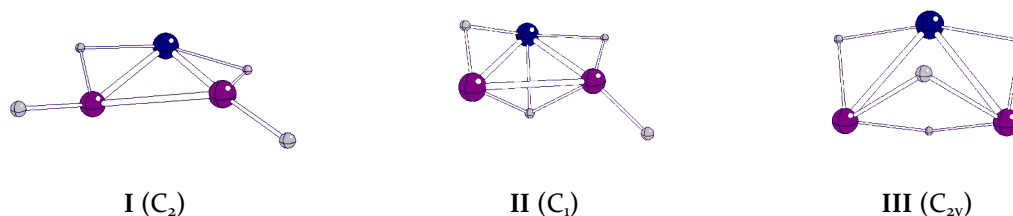


Figure 1: Structure of the most stable isomers of $[\text{LiAl}_2\text{H}_4]^-$ complex anions (molecular symmetry in parentheses, Al – magenta, Li – blue, H – gray)[1]

Using the Gaussian09 program [2] we have investigated the electron structure of *trans*- Al_2H_2 (C_{2h} symmetry), Al_2H_4 (D_{2d} symmetry) and of three most stable $[\text{LiAl}_2\text{H}_4]^-$ isomers (Fig. 1) obtained at DFT level of theory by a hybrid PBE0 functional using standard 6-311++G** and 6-311G basis sets in terms of Quantum Theory of Atoms-in-Molecule (QTAIM) [3] in order to compare possible Al-Al bonding in these compounds. We have demonstrated that non-nuclear attractors at the center of Al-Al bonds are only the artefacts of non-physical diffusion and polarization functions in unbalanced 6-311++G** basis sets. Our results do not exclude the existence of the double Al=Al bond in the most stable isomer I of $[\text{LiAl}_2\text{H}_4]^-$ (C_2 symmetry) but this bond is very weak in comparison with other bonds and its stabilizing role in the whole complex is questionable.

This study is supported by the Slovak Grant Agency VEGA (contract no. 1/0598/16) and by the Ministry of Education, Science, Research and Sport of the Slovak Republic within the Research and Development Operational Programme for the project “University Science Park of STU Bratislava”, ITMS 26240220084, co-funded by the European Regional Development Fund.

[1] K. A. Lundell, X. Zhang, A. I. Boldyrev, K. H. Bowen, *Angew. Chem. Int. Ed.* **56** (2017) 16593

[2] M. J. Frisch *et al.*, Gaussian09 (Revision D.0.1), Gaussian, Inc., Wallingford CT (USA), 2013

[3] R. F. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, 1994

Calculations of pK_a value of lysine in biological membranes

Zlatko Brkljača, Mario Vazdar

¹Ruđer Bošković Institute, Bijenička 54, 10 000 Zagreb, Croatia

The physicochemical properties of amino acids in biological environment represent a crucial element in the transmembrane protein functionality. These properties govern both physical (i.e. orientation and helical configuration) and chemical (i.e. reactivity and substrate specificity) properties of transmembrane proteins [1]. In this study we focus on the essential amino acid lysine, which is usually found both in extracellular side of transmembrane proteins and in β -barrels where it often forms pore linings [2]. As such, this amino acid is subject to different surroundings which can have significant effect on its properties, such as pK_a , in turn changing its functionality. Motivated by this we decided to calculate pK_a values of lysine in three different microenvironments, namely in water (reference system), at the membrane/water interface (imitating extracellular side of the protein), and in the membrane (emulating β -barrel/pore environment). We performed here all-atom QM/MM molecular dynamics simulations for three chosen biological surroundings, where lysine and water molecules closest to it were treated quantum mechanically (SCC-DFTB level of theory), with the remainder of the system being treated classically. More precisely, by using umbrella sampling technique we calculated free energy profiles for the deprotonation of lysine, thereby elucidating the influence of different biological surroundings on the thermodynamics (pK_a value) and also kinetics of this reaction. The obtained results provide new insights on the extent of microenvironment effects on the biological function and reactivity of membrane proteins.

[1] Panahi, A.; Brooks, C. L. III, J. Phys. Chem. B **119** (2015) 4601-4607.

[2] Ulmschneider M. B.; Sansom, M. S. P., Biochim. Biophys. Acta **1512** (2001), 1-14.

DFT study of the effect of chemical modification on the electronic structure and drift mobilities of selected pentacene and bis-benzothiadiazole derivatives

Cagardová Denisa¹, Michalík Martin¹, Poliak Peter¹ and Lukeš Vladimír¹

¹Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, SK-812 37 Bratislava, Slovakia

Organic semiconductors based on linear acenes and heteroacenes represent important materials for organic field effect transistors, which often show high charge mobilities due to their fused planar structures.

Density functional theoretical (DFT) study of pentacene derivatives provides description of the side-specific symmetric fluorine substitution effect. Electronic structure was characterized by the frontier molecular orbitals in comparison with the typical p- and n-type semiconductors, pentacene and perfluorinated pentacene, respectively. The presented theoretical results allowed us to predict hypsochromic shift of the optical bandgap by partial fluorine substitution of outermost condensed rings. Interaction energies of model parallel-stacked and parallel-displaced dimer configurations were obtained, and it has been found that there is a significant role of hydrogen bonding between fluorine and hydrogen atoms [1].

Moreover, the consequences of central core variation in selected symmetric linear condensed bis-benzothiadiazole derivatives were studied as well. Depending on the central rings modification, the potential role of intermolecular bonds stabilizing the stacking structures in real bulk was estimated by mutual comparison of interaction energies for model parallel-stacked and parallel-displaced dimer configurations.

In addition, the local aromaticity of bis-benzothiadiazole and pentacene moieties as well as the global molecular aromaticity was described using the HOMHED aromaticity indices [2]. Drift mobilities of the studied theoretical and X-ray dimer configurations were evaluated using the Marcus theory [3] and Einstein relation.

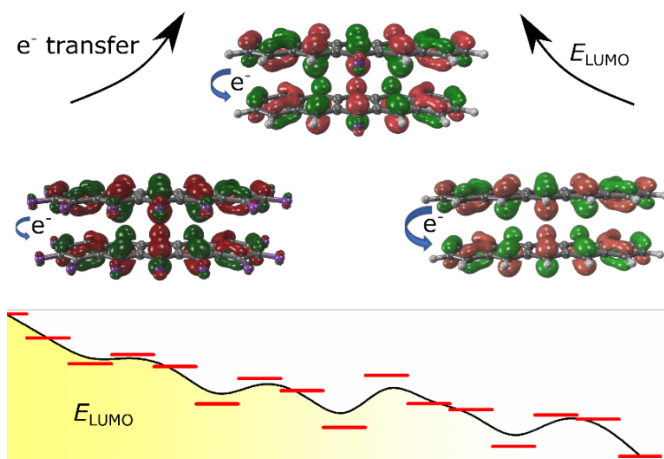


Figure 1: The substitution effect on the LUMO energy levels and simulated drift mobilities of pentacene derivatives

Acknowledgment

The work has been supported by Slovak grant agency No. 1/0594/16.

References

- [1] V. Lukeš, D. Cagardová, M. Michalík, P. Poliak, *Synth. Met.* **240** (2018) 67-76.
- [2] C.P. Frizzo, M.A.P. Martins, *Struct. Chem.* **23** (2012) 375-380.
- [3] R.A. Marcus, *Rev. Mod. Phys.* **65** (1993) 599-610.

Chiral Resolution of the Active Pharmaceutical Intermediates on the Selected Stationary Phases

Michał Chojecki¹, Dorota Rutkowska-Żbik², Tatiana Korona¹

¹Faculty of Chemistry, University of Warsaw, Warsaw, Poland

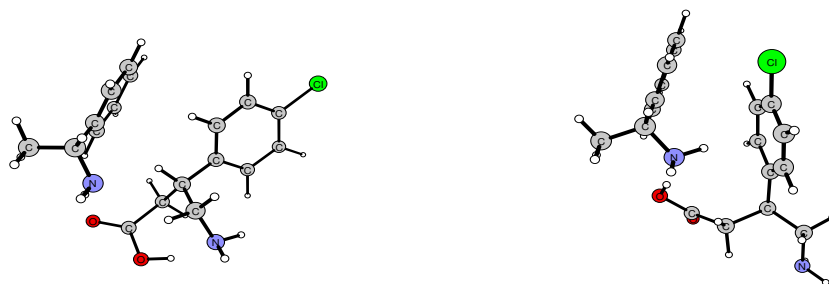
²Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Kraków, Poland

Many bioactive compounds exist in two forms which only differ with the way they rotate light. These forms have identical chemical and physical properties but interact differently with other chiral molecules, including many important biochemicals. Therefore, when a new candidate for an active pharmaceutical intermediate (API) molecule is identified, a synthetic route that produces solely the desired enantiomer must be developed.

To this end, we aim to study the effectiveness of modelling of the interaction energy differences between the pair of the same enantiomers of the selected stationary phases, such as: phenylethylamine, glucose, and proline with selected APIs molecules such as: baclofen or ibuprofen. We utilise several popular theoretical methods, which allow for the energy partitioning, like symmetry-adapted perturbation theory (SAPT) [1] and functional-group SAPT (F-SAPT) [2], as well as a supermolecular MP2. The F-SAPT approach turns out to be especially useful for this analysis since it enables for an identification of a specific spot of the molecule responsible for the increased or decreased attraction or repulsion.

Figure 1: Optimised complexes of the baclofen enantiomers with phenylethylamine.

(a) R-baclofen \cdots (1R)-1-phenylethylamine (b) S-baclofen \cdots (1R)-1-phenylethylamine



The support from the National Science Centre of Poland through grant 2015/19/B/ST4/01812 is gratefully acknowledged. This research was supported in part by PL-Grid Infrastructure.

[1] B. Jeziorski, R. Moszynski, K. Szalewicz, Chem. Rev. **94** (1994) 1887.

[2] R.M. Parrish, T.M. Parker, C.D. Sherill, J. Chem. Theory Comput. **10** (2014) 4417.

Adjusting dispersion coefficients for the accurate DFTB+D₃ treatment of structural and energetic properties of molecular crystals

Grygoriy A. Dolgonos¹, A. Daniel Boese¹

¹*Institute of Chemistry, University of Graz, Heinrichstrasse 28/IV, 8010 Graz, Austria*

Accounting for dispersion interactions is indispensable to accurate modeling of properties of weakly-bound systems, in particular, of molecular crystals. Among various low-level quantum mechanical methods, empirical corrections to the total electronic energies are typically applied. One of the commonly used dispersion corrections applied to density-functional theory (DFT) or density-functional tight-binding (DFTB) is the D₃ correction of Grimme [1] together with the Becke-Johnson damping [2,3]. Although the performance of DFT+D₃ methods has already been intensively investigated [4,5], there is not much known about DFTB+D₃ and to which extent its dispersion parameters can be improved to better approach reference experimental data.

In this contribution, we investigate the role of DFTB+D₃ dispersion coefficients on the final lattice energies and cell volumes of the X₂₃ set [6] of molecular crystals. By minimizing the mean absolute errors in the cell volumes, we propose new dispersion coefficients which lead to more accurate cell volumes than in the case of originally proposed parameters [7]. This finding is important for further application of DFTB+D₃ as a low-level method to explore the properties of various polymorphic forms of molecular crystals. We also test the performance of new parameters on lattice energies and cell volumes of much broader G₆₀ and K₇ sets [8] of periodic systems.

- [1] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J Chem Phys* 132 (2010) 154104.
- [2] A. D. Becke, E. R. Johnson, *J Chem Phys* 123 (2005) 154101.
- [3] E. R. Johnson, A. D. Becke, *J Chem Phys* 123 (2005) 024101.
- [4] G. J. O. Beran, *Chem Rev* 116 (2016) 5567 and references therein.
- [5] G. A. Dolgonos, O. A. Loboda, A. D. Boese, *J Phys Chem A* 122 (2018) 708.
- [6] A. M. Reilly, A. Tkatchenko, *J Chem Phys* 139 (2013) 024705.
- [7] J. G. Brandenburg, S. Grimme, *J Phys Chem Lett* 5 (2014) 1785.
- [8] M. Cutini, B. Civalleri, M. Corno, R. Orlando, J. G. Brandenburg, L. Maschio, P. Ugliengo, *J Chem Theory Comput* 12 (2016) 3340.

Is visible fluorescence in non-aromatic peptidic chains possible?

Luca Grisanti^{1,2}, Marin Sapunar³, Nada Došlić³, Ali Hassanali¹

¹SISSA-Scuola Internazionale Superiore di Studi Avanzati, via Bonomea 265, Trieste, Italy

²International Centre for Theoretical Physics, Strada Costiera 11, Trieste, Italy

³R. Bošković Institute, Bijenička 54, Zagreb, Croatia

The understanding of the fundamental behaviors of biological matter in the processes of interaction with light receives constant attention from several fields, such as biophysics, biological physical chemistry, spectroscopy and biology. Recently, fluorescence from proteins in form of aggregates and fibrils has been reported by several groups, [1] with similar properties in presence or in absence of aromatic amino acids. However, while for aromatic and conjugated groups an emission in the visible is easy to be theoretically understood, little has been clarified about the details of the mechanism for chains containing only non-aromatic residues.

Here we report the first results of excited state static and non-adiabatic dynamics calculations for a series of model peptides containing only non-aromatic residues.

Acknowledgments:

The author acknowledges the Croatian Science Foundation for financial support.

References

- [1] Chen, X.; Luo, W.; Ma, H.; Peng, Q.; Yuan, W. Z.; Zhang, Y. *Prevalent intrinsic emission from nonaromatic amino acids and poly(amino acids)*. *Science China Chemistry* 2018, 61, 351–35

Gaussian basis set saturation in fixed-node diffusion Monte Carlo

M. Dubecky

Department of Physics, University of Ostrava, 30. dubna 22, 701 03 Ostrava, Czech Republic

Fixed-node diffusion Monte Carlo (FNDMC) is a promising many-body electronic structure quantum Monte Carlo method that complements traditional benchmark methodologies like coupled cluster in noncovalent systems for its accuracy, direct treatment of periodicity, low-order polynomial CPU cost scaling, and massive parallelism [1].

Although the nodes of many body trial wave functions play an important role in FNDMC as they dominate its accuracy, only little is known about their convergence with respect to the saturation of one-particle basis sets used to express orbitals in Ψ_T s [1]. Here we explore the convergence of nodal shapes and noncovalent interaction energies vs the Gaussian basis set saturation level in HF and CH₄ dimers within FNDMC employing single-determinant Slater-Jastrow Ψ_T s [2].

The tested 25 distinct basis sets obtained by stepwise trimming of aug-VDZ and aug-VTZ bases show rapid convergence in presence of a single diffuse function per center and suggest thus minimum basis set requirements to achieve reasonable results within FNDMC. A single selected trimmed basis set, about 2 times smaller in size than aug-VTZ, is extensively tested on a set of 12 noncovalent complexes including formic acid dimer, benzene-methane, or coronene-H₂. The results indicate that accurate noncovalent FNDMC energy differences are available at cost lower than assumed before [2].

[1] M. Dubecky, P. Jurecka, L. Mitas, Chem. Rev. 116, 5188, 2016

[2] M. Dubecky, J. Chem. Theory Comput. 13, 3626-3635, 2017

Tilde transformation for quantum resonances

Philippe Durand¹, Ivana Paidarová²

¹*IRSAMC, Université de Toulouse, 31062 cedex 4, Toulouse, France*

²*UFCH JH, AS CR, Dolejškova 3, 182 23, Praha, Czech Republic*

The Heaviside's and Mikusiński's operational calculus [1, 2] is extended and applied to the theory of quantum resonances. A "tilde" transformation transforms the time-dependent Schrödinger equation into an inhomogeneous equation containing smoothed initial conditions. The approach is much simpler than the Schwartz's theory of distributions [3]. A brief numerical illustration is presented.

- [1] J. Mikusiński, *Operational Calculus*, Pergamon Press, 1959, 5th edition.
- [2] A. Erdélyi, *Operational Calculus and Generalized Functions*, Holt, Rinehart and Winston, New York, 1962.
- [3] L. Schwartz *Théorie des distributions*, Hermann, 1966.

IP acknowledges the Czech Science Foundation (grant No. 17-14200S) for financial support

Benchmark computations of infinite linear chain of HF molecules

Roman Fanta, Matúš Dubecký

Department of Physics, University of Ostrava, 30. dubna 22, 701 03 Ostrava, Czech Republic

One of the promising methods of nonempirical quantum chemistry of non-covalent interactions for large systems is the fixed-node diffusion Monte Carlo (FNDMC) method. To determine the accuracy of this method for periodic systems, high-quality reference data are required for cross-validation. We used calculations based on truncated many-body expansion together with high accuracy theory such as CCSD(T) with extrapolation to the complete basis set (CBS) limit. We approximated the endless chain of HF molecules with sizes of up to $N = 14$ molecules, and the intermolecular interactions were truncated at the four-body level. By extrapolation, we obtained an estimate of interaction energy ΔE per molecule in the thermodynamic limit ($1/N \rightarrow \infty$). Our current best estimate for the used model amounts to $\Delta E = 7.08 \pm 0.02$ kcal/mol. These results will be used for FNDMC accuracy cross-checks vs. current CCSD(T)/CBS results.

Theoretical spectrum of the HD-CO complex to guide the microwave measurements

Ewelina Grabowska¹, Piotr Jankowski¹

¹*Faculty of Chemistry, Nicolaus Copernicus University, Jurija Gagarina 7, 87-100 Toruń, Poland*

In this work we present the first observation of the theoretical rovibrational spectrum of the HD-CO van der Waals complex in the microwave range. Rovibrational transitions of the H₂-CO and D₂-CO weakly bound complexes have been analyzed very intensively during the last years [1,2,3,4], primarily due to their astrophysical importance. The knowledge of spectra of the H₂-CO and its isotopologues can help mapping of interstellar matter [4].

The experimental rotational spectrum of the HD-CO van der Waals complex was first measured in 2015 by Potapov *et al.* [5]. Three transitions were observed in the millimeter-wave region. A comparison to the three measured transitions shows that the agreement to within 0.01 cm⁻¹ between theory and experiment has been achieved. Moreover, the experimental assignment of these lines has been confirmed.

We also obtained the first infrared spectrum of HD-CO van der Waals complex. Our results show that the high-accuracy quantum mechanical computations can be useful for planning and interpretation of experiments.

[1] A. R. W. McKellar, J. Chem. Phys., 108 (1998) 1811

[2] A. R. W. McKellar J. Chem. Phys., 112 (2000) 9282

[3] P. Jankowski, A. R. W. McKellar, K. Szalewicz, Science, 336 (2012) 1147

[4] P. Jankowski, L. A. Surin, A. V. Potapov, S. Schlemmer, A. R. W. McKellar, K. Szalewicz, J. Chem. Phys., 138 (2013) 084307

[5] A. V. Potapov, L. A. Surin, S. Schlemmer, Journal of Molecular Spectroscopy, 307 (2015) 18

Practical, accurate, cost- and implementation-free method (Δ MP2-SCS(IP)) for the calculation of vertical ionization potentials

Ireneusz Grabowski, Szymon Śmiga

*Institute of Physics, Faculty of Physics, Astronomy and Informatics
Nicolaus Copernicus University in Torun
Grudziadzka 5, 87-100 Torun, Poland
ig@fizyka.umk.pl*

A practical, accurate, cost- and implementation-free method (Δ MP2-SCS(IP)) for the calculation of vertical ionization potentials is proposed [1]. The simple method is based on a single step, a diagonal, frequency-independent approximation to the second-order self-energy expression combined with the spin-component-scaled technique. A new optimal parametrization for the spin-resolved Δ MP2 methods is proposed to accurately predict IPs. The new methods have been tested for set of 100 moderately-sized molecules and additionally benchmarked against a set of 24 organic molecules. As we have shown, the IPs calculated using our new methods are of almost Δ -CCSD(T) or IP-EOM-CCSD quality and are better than computationally more demanding EP methods. Moreover, the Δ MP2-SCS(IP) and Δ MP2-SOS(IP) require only single step post HF calculation which scales like $O(N^3)$.

[1] S. Śmiga, I. Grabowski JCTC XX,XX (2018),

Benchmark CCSD(T)/CBS interaction energies of coinage metal atoms on benzene

Jaroslav Granatier

Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic

The complexes of open-shell metal atoms (coinage metals) with closed-shell molecules (benzene) are characterized by weak van der Waals interaction. The study of such systems requests more accuracy approaches than CCSD(T) method, which describes the electron correlation and provides correct nature of interaction. However, the CCSD(T) due to more computational demanding allows to study only the simplest models. Consequently, the large systems (the metal atoms bonded on the graphene surface) are usually studied in terms of the density functional theory (DFT) method.

Our previous work¹ showed to different nature of binding of Ag and Au metal atoms on benzene. While the silver binds predominantly through dispersion interactions, the binding of gold involves a subtle combination of dispersion interaction and charge transfer interaction between the electron donor (benzene) and the electron acceptor (the gold atom). Consequently, the most stable structure for Ag...benzene complex is the hollow (site above the center of the aromatic ring), while the gold atom prefers the top (site directly above a C atom) and the bridge (site above the midpoint of a C-C bond) positions. The relativistic effects dramatically increase the stability of Au...benzene complex due to relativistic increase of electron affinity of metal atom.

In this work we demonstrate the CCSD(T)/CBS benchmark binding energies for complexes of coinage metals with benzene. The CCSD(T)/CBS binding energies were obtained from MP2/CBS interaction energies and by adding of difference between CCSD(T) and MP2 binding energies evaluated in small basis sets. The relativistic effects have been included by using Douglas-Kroll-Hess approximation. All wave function binding energies were treatment by counterpoise correction.

This work is supported by the Slovak Grant Agency VEGA, project No. 1/0598/16. Also we are grateful to the HPC center at the Slovak University of Technology in Bratislava, which is a part of the Slovak Infrastructure of High Performance Computing (SIVVP project, ITMS code 26230120002, funded by the European region development funds, ERDF), for the computational time and resources made available.

¹ Granatier, J., Lazar, P., Otyepka, M., Hobza, P.: *J. Chem. Theory Comp.*, 7 (11), 3743–3755 (2011).

Molecular modelling of bioorganoclays

Peter Grančič¹, Daniel Tunega¹

¹*Institute of Soil Research, University of Natural Resources and Life Sciences,
Peter-Jordan-Straße 82, 1190 Vienna, Austria*

Interaction of microorganisms and their metabolic products with clay minerals is a common interfacial phenomenon in the environment. However, fundamental mechanisms governing all types of interactions are still poorly understood. The objective here is to elucidate the complex mechanisms responsible for the formation of bioorganoclays via molecular dynamics simulations. This includes the determination of probable molecular configurations and the identification of the corresponding binding sites and energies under various physical conditions. Our calculations explain how the phosphatidylcholine molecules arrange at the surface of the clay montmorillonite and reveal that their conformational structure strongly depends on the phosphatidylcholine loading.

HB49: How accurate is DFT?

Robin Guttman¹, Adrian Daniel Boese¹

¹*Institute of Chemistry, University of Graz, Heinrichstrasse 28, 8010 Graz, Austria*

In recent years many theoretical methods were developed to describe weak, intermolecular interactions. In our study we used different density functionals like B3LYP, PBE0, TPSS, SCAN and b97-3c together with dispersion correction D3(BJ)^[1] to investigate several neutral, weakly bound complexes, which were taken from the HB49 benchmark.^[2,3] This set offers highly accurate geometries and interaction energies for equilibrium structures of small, interacting molecules.

Most of the tested methods show an overbinding, which can be attributed to the dispersion correction used. The resulting error is high for several not so common complexes like HCl---NH₃, OC---HF or some of the larger complexes.

Additionally, four of those systems were chosen and the intermolecular distance was varied. According to the protocol of the HB49 we obtain reference interaction energies. Around the minimum most of the used DFT methods can reproduce the values quite well, but at low distances the error can be huge.

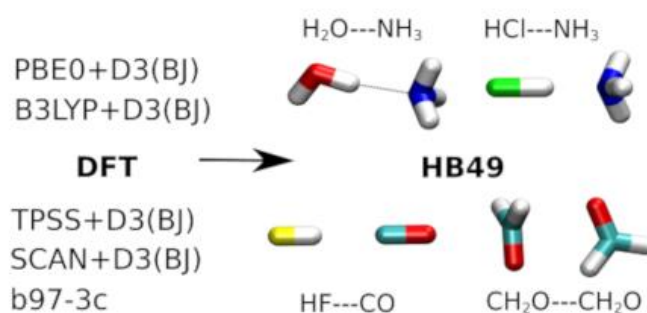


Figure 1: Used DFT methods on the subset of the HB49 benchmark (the four molecules shown are used for the study of distance dependency).

[1] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **32** (2011) 1456-1465

[2] A. D. Boese, *Molecular Physics* **14** (2015) 1618-1629

[3] A. D. Boese, *ChemPhysChem* **140** (2015) 978-985.

Interaction-induced electric properties of hydrated uracil molecule.

Tomáš Hrivnák¹, Šimon Budzák², Heribert Reis³, Robert Zalešný⁴, Philippe Carbonniere⁵ and Miroslav Medved²

¹ Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Mlynska dolina, Ilkovičova 6, SK-842 15 Bratislava, Slovakia

² Department of Chemistry, Faculty of Natural Sciences, Matej Bel University, Tajovského 40, SK-97400 Banská Bystrica, Slovakia

³ Institute of Organic and Pharmaceutical Chemistry, National Hellenic Research Foundation, Vasileos Constantinou 48, GR-11635 Athens, Greece

⁴ Department of Physical and Quantum Chemistry, Faculty of Chemistry, Wrocław University of Science and Technology, Wyb. Wyspiańskiego 27, PL-50370 Wrocław, Poland

⁵ Equipe de Chimie Physique, IPREM UMR 5254, Université de Pau et des Pays de L'Adour, 2 Avenue du président Angot, F-64000 Pau, France

Changes of the dipole moment and dipole polarizability of the uracil molecule induced by the presence of water molecules have been investigated in micro- and macrohydration regimes. In the case of the former, all relevant conformers generated by the Global Search Algorithm of Minima (GSAM)¹ level have been considered. Both induced dipole moment and isotropic dipole polarizability values gradually increase with the increasing $U \cdot nH_2O$ cluster size up to $n = 5$ followed by a dramatic decrease of polarizability in the case of $U \cdot 6H_2O$. These observations were explained in terms of the changes of collective behavior of water molecules. To represent the macrohydrated system we applied supermolecular (SM) and rigorous local field (RLF) explicit solvation models with representative structure generation by molecular dynamics. The SM approach predicts the evolution of properties with the cluster size consistent with the results obtained by the microhydration model, reaching the maximum value of induced polarizability of uracil for smaller clusters followed by decrease of this property with the increasing cluster size. To reach the electrostatic contribution convergence we applied the RLF model and then combined this result with converged non-electrostatic contributions from the SM model. This approach shows that a decrease of total polarizability of uracil molecule in water can be expected.

[1] Marchal, R., Carbonnière, P. & Pouchan, C. A global search algorithm of minima exploration for the investigation of low lying isomers of clusters from density functional theory-based potential energy surfaces: The example of Sin ($n=3,15$) as a test case. *The Journal of Chemical Physics* **131**, 114105 (2009).

Theoretical Study of Molecular and Adsorption Properties of Group 6, 7 and 8 Heavy and Super-heavy Metal Carbonyls

Miroslav Iliaš^{1,2,3}, Valeria Pershina²

¹*GSI Helmholtzzentrum für Schwerionenforschung GmbH, 64291 Darmstadt, Germany*

²*Helmholtz Institute Mainz, 55099 Mainz, Germany*

³*Matej Bel University, 97401 Banská Bystrica, Slovakia*

Calculations of the first bond dissociation energies (FBDEs) and other molecular properties of (i) $M(\text{CO})_6$, where $M = \text{Mo}, \text{W},$ and Sg (group 6), Ref. [1], of (ii), $M(\text{CO})_5$ and $M\text{H}(\text{CO})_5$, where $M = \text{Tc}, \text{Re}, \text{Bh}$ (group 7) and of, (iii), $M(\text{CO})_5$, where $M = \text{Ru}, \text{Os},$ and Hs (group 8), Ref. [2], have been carried out using a variety of nonrelativistic and relativistic methods, such as ZORA-DFT, X2c+AMFI-CCSD(T), and Dirac-Coulomb DFT.

The aim of the study is to assist experiments on the measurements of the FBDEs. The obtained results show that trends in spectroscopic properties of the given species follow the same pattern as that of other compounds of group 4 through group 8 elements.

[1] M. Iliaš and V. Pershina, *Inorg. Chem.* **56** (2017) 1638

[2] V. Pershina and M. Iliaš, *J. Chem. Phys.* **146** (2017) 184306.

Relativistic four component DFT and CC calculations of potential energy curves of Zn₂, Cd₂ and Hg₂ dimers.

Katarzyna Jakubowska¹, Magdalena Pecul-Kudelska¹

¹*Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*

The aim of this project is to study effects of electron correlation and to choose correlation-exchange functional used in DFT calculations that would most accurately describe correlation energy for metal clusters from XII group of periodic table: zinc, cadmium and mercury in case of relativistic four-component calculations that base on Dirac-Coulomb Hamiltonian.

XII group metal dimers have been chosen to be the test systems. First, potential energy curves have been computed with the use of coupled-cluster (CC) method and four-component Dirac-Coulomb Hamiltonian. CC theory is one of the most mathematically elegant techniques for estimating electron correlation energy and, thus, it is also one of the most popular methods of computations in cases, where correlation energy plays a key role in obtaining results in agreement with experiment. That is why, the CC results are considered benchmark for further density functional theory (DFT) calculations with the use of a wide variety of exchange-correlation functionals, for example, B₃LYP, BLYP and PBEo.

Moreover, in order to obtain more accurate results the basis set superposition error (BSSE) has been estimated by performing subsystem calculations using ghost atoms with basis sets of the full system. A number of different basis sets has been used so as to study the dependence of BSSE on the chosen basis set.

Accurate description of electron correlation, in addition to accounting for relativistic effects in case of systems including heavy atoms, is one of the key factors affecting accuracy of the results. In many cases relativistic quantum chemical calculations of molecular properties with the use of CC method cannot be carried out because of high computational effort that prevents this method from being used routinely or the fact that there is currently no implementation of four-component coupled-cluster theory for calculating a given molecular property, for example spin-spin coupling constant. In such cases the only method that is available is the DFT method and, that is why, choosing the most suitable exchange-correlation functional is of great importance.

Failure of the dispersion-corrected density-functional theory for three-body intermolecular interactions.

Wojciech Jankiewicz¹, Henryk Witek², and Rafał Podeszwa¹

¹ Institute of Chemistry, University of Silesia, Katowice, Poland

² Department of Applied Chemistry and Institute of Molecular Science,
National Chiao Tung University, Hsinchu, Taiwan.

Although a number of computational methods can be used for describing three-body intermolecular interactions, none of them are both accurate and robust. The best of the techniques based on the coupled-cluster method can only be applied to systems consisting of about a dozen atoms per monomer. The second-order Møller–Plesset perturbation theory (MP2) can be applied to larger systems but it fails to describe the non-additive dispersion contribution. It may be, therefore, tempting to use the density-functional theory with empirical dispersion correction (DFT-D), a method that has been successfully applied to studies of molecular dimers and condensed phases.

We present a detailed analysis of the performance of a wide range of DFT-D methods for three-body interaction energies for a 3B-69 benchmark. We also test the behavior of the methods for cross-sections of illustrative systems dominated by induction, exchange, or and dispersion. We show that none of the DFT-D methods work satisfactorily, except for the induction-dominated configurations. On the other hand, the MP2 method can be corrected for dispersion and provide good accuracy for three-body interaction energies.

Fluorographane C₂FH: stable and wide band gap insulator with huge excitonic effect

František Karlický, Josef Turoň

University of Ostrava, 30. dubna 22, 30. dubna 22, 701 03 Ostrava, Czech Republic

2D materials derived from graphene by attachment of hydrogen and halogens have attracted considerable interest because of their potential applications [1]. We present structural, vibrational, electronic and optical properties of recently prepared [2] fully fluorinated and hydrogenated graphene, called fluorographane [3]. We consider 1:1 ratio of F and H adatoms and we carefully investigate possible structural conformers in C₂FH stoichiometric material. We show that all conformers are dynamically stable and homogeneous structures with F and H atoms on both sides of carbon honeycomb structure are more stable than the Janus structures with F atoms on one side and all H atoms on the other. While the main structural and vibrational features are roughly similar for various conformers, electronic and optical properties are very sensitive to local structure (namely specific combinations of F and H adatoms on the graphene surface) and differ significantly. Our highly accurate results based on many-body methods (GW and BSE) indicate that homogeneous fluorographane has unusually wide indirect electronic band gap of ~10 eV [3] (larger than both pure graphane CH and pure fluorographane CF [4]) and embodies a huge excitonic effect (~3 eV). Fluorographane C₂FH is therefore a material with the widest electronic gap and a largest binding energy of exciton in the class of currently known 2D materials.

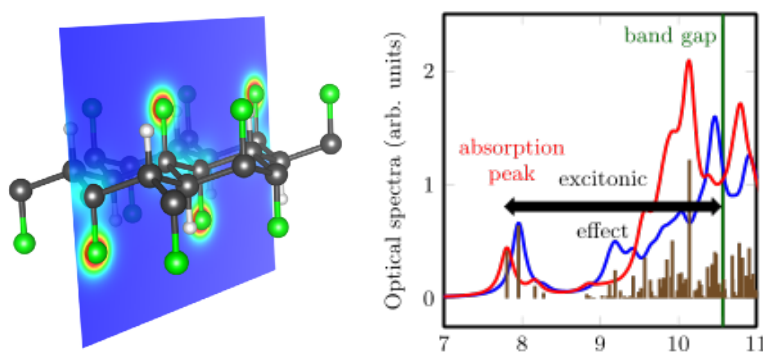


Figure 1: Optimized structure of the most stable conformer of fluorographane C₂FH including a cut through an electron density. Optical absorption spectra and the band gap of fluorographane C₂FH.

- [1] Karlicky F., Datta KKR., Otyepka M., Zboril R., ACS Nano 7 (2013) 6434
- [2] Sofer Z., Simek P., Mazanek V., *et al.*, Chem. Commun. 51 (2015) 5633.
- [3] Karlicky F., Turoň J., Carbon 135 (2018) 134
- [4] Karlicky F., Otyepka M., J. Chem. Theory Comput. 9 (2013) 4155

Calculations of electronic excited states of CsMo molecule

Dávid Vrška, Katarína Rišková, Ivan Černušák, Vladimír Kellö

Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Ilkovičova 6, SK-842 15 Bratislava, Slovakia

Interaction of caesium with molybdenum attracted recently more detailed research because of its particular importance in nuclear fusion reactors [1]. In this work we present more accurate calculations of Cs-Mo interaction using the RASSCF and CASPT₂ method. Scalar relativistic effects are accounted for by Douglas-Kroll-Hess method. Previous studies indicate that multiplicity of the lowest state is sextet and octet is higher. We carried out calculations for all possible multiplicities and their stabilities are in the order; sextet, octet, quartet and doublet, see Figure 1. We calculated potential energy curves for three lowest electronic levels for the every multiplicity.

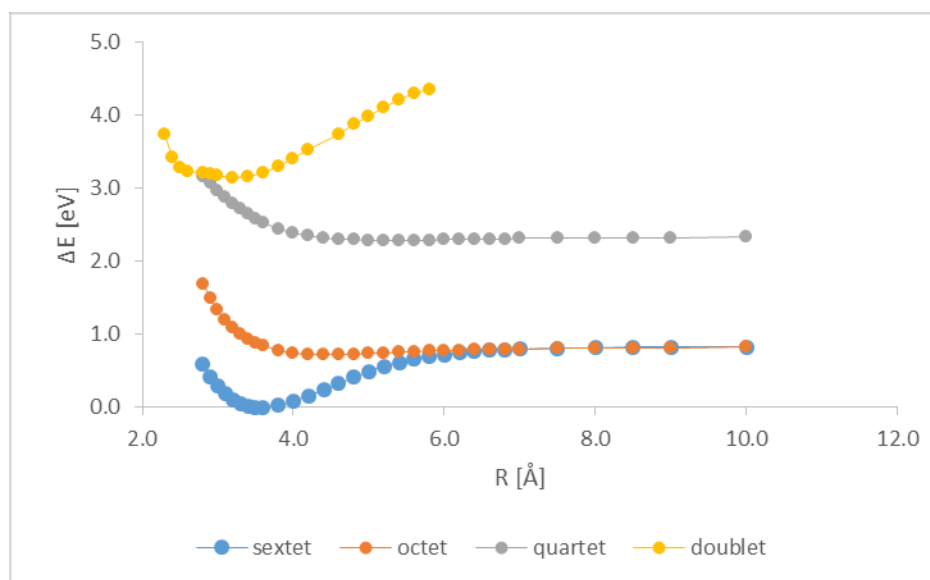


Figure 1: CASPT₂ potential energy curves for the CsMo molecule for the lowest sextet, octet, quartet and doublet state

[1] A. Damone and A. Panarese, *et al.*, Plasma Phys. Control. Fusion **57** (2015) 035005.

Theoretical Study on Fe(III) and Cu(II) complexes of 4-Quinazolinone in Water and DMF

René Zach ¹, Anne-Marie Kelterer ¹, Sándor Kunsági-Máté ²

¹*Institute of Physical and Theoretical Chemistry, Graz University of Technology, NAWI Graz, Stremayrgasse 9, 8010 Graz, Austria*

²*Department of Pharmaceutical Chemistry, University of Pécs, Rokos Utca 2, 7624 Pécs, Hungary*

Quinazolinone derivatives are of particular importance in medicine because of their various biological properties. Recently a new 4-quinazolinone was synthesized as DNA enzyme repair inhibitor.[1] In the presence of water, experimental measurements show different behavior of its iron and copper complexes when included in a cavitant. Our quantum chemical calculations try to explain the solvent dependent differences.

The octahedral Cu(II) complex was modelled with different positions of the Cu(II) ion at various tautomeric forms of 4-quinazolinone with water or DMF. Both spin states were calculated for the Fe(III) complexes in water. Density Functional Theory was applied using B₃LYP-D₃BJ with the def2-TZVP basis set throughout this study.

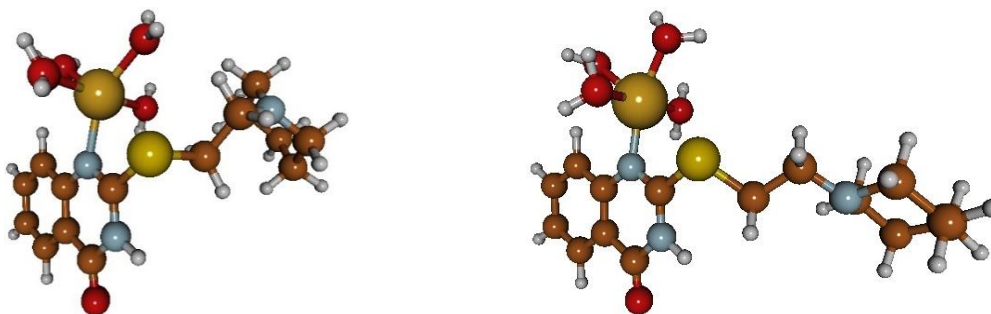


Figure 1: Complex of the 4-quinazolinone complex with Fe³⁺ (left) and Cu²⁺ (right) in water

This poster presents the conformations of the various complexes with water and DMF and compares the Cu(II) and Fe(III) binding situations including their interaction energies. Both high spin and low spin iron(III)-complexes are shown. The poster tries to explain why the Cu(II)-4-quinazolinone-water complex is expected to bind differently to a cavitant molecule than the respective Fe(III) complex.

[1] Kulcsár, Gy.; Kálai, T.; Ósz, E.; Sár, C.P.; Jekő, J.; Sümegi, B.; Hideg, K., *Arkivoc* 4 (2003) 121.

Adsorption of Trichloroethylene on modified zero-valent nanoparticles of iron

Miroslav Kolos^{1,2}, Daniel Tunega¹, Frantisek Karlicky²

¹*Institute for Soil Research, Department of Forest and Soil Sciences, University of Natural Resources and Life Sciences Vienna, Austria*

²*Department of Physics, Faculty of Science, University of Ostrava, Czech Republic*

Degradation of toxic trichloroethylene (TCE) from ground water using conventional methods is very slow and expensive, so it is crucial to develop new effective methods for TCE removing. Zero-valent iron in a form of nanoparticles (nZVI) is very promising and reactive material having a capability to degrade TCE. However, nZVI particles are not very stable in water what decreases their surface reactivity. Chemical modification of nZVI nanoparticle surfaces (e.g. by sulfidization) can increase the surface stability without significant loss of reactivity with respect to TCE. We performed quantum chemical calculations (at density functional theory level, DFT) of interactions and reactions of TCE molecule with surface models of pure nZVI and mackinawite mineral (FeS), which is, according to experiments, formed on nZVI surface after the sulfidization. DFT calculations showed that nZVI can degrade TCE spontaneously with no energetic barrier. On the other hand, the calculations showed that theoretical dissociation of the first Cl atom from the TCE molecule on mackinawite (001) surface has an energetic barrier of about 54 kcal/mol and endothermic character. The barrier seems to be relatively high but it is about half less than the dissociation of the TCE in a gas phase.

Relativistic two- and four-component electron dynamics approach to chiroptical spectroscopies

Lukas Konecny^{1,2}, Marius Kadek¹, Stanislav Komorovsky³, Kenneth Ruud¹, Michal Repisky¹

¹*Hylleraas Centre for Quantum Molecular Sciences, Department of Chemistry, UiT—The Arctic University of Norway, NO-9037, Tromsø, Norway*

²*Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University, Ilkovicova 6 Bratislava, Slovakia*

³*Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dubravska cesta 9, Bratislava, Slovakia.*

We present an implementation and application of electron dynamics based on real-time time-dependent density functional theory (RT-TDDFT) and relativistic 2-component (X2C) and 4-component (Dirac–Coulomb) Hamiltonians [1, 2] to the calculation of electron circular dichroism (ECD) and optical rotatory dispersion (ORD) spectra. To reduce the computational cost, the resolution-of-identity approximation for the Coulomb term (RI-J) is introduced into RT-TDDFT.

We have calculated the ECD and ORD spectra of the dimethylchalcogenirane series, $(C_2H_2)X(CH_3)_2$ ($X = O, S, Se, Te, Po, Lv$). [3] The spectra obtained by non-relativistic and relativistic methods start to disagree for Se and Te, while dramatic differences are observed for Po and Lv. Most notably, in the case of Po, the non-relativistic ECD spectrum gives the visual impression of being the mirror image of the relativistic spectrum in a certain frequency region, clearly demonstrating the need for a relativistic approach. The X2C approach reproduces the reference 4-component results surprisingly well across the entire series while offering an 8-fold speed-up. An overall acceleration of RT-TDDFT achieved by means of the combination of X2C and RI-J increases with system size and approaches a factor of almost 25 when compared to the full 4-component treatment, without compromising accuracy of the final spectra. These results support (relativistic) electron dynamics as a viable and perspective tool for molecular property calculations. [4]

- [1] M. Repisky, L. Konecny, M. Kadek, S. Komorovsky, O. L. Malkin, V. G. Malkin, and K. Ruud, *J. Chem. Theory Comput.* **11** (2015) 980.
- [2] L. Konecny, M. Kadek, S. Komorovsky, O. L. Malkin, K. Ruud, and M. Repisky, *J. Chem. Theory Comput.* **12** (2016) 5823.
- [3] L. Konecny, M. Kadek, S. Komorovsky, K. Ruud, and M. Repisky, submitted to *J. Chem. Theory Comput.*
- [4] J. J. Goings, P. J. Lestranger and X. Li, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **8** (2018) 1.

DFTB parametrization for intermolecular interactions

Magdalena Krzuś¹, Chien-Pin Chou², Rafał Podeszwa³, Henryk Witek⁴

¹*Jagiellonian University, Gołębia 24, 31-007 Kraków, Poland*

²*Waseda University, Shinjuku, Totsukamachi, 1 Chome-104, 169-8050 Tokyo, Japan*

³*University of Silesia, Bankowa 12, 40-007 Katowice, Poland*

⁴*National Chiao Tung University, No. 1001 Daxue Road, 30010 Hsinchu City, Taiwan*

The last years have seen the growing interest in theoretical calculations for intermolecular interactions of complex organic compounds which have heightened the need for quick, universal and inexpensive computing methods. The main drawback of the currently used methods is high computational cost. Even the most computational accessible method, namely density functional theory with empirical dispersion (DFT-D), is too expensive for large systems. These obstacles might be overcome by simplifying the calculation method and using some empirical parameter sets.

Density functional tight binding method (DFTB) can be regarded as an approximation to DFT with much lower computational costs and accuracy acceptable for many applications. In the present work, DFTB parametrization was optimized for intermolecular interactions by fitting dispersionless interaction energies (i.e. energy with the dispersion energy subtracted) and adding empirical dispersion. The resulting DFTB-D interaction energies were compared with several benchmarks and with other approaches, including DFT-D. The data show that with careful optimization the DFTB-D accuracy can become competitive for some systems with the DFT-D approaches with significantly lower computational complexity.

Two- and three-body energies from DLPNO-CCSD(T) method

M. Krzyżowska¹, R. Podeszwa¹

¹*Institute of Chemistry, University of Silesia, Szkolna 9, 40-006 Katowice, Poland*

Domain-based local pair natural orbital coupled cluster theory with single, double, and perturbative triple excitations [DLPNO-CCSD(T)] method [1] was applied to calculations of two- and three-body intermolecular interactions energies of van der Waals complexes. The results were compared with the coupled cluster method with single, double and non-iterative triples excitations with the complete basis set extrapolation [CCSD(T)/CBS] benchmarks and several density functional theory plus dispersion approaches (DFT-D) [2, 3]. The accuracy of the DLPNO-CCSD(T) method for two-body energies was tested for several local cut-off thresholds with standard basis sets and with explicitly correlated DLPNO-MP2-F12 method [4] used with a DLPNO-CCSD(T) correction. The huge computational speed-up of the DLPNO-CCSD(T) method compared to the canonical CCSD(T) method results in decrease of the accuracy but the the quality of the two-body energies was found to be competitive with the DFT-D methods. For three-body non-additive energies, the DLPNO-CCSD(T) offers similar overall accuracy to the MP2 method which is rather disappointing but for the three-body energies DFT-D methods do not work well, either. Overall, DLPNO-CCSD(T) can be used for intermolecular interactions with careful selection of cut-offs and basis sets.

- [1] C. Riplinger, B. Sandhoefer, A. Hansen, F. Neese, *J. Chem. Phys.*, **139** 134101 (2013).
- [2] D. E. Taylor, J.G. Ángyán, *et al.*, *J. Chem. Phys.*, **145** 124105 (2016).
- [3] J. Řezáč, Y. Huang, P. Hobza, G. J. Beran, *Journal of Chemical Theory and Computation*, **11** 3065-3079 (2015).
- [4] F. Pavošević, P. Pinski, *et al.*, *J. Chem. Phys.*, **144** 144109 (2016).

New theoretical approaches for strongly-correlated systems

Aleksandra Lachmanska¹ and Katharina Boguslawski²

¹*Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland*

²*Faculty of Chemistry, Nicolaus Copernicus University, Gagarina 11, 87-100 Torun, Poland, email: k.boguslawski@fizyka.umk.pl*

The pair Coupled Cluster Doubles (pCCD) model combined with a (variational) orbital optimization protocol [1, 2] has been shown to capture the major part of the static correlation in small molecules, like diatomics or heavy-element-containing compounds [3]. The orbital-optimized pCCD method is size-consistent and computationally inexpensive in comparison to various multi-reference approaches. However, it does not account for all electron correlation effects. [4] One way to include the missing (dynamic) electron correlation effects is to use a (linearized) Coupled Cluster correction on top of the pCCD wave function. [5, 6] The frozen-pair Coupled Cluster Singles Doubles (fpCCSD) method is one efficient way to improve the wave function with the cost of CCSD. [5] In fpCCSD or its linearized variant, the singles and non-pair doubles amplitudes are optimized, while the pair doubles amplitudes are kept frozen. Such an optimization routine provides a balanced description of strongly-correlated systems, where traditional CCSD usually fails. In this work, we will scrutinize the performance of various Coupled Cluster corrections on top of pCCD.

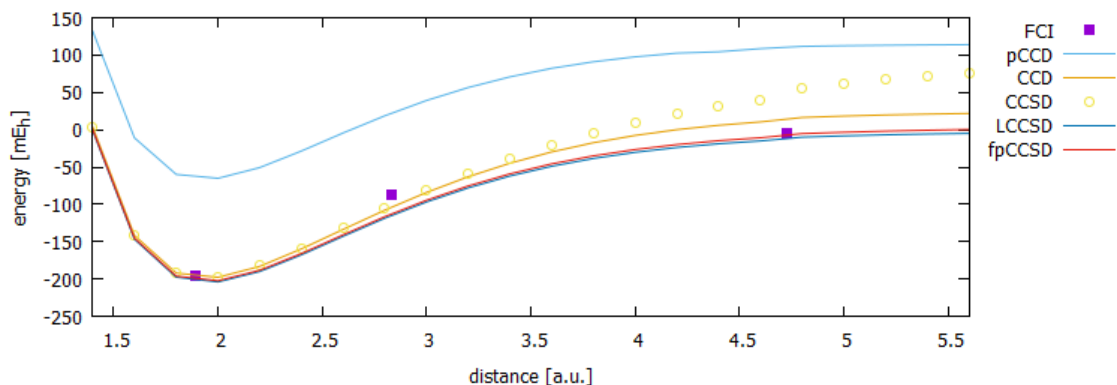


Figure 1: The dissociation process of the HF molecule

- [1] K. Boguslawski, P. Tecmer, *et al.*, Phys. Rev. B **89** (2014) 201106.
- [2] T. Stein, T.M. Henderson, and G.E. Scuseria, J. Chem. Phys. **140** (2014) 214113.
- [3] P. Tecmer, K. Boguslawski, and P.W. Ayers, Phys. Chem. Chem. Phys. **17** (2015) 14427.
- [4] K. Boguslawski, P. Tecmer, and Ö. Legeza, Phys. Rev. B **94** (2016) 155126.
- [5] T. Stein, T.M. Henderson, and G.E. Scuseria, J. Chem. Phys. **140** (2014) 214113.
- [6] K. Boguslawski, and P.W. Ayers *et al.*, J. Chem. Theory Comput. **11** (2015) 5252.

Perturbative Triples Correction to DLPNO-MkCCSD

Jakub Lang^{1,2}, Jiri Brabec¹, Masaaki Saitow³, Jiří Pittner¹, Frank Neese³, and Ondřej Demel¹

¹*J. Heyrovský Institute of Physical Chemistry, v.v.i., Academy of Sciences of the Czech Republic, Dolejškova 3, 18223 Prague 8, Czech Republic*

²*Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University of Prague, Hlavova 2030, 12840 Prague 2, Czech Republic*

³ *Max Planck Institute of Chemical Energy Conversion, Mülheim an der Ruhr, Germany*

The multireference coupled cluster (MRCC) methods are a highly accurate approach for systems with quasidegeneracies, where a high portion of the correlation energy is a static correlation. However, while canonical MRCC is highly successful for many systems, it can be used only for small systems[1]. Nonetheless, it was shown that this obstacle can be bypassed with the domain-based pair natural orbital approach (DLPNO)[2].

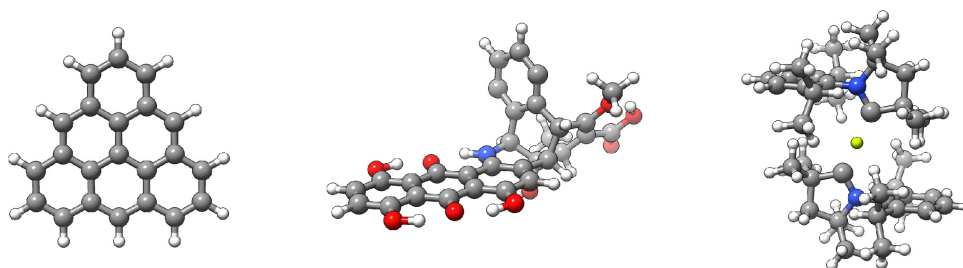


Fig. 1 The molecules (a) triangulene, (b) dynemicin A, and (c) $[\text{Be}^{\text{MeL}}_2]$.

In this poster we report an implementation of the perturbative triples correction to Mukherjee's state-specific multireference coupled cluster method based on the domain-based pair natural orbital approach (DLPNO-MkCC). We test the performance of DLPNO-MkCCSD(T) on calculations of tetramethyleneethane and isomers of naphthyne. These tests show that more than 97% of triples energy was recovered with respect to the canonical MkCCSD(T) method, which together with the DLPNO-MkCCSD part accounts for about 99.8% of the total correlation energy. Furthermore, calculations needed only small fraction of canonical computational time.

The applicability of the method is demonstrated on calculations of singlet-triples gaps for several large systems (triangulene, dynemicin A, beryllium complex (Fig.1.)).

[1] J. Lang, M. Svana, *et al.*, *Mol. Phys.* **115** (2017) 2743.

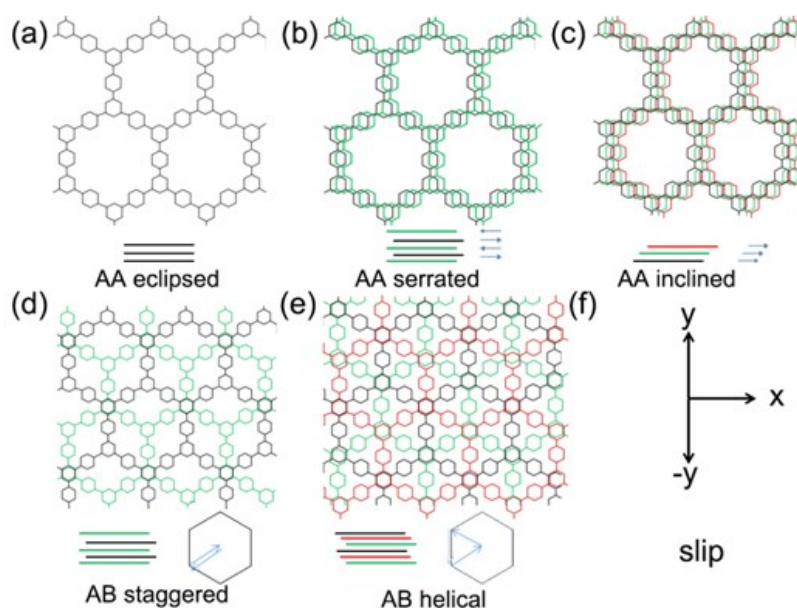
[2] J.Brabec, J. Lang *et al.* *JCTC* **14** (2018) 1370.

Theoretical investigation of COF stacking and effects on photocatalysis

P. Lyu, P. Nachtigall

Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, 128 43 Prague 2, Czech Republic, e-mail: petr.nachtigall@natur.cuni.cz

To meet the demand for clean energy from solar radiation, an important task is to find out efficient, highly active and low-cost semiconductor photocatalysts. [1,2] Covalent organic frameworks (COFs) have drawn an increasing attention in this aspect. In this work, the inter-layer arrangement of 2D COFs with different nitrogen content (C: N=4:1, 9:1, 1:0, respectively) is investigated. Different stacking patterns, AA eclipsed, AA inclined, AA serrated, AB staggered and AB helical have been taken into account. [3] The nitrogen content is found to influence the planarity and in turn the interaction between linkers from neighboring layers. The stabilities of COFs with different stacking patterns depend on the competition of electrostatic and dispersion interactions between adjacent COF layers. The effects of COF stacking on band gaps and band edge alignment are also discussed.



[1] A. J. Bard, *Journal of the American Chemical Society* 2010, 132, 7559-7567.

[2] Y. Li, Y.-L. Li, B. Sa, R. Ahuja, *Catalysis Science & Technology* 2017, 7, 545-559.

[3] B. Lukose, A. Kuc, J. Frenzel, T. Heine, *Beilstein Journal of Nanotechnology* 2010, 1, 60-70.

Benchmarking weakly-bound open-shell system: design of dataset

K.Madajczyk, P. Żuchowski

Nicolaus Copernicus University, Gagarina 11, 87-100 Toruń, Poland

The research is aimed at creating a standard database for open-shell's molecules to better understand the interaction between them. Compounds which are studied are often found in the Earth's atmosphere as well as extraterrestrial bodies and their spectroscopic properties are provided by ExoMol, BaseCol and Hitran databases.

In the first stage, calculations were performed using the methods RHF, UHF, MP2, UMP2, CCSD, CCSD(T), UCCSD, UCCSD(T). All methods carried out on a number of different bases, from aug-cc-pvdz to aug-cc-pv5z. In further stages, calculations are planned using the F12 and midbond methods. The next step will be the calculation of SAPT-0 correction.

Thanks to this, it will be possible to know what kind of interaction dominates in a given pair of compounds. In addition, it will be possible to choose such compounds so that the base is as rich as possible in various types of interactions between molecules.

Acknowledgments: I want to acknowledge to FONDECYT for financial support.

[1] K. Patkowski, *Annual Reports in Computational Chemistry*, 13, 3-91(2017)

[2] P.R.Tentscher, J.S.Arey, *J. Chem. Theory Comput.*, 9 (3), 1568–1579(2013)

Formation of tungsten clusters.

Ján Matúška¹, Ivan Sukuba²

¹*Institute of Physical Chemistry and Chemical Physics, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic*

²*Department of Nuclear Physics and Biophysics, Faculty of Mathematics, Physics and Informatics, Comenius University, SK-84248, Bratislava, Slovak Republic*

The materials that face hot plasmas like the ones in present and future thermonuclear fusion reactors have to withstand challenging conditions[1], in order to achieve the goal of maintaining long-term stable source of energy out of fusion reaction. Tungsten is already projected to be used in ITER as a divertor due to its unique chemical and physical properties, i.e. extremely high melting point and low thermal expansion. Therefore, the properties of the tungsten under conditions in the fusion reactor are studied intensively to minimize the divertor erosion and subsequent plasma contamination or dust creation.

Formation of the tungsten clusters up to 20 atoms have been studied using molecular dynamics trajectory simulations. The aim of the study was to describe the process of the single W atom attachment to W_n clusters, where $n=2-10$. Additionally, the corresponding reaction cross sections as a function of the translational collision energy and the thermal rate constants were evaluated and compared to our previous results that were obtained under conditions of high-pressure limit.

Interatomic interactions were described by the analytical bond-order potential (ABOP) with set of parameters for W[2]. ABOP was implemented into ANT 16 computational code[3] which we used for Molecular dynamics simulations.

[1] G. Pintsuk, *Compr. Nucl. Mater.*, (2012) 551

[2] N. Juslin, P. Erhart, et al., *J. Appl. Phys.* **98** (2005) 12352

[3] J. Zheng, Z.-H. Li, et al., *ANT* 2016, <http://comp.chem.umn.edu/ant>

Photoswitching mechanism of Donor-acceptor Stenhouse adducts (DASAs): Theoretical aspects

Miroslav Medved¹, Adèle D. Laurent², Michael Lerch³, Mariangela Di Donato⁴, Wiktor Szymański³, Wybren Jan Buma⁵, Ben L. Feringa³

¹*Department of Chemistry, Faculty of Natural Sciences, Matej Bel University, Tajovského 40, SK-97400 Banská Bystrica, Slovakia*

²*CEISAM, UMR CNRS 6230, BP 92208, 2 Rue de la Houssinière, 44322 Nantes, Cedex 3, France*

³*Centre for Systems Chemistry, Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands*

⁴*LENS (European Laboratory for Non Linear Spectroscopy), via N. Carrara 1, 50019 Sesto Fiorentino, Italy*

⁵*Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098XH Amsterdam, The Netherlands*

Donor-acceptor Stenhouse adducts (DASAs) are an emerging class of T-type photoswitches [1]. They are particularly attractive due to their modular nature, rapid synthesis and also due to large structural changes upon photoswitching with visible light. The key to optimize their switching properties is an in-depth understanding of the photoswitching mechanism.

In our combined experimental and theoretical studies [2,3], we fully characterized actinic and thermal steps of DASA-photoswitching and its key intermediates. The first intermediate was trapped and studied using ultrafast visible and IR pump-probe spectroscopies and TD-DFT calculations. Comparison of the ultrafast TRIR spectra with DFT computations allowed to unambiguously identify the structure of the intermediate, confirming that light absorption induces a sequential reaction path in which *Z-E* photoisomerization is followed by a thermal single-bond rotation.

We also employed TD-DFT calculations and spectroscopic analyses to disentangle various factors determining the solvent-dependence of DASA's photoswitching [4], which is crucial for the rational development of applications in a wide range of different media.

Acknowledgments: The authors acknowledge financial support from Laserlab-Europe (LENS002289), The Netherlands Organization for Scientific Research (NWO-CW, Top grant to B.L.F., VIDI grant no. 723.014.001 for W.S.), the European Research Council (Advanced Investigator Grant, no. 227897 to B.L.F.) and the Royal Netherlands Academy of Arts and Sciences Science (KNAW). M.M. acknowledges the financial support of the Slovak Research and Development Agency (project No. APVV-15-0105), the Research Grant Agency of the Slovak Republic (VEGA project No. 1/0737/17), and CMST COST Action CM1405 MOLIM: MOLEcules In Motion.

[1] Helmy, S., Leibfarth, F. A., *et al.*, *J. Am. Chem. Soc.* 136 (2014) 8169.

[2] M. Di Donato, M. M. Lerch, *et al.*, *J. Am. Chem. Soc.* 139 (2017) 15596–15599.

[3] M. M. Lerch, M. Medved', *et al.*, *J. Phys. Chem. A* 122 (2018) 955–964.

[4] M. M. Lerch, M. Di Donato, *et al.*, *Angewandte Chemie* 130 (2018) 8195.

Theoretical prediction of electronic structure and drift mobilities of organic semiconductors

Martin Michalík¹

¹*Institute of Physical Chemistry and Chemical Physics, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovakia*

Organic π -conjugated molecules are nowadays frequently used as semiconductors due to its cheaper and less complex fabrication. However, they come with a few downsides – poor longevity and charge transfer mobility. Therefore, the current research is oriented towards the development of more stable organic molecules with molecular structure tuned for desired physical properties [1]. Besides tedious organic syntheses and experimental work seeking better performing derivatives, theoretical and computational chemistry might help as well.

Quantum chemistry can prove highly valuable not only for the interpretation of the spectroelectrochemical data but also for designing novel materials with tailored properties prior to any chemical synthesis. For example, the electric drift mobility μ can be estimated from the combination of Marcus formula and Einstein–Smoluchowski relation in the hopping mechanism approximation. In this context, theoretical calculations based on Density Functional Theory (DFT) methods on isolated molecules or model subsystems are frequently used. Specifically, the calculations give a far richer understanding of the structure-property relationships with respect to the molecular size, substituent effects and oxidation-reduction processes.

The main goal of this contribution is to present the basic chemical models and approaches used for the prediction and interpretation of spectroelectrochemical experiments and electric mobility measurements. Next, the problem of aromaticity characterization will be shortly discussed. Finally, the chemical accuracy of the theoretically evaluated data will be also estimated.

Acknowledgement

The authors would like to thank for financial contribution from the STU Grant scheme for Support of Young Researchers.

[1] Kordt, P. Charge Dynamics in Organic Semiconductors: From Chemical Structures to Devices. Walter de Gruyter GmbH & Co KG (2016) ISBN: 3110473607

Convergence issues in Rayleigh-Schrödinger Perturbation Theory – The inverse boundary value problem

Zs. É. Mihálka^{1,2}, Péter R. Surján², Ágnes Szabados²

¹*Doctoral School of Chemistry, Faculty of Science, Eötvös Loránd University, Budapest, Hungary*

²*Laboratory of Theoretical Chemistry, Faculty of Science, Eötvös Loránd University, H-1518 Budapest 112, P.O.B. 32*

In Rayleigh-Schrödinger perturbation theory, a perturbation parameter z can be used to control the strength of the perturbation. Writing the Hamiltonian as

$$\hat{H}(z) = \hat{H}^{(0)} + z\hat{W}, \quad (1)$$

the case $\hat{H}(z = 1)$ corresponds to the Hamiltonian of the original problem, while $\hat{H}^{(0)}$ is the zero-order Hamiltonian which defines the partitioning. With this formulation the energy also becomes a function of z , and we obtain the energy as an infinite power series w.r.t. this parameter: $E(z) = \sum_n E^{(n)} z^n$. Allowing z to have complex values, $E(z)$ also becomes a complex function. Although this leads to $E(z)$ not necessarily having a physical meaning, still, the tools of complex analysis can be put to use.

The above series may not converge for $z = 1$, i.e. the radius of convergence, r_0 can be less than 1. This is often the case for the Møller-Plesset (MP) partitioning applied to molecules with elongated bond lengths, or if one uses extended bases with diffuse basis functions ([1]). Even in that case, the numerical value of $E(z)$ inside the region of convergence (i.e. for z such that $|z| < r_0$) can be calculated from the MP $_n$ terms. Inside the convergence region the function $E(z)$ has no singularity, therefore both its real and imaginary parts (u and v , considered as bivariate real-valued functions) are harmonic, i.e. they satisfy

$$\begin{aligned} \Delta u &= 0 \\ \Delta v &= 0. \end{aligned} \quad (2)$$

Choosing a contour that contains the point of interest $z = 1$, an algorithm is discussed to find boundary conditions on part of this contour so that the solution to the partial differential equations (2) is as close as possible to the known values of the exact solution inside the convergence region and the domain enclosed by the boundary. The method is used as a tool of analytic continuation to complement a method proposed recently([2]) for finding resummed values of divergent perturbation series. As a result of this procedure, an eventually divergent PT series can be summed up, often providing good approximation to the full-CI energy.

This work was completed in the ELTE Excellence Program supported by the Hungarian Ministry of Human Capacities, and was partly supported by the grant NKFIH-K115744. Zs. É. M. acknowledges the Grant New National Excellence Program of the Ministry of Human Capacities.

[1] Olsen, J., Roos, B. O., Jørgensen, P., Jensen, J. A. *J. Chem. Phys.* **89**, 2185 (1988)

[2] Mihálka, Zs. É., Surján P. R. *Phys. Rev. A* **96**, 062106 (2017)

Electronic structure of electrolyte solutions

Eva Muchová, Petr Slavíček

*Department of Physical Chemistry, University of Chemistry and Technology, Prague, Technická 3.
Prague, eva.muchova@vscht.cz*

Ions are known to profoundly alter the geometry of liquid water and water alters the electronic structure of ions. Yet the answer of a reverse question – how ions change the electronic structure of water – has not been addressed so far. The electronic structure differences induced by ions were experimentally studied by photoemission spectroscopy. Theoretical interpretation of the measured ionization energies in solutions represents a challenging problem. In our simulations, we employ the density functional theory DFT and we introduced a new, efficient technique to calculate liquid-state photoemission spectra based on the ionization-as-an-excitation-into-a-distant-center (IEDC) concept combined with the Mulliken type projection. In addition, our data points to the importance of considering concentration-dependent screening length for a correct description of the electronic structure of solvated systems.

The support by Czech Science Foundation (project No. 18-23756S).

Dissecting electron correlation effects in geminal-based wave function method.

Artur Nowak¹, Katharina Boguslawski²

¹*Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland.*

²*Faculty of Chemistry, Nicolaus Copernicus University, Gagarina 7, 87-100 Torun, Poland.*

The compromise between the computational cost of quantum-many-body methods and their accuracy and reliability is a central issue in quantum many body physics and chemistry. Specifically in electronic structure theory, we require methods that allow us to efficiently describe the correlated motion of electrons. Difficulties originate from the different contributions that govern the correlated motion of electrons, commonly referred to as strong and weak correlation. One group of approaches suitable for strongly-correlated electrons uses non-interacting electron pairs, so-called geminals, to construct the electronic wave function, which is an antisymmetric product of geminals [1]. Numerical studies suggest that geminal-based approaches can accurately model systems where strong correlation is important, like molecules with stretched bonds [2] as well as complexes or clusters containing actinide atoms [3]. However, all geminal-based methods miss (some fraction of the) weak correlation energy and therefore corrections are required that compensate their deficiencies. One possibility to account for weak correlation is to use an *a posteriori* (linearized) Coupled Cluster (LCC) correction with a geminal-based reference function[4-5]. One example is the AP1roG-LCCSD (antisymmetric product of 1-reference orbital geminals) approach (or pair CC Doubles-LCCSD), which represents a linearized coupled cluster correction with single and double excitations. In this work, we will scrutinize the performance of pCCD-LCCSD in capturing weak (or dynamic) electron correlation effects. Our approach is based on concepts of Quantum Information Theory that will allow us to dissect inter-orbital correlations. Specifically, we highlight how the orbital correlation measures can be extracted from Coupled-Cluster-type wave functions.

- [1] Boguslawski, K.; Tecmer, P.; Ayers, P. W.; Bultinck, P.; De Baerdemacker, S.; Van Neck, D. *Phys. Rev. B* **2014**, 89, 201106(R).
- [2] Tecmer, P.; Boguslawski, K.; Limacher, P. A.; Johnson, P. A.; Chan, M.; Verstraelen, T.; Ayers, P. W. *J. Phys. Chem. A* **2014**, 118, 9058–9068.
- [3] Tecmer, P.; Boguslawski, K.; Ayers, P. W. *Phys. Chem. Chem. Phys.* **2015**, 17, 14427–14436.
- [4] Henderson, T. M.; Bulik, I. W.; Stein, T.; Scuseria, G. E. *J. Chem. Phys.* **2014**, 141, 244104.
- [5] Boguslawski, K.; Ayers, P. W. *J. Chem. Theory Comput.* **2015**, 11 (11), 52525261.

The state-selected reactions of electronically excited oxygen ions with methane: the role of the spontaneous emission at the long distance region

Ivana Paidarová, Jan Hrušák

J. Heyrovský Institute of Physical Chemistry of the Academy of Sciences of the Czech Republic, v. v. i., Dolejškova 3, 182 23 Prague, Czech Republic

The O^+ ions are starting point of chemistry in Titan atmosphere and it appears important to fully understand reaction of O^+ with most abundant neutrals N_2 and CH_4 . The absolute $O^+/CH_4(CD_4)$ cross sections at selected collision energies were measured in experiments on the state-selected $O^+(^4S, ^2D, ^2P)$ atomic ions with CH_4 (and CD_4) [1]. They revealed a reduction of the total cross section and a complete inversion of the branching ratio between the main products (CH_4^+ and CH_3^+) for the ground state and the excited states. (Left panel of fig.). A computational strategy that would allow chemically reasonable and computationally feasible treatment of the $CH_4(X)/O^+(^2D, ^2P)$ system developed in [2] requires careful examination of the corresponding 19 potential energy surfaces. Before entering the discussion of the rich (photo)chemistry, we found it useful to inspect first the long range behavior of the system, as our preliminary calculations [3] showed nonzero probability for the reactants to decay before entering the multiple avoided crossings region of the $[CH_4 + O^+ \rightarrow \text{products}]^+$ reaction. The probability of spontaneous emission can be characterized by Einstein coefficients [4] evaluated and discussed in this contribution.

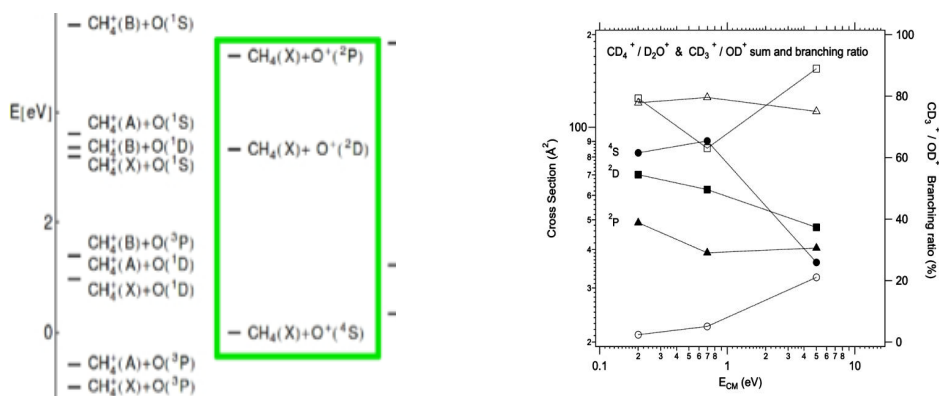


Fig. *Left panel*: The part relevant to the charge transfer of the energy diagram for the thermodynamically accessible reaction products of the O^+/CH_4 collision. *Right panel*: Sum (solid symbol and left scale) of the absolute reaction cross sections for the production of CD_4^+/D_2O^+ and CD_3^+/OD^+ as a function of collision energy for the reaction of $O^+ (^4S)$, $O^+ (^2D)$ and $O^+ (^2P)$ with CD_4 . The branching ratios CD_3^+/OD^+ are displayed with open symbols on the right scale.

The financial support of the Czech Science Foundation grant No. 17-14200S is acknowledged.

- [1] B. Cunha de Miranda, C. Romanzin, et al., *J. Phys. Chem. A*, **119**, 6082 (2015)
- [2] J. Hrušák, I. Paidarová, *Int. J. Mass. Spec.*, **354**, 372 (2013)
- [3] J. Hrušák and I. Paidarová, *Orig. Life. Evol. Biosph.*, **46**, 419 (2016)
- [4] M. Mostafanejad, A. Shayesteh, *Chem. Phys. Letters*, **551**, 13 (2012)

Dynamic polarizability of the thiophene dimer

Tadeusz Pluta, Grzegorz Skrzyński

Institute of Chemistry, University of Silesia, Szkolna 9, 40-008 Katowice, Poland

Dynamic dipole polarizability $\alpha(\omega)$ is a complex quantity. Its imaginary part is needed, *i.a.*, for evaluation of the linear absorption cross section of a given system $\sigma(\omega)$.

$$\sigma(\omega) = \frac{4\pi}{c} \omega \text{Im}[\alpha_{ave}(\omega)]$$

Where c is the speed of light, and $\text{Im}[\alpha_{ave}(\omega)]$ denotes the average of the imaginary part of the polarizability $\alpha(\omega)$. Dynamic polarizability calculated at frequencies far from the electronic resonances can be calculated using a variety of quantum chemical methods, including accurate Couple Cluster methods. In order to avoid divergent results occurring in the vicinity of the electronic resonances, and to obtain well behaving molecular response functions, the lifetime of electronically excited states must be introduced, at least as an empirical parameter. This formalism then yields also the imaginary part of the polarizability α .

We used the complex polarization propagator approach (CPP) [1] known also as damped response theory to calculate $\alpha(\omega)$ for a wide range of frequencies ω for the thiophene molecule and two conformers of the thiophene stacked dimers (Figs 1. and 2.) using the cam-QTP [2] functional.

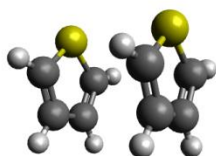


Fig. 1. Thiophene dimer A

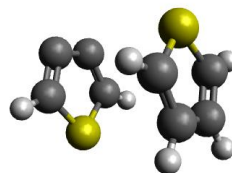


Fig. 2. Thiophene dimer B

We studied intermolecular interaction energies of the two conformers of the stacked dimers, and the change of dipole polarizability accompanying the formation of the dimers.

All calculations were performed using the Dalton package [3] using the Pol basis set of Sadlej [4]. The analysis of the interaction energy, and the interaction induced static and dynamic polarizabilities $\Delta\alpha$ of the dimers will be presented and discussed.

[1] P. Norman, D.M. Bishop, H.J.Aa. Jensen, J. Oddershede, *J.Chem.Phys.* **123** (2005) 194103

[2] Y. Yin, and R.J. Bartlett, *J.Chem.Phys.* **145** (2016) 034107

[3] Dalton, a Molecular Electronic Structure Program, Release 2016.2(2016), see <http://daltonprogram.org>

[4] A.J. Sadlej, *Coll.Czech.Chem.Commun.*, **53** (1988) 1995

Towards accurate calculations of adsorption energies

Kyrylo Prokofiev, Jiří Klimeš

¹ Charles University, Dept. of Chemical Physics and Optics, Ke Karlovu 3 121 16, Praha 2

Understanding of interactions between molecules and surfaces are important for catalysis and the process of ice formation.

Our aim is using recently developed theoretical methods such as random phase approximation (RPA) to develop efficient techniques for calculating adsorption energies.

Also we use couple-cluster method (CC) which provides possibility to obtain reference quality data. Combination of two different methods - RPA, implying periodic structure and finite cluster will allow to clarify the avenues for leveling disadvantages of two distinct approaches.

The adsorption energy is implied to be equal to the sum of energy of the periodic structure, calculated by RPA and difference between energies of finite cluster, obtained with two above methods.

$$E_{ads}^{CC} = E_{ads}^{RPAperiodic} - E_{ads}^{RPAcluster} + E_{ads}^{CCcluster}$$

For this we will use specialized software, actually VASP and Molpro packages. We present our initial results for water adsorption on MgO.

The electronic structure, UV/Vis transitions and CO₂ affinity of Ni(II) macrocyclic complexes

Ingrid Puškárová¹, Barbora Vénosová¹, Dana Dvoranová¹, Lukáš Bučinský¹, Michal Šoral¹, Peter Rapta¹, Vladimír Arion²

¹*Institute of Physical Chemistry and Chemical Physics, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republik*

²*Institute of Inorganic Chemistry, University of Vienna, Währinger Strasse 42, A-1090 Vienna, Austria*

Ni(II) macrocyclic complexes are new candidates for electrocatalytic CO₂ reduction [1]. Standard B₃LYP/6-311G* (6-311+G*) geometry optimization in various charge and spin states was performed using the Gaussian09 [2] program package. Solvent effects in dichloromethane, acetonitrile and N,N-dimethylformamide were 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). The obtained electron density at the central nickel atom was evaluated in terms of Mulliken population analysis. ¹³C, ¹H and ¹⁵N NMR chemical shifts were calculated using the Gauge - Including Atomic Orbital method. To elucidate the affinity towards CO₂, the obtained results were compared with the study of Froehlich and Kubiak on the affinity of [Ni(cyclam)]²⁺ towards CO₂ [3].

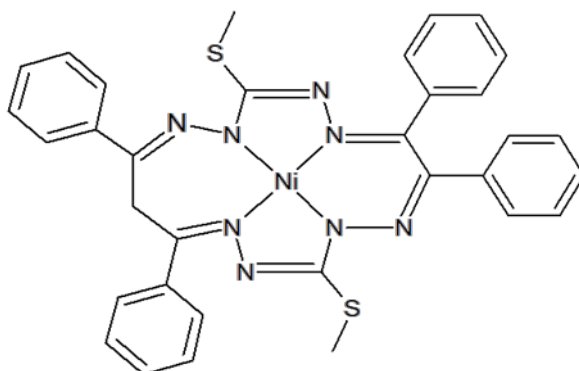


Figure 1: structure of the Ni(II) macrocyclic complex under study

Acknowledgements

We thank the Slovak Grant Agencies APVV (contracts No. APVV-15-0053 and APVV-15-0079), VEGA (contract No. 1/0598/16) and SIVVP (project ITMS 26230120002).

[1] P. Rapta, I. Puškárová, *et al.*, to be published.

[2] M. J Frisch, G. W Trucks, *et al.*, Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.

[3] J. D. Froehlich, C. P. Kubiak, *J. Am. Chem. Soc.* **137** (2015) 3565–3573.

DFT modelling of V-containing BEA zeolite

Dorota Rutkowska-Zbik¹, Agnieszka Drzewiecka-Matuszek¹

¹*Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, ul. Niezapominajek 8, 30-239 Krakow, Poland*

The aim of this work was to gain understanding in the nature of the V species introduced into the BEA zeolite by two-step post-synthesis method [1].

Our motivation arises from the activity and selectivity of these materials in oxidative dehydrogenation (ODH) of propane to propene. ODH is a reaction in which lower alkenes can be produced. Nowadays, the process is of increasing interest because lower unsaturated hydrocarbons are important materials for the chemical industry. The energy demand for ODH reaction is much lower than that for conventional catalytic cracking and even of dehydrogenation processes. The oxidative dehydrogenation pathway exhibits many advantages: the pathway is exothermic and thermodynamically not restricted, the reaction temperature is lower compared to the non-oxidative dehydrogenation processes and coke deposition is minimized in oxidizing atmospheres.

In order to study the nature of the introduced vanadium, we performed Density Functional Theory (DFT) calculations using Perdew-Burke-Ernzerhof (PBE) functional, resolution-of-identity approximation (RI), and the def2-TZVP basis set with Turbomole computer code. Cluster models of increasing size comprising of V centre introduced into nine structurally different positions in BEA framework were constructed, based on the available literature data as to the geometry and environment of the V-sites in zeolites, in particular theoretical studies regarding SOD and BEA zeolites [3]. Additionally, two possible forms of the active centres were considered, i.e. bearing vanadyl oxo group or vanadyl hydroxo group, and their relative stability was compared. Theoretical calculations enabled to characterize the nature of the introduced vanadium centres in terms of their coordination environment, charges, reactivity indices, and partial Density Of State (pDOS) plots.

[1] Dzwigaj, M.J. Peltre, *et al.*, Chem. Commun. (1998) 87

[2] F. Cavani, N. Ballarini, *et al.*, Catal. Today **127** (2007) 113

[3] A. Wojtaszek, M. Ziolek, *et al.*, Chem. Phys. Lett. **514** (2011) 70.

Acknowledgements: This work was supported by the National Science Centre, Poland within project no 2016/23/B/ST4/02854.

A DFT Study of Radical Z/E Isomerization of $\text{BBr}_2\text{C}_2\text{H}_2\text{Br}$

Hugo Semrád and Markéta Munzarová

Department of Chemistry, Faculty of Science, Kotlářská 2, CZ-602 00 Brno, Czech Republic

Haloboration reactions of alkynes represent key elements in many organic synthetic routes, as evidenced in a series of 21 papers by A. Suzuki through 1983-1992.¹ During an acetylene bromoboration reaction, (Z)-alkene is formed by the direct addition of boron tribromide to acetylene which undergoes a subsequent isomerization into (E)-dibromo(2-bromovinyl)borane cf. **Figure 1**.

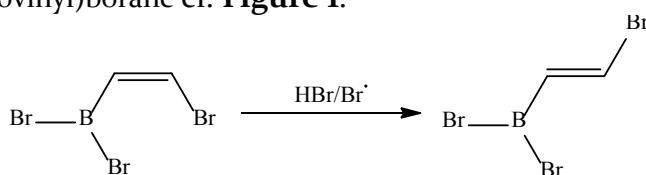


Figure 1: Z/E isomerization of (Z)-dibromo(2-bromovinyl)borane.

Wang and Uchiyama have proposed a polar isomerization mechanism catalyzed by another BBr_3 molecule with a barrier of ca. 26 kcal/mol.² This is in contrast with recent experimental findings obtained in our department.³ The present DFT study with results summarized in **Figure 2** concentrates on an alternative mechanism initiated by a reaction of Z-alkene with the radical $\text{Br}\cdot$, whose presence is expected due to the interaction with residual air humidity.

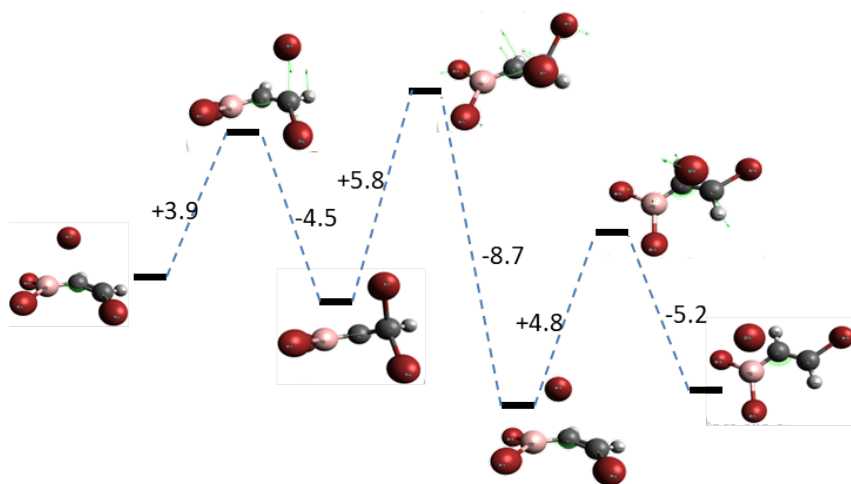


Figure 2: Gibbs free energy (kcal/mol) profile of Z/E radical isomerization of dibromo(2-bromovinyl)borane at the $\text{B}_3\text{LYP}+\text{GD}_3\text{BJ}/6\text{-}31+\text{G}^*/\text{PCM}(\text{CH}_2\text{Cl}_2)$ level.

[1] Suzuki, A. *Heterocycles* **80** (2010) 15.

[2] Wang, C., Uchiyama, M. *Eur. J. Org. Chem.* **2012** (2012) 6548.

[3] Polášek, J., *Bachelor's thesis, MU Brno* (2014).

Thermochemical Hierarchy of Homodesmotic Reactions Extended for Hydrocarbons Containing Heteroatoms

Ján Šimunek^{1,2}, Lukáš F. Pašteka³, Lucia Demovičová⁴, Jozef Noga^{1,5}

¹ Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University, Bratislava, Slovakia

² Department of Physics, Faculty of Science, University of Ostrava, 30. dubna 22, 70103 Ostrava, Czech Republic

³ Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Slovakia

⁴ Institute of Chemistry, Center of Glycomics, Slovak Academy of Sciences, Bratislava, Slovakia

⁵ Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-84536 Bratislava, Slovakia

The basic bond separation scheme was proposed by Pople et al. [1]. It was based on isodesmic reactions with controlled fragmentation that provide accurate thermochemistry data. Many more bond separation schemes emerged and all were later summarized and redefined in a simple hierarchy by Allen et al. [2]. We propose an extension to this hierarchy for hydrocarbons containing heteroatoms. For testing purposes we define a small set of saturated and unsaturated hydrocarbon molecules containing oxygen and nitrogen. For these we compute very accurate enthalpies of formation using the Focal Point Analysis (FPA) [3] with incrementally controlled precision. We then form a set of reactions relying on the extended bond separation schemes and test the validity of proposed definitions. Fragmentation methods should be extremely useful in biochemistry, where one encounters large molecules. However, almost none biomolecules are pure hydrocarbons, so extension to hydrocarbons with heteroatoms is simply a necessity.

[1] Hehre, Ditchfield, Radom, Pople, J. Am. Chem. Soc. 92 (1970) 4796

[2] Wheeler, Houk, Schleyer, Allen, J. Am. Chem. Soc. 131 (2009) 2547

[3] Schuurman, Muir, Allen, Schaefer, J. Chem. Phys. 120 (2004) 11586

Enzyme activity of *Candida antarctica* lipase B in organic solvents

Zuzana Sochorová Vokáčová¹, Damien Laage², Eva Pluhařová¹

¹J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 2155/3, 18223 Prague 8 Czech Republic

²École Normale Supérieure – PSL Research University, Département de Chimie, Sorbonne Universités – UPMC Univ Paris 06, CNRS UMR 8640 PASTEUR, 24 rue Lhomond, 75005 Paris, France

Enzymes are extraordinary catalysts satisfying the needs of living organisms. Enzyme efficiency and selectivity is also appealing for utilizing them in technological applications [1]. Perhaps surprisingly, a wide range of enzymes do not denature and moreover retain catalytic activity in organic solvents. This opens a path for carrying out new unnatural reactions. The change of reaction medium moreover significantly alters enzyme activity, chemo- and regio- and enantioselectivity. In spite of achirality of the solvent its effects on enantioselectivity are complex; different types of enzymes exhibit qualitatively different behavior [2,3] and simple rules for rationalization are still missing.

Our aim is to systematically investigate an intriguing non-monotonic dependence of enantioselectivity on composition of reaction medium. Specifically, we study a transesterification reaction catalyzed by *Candida antarctica* lipase B in acetonitrile, toluene and their mixtures. First, we examine the detailed nature of the rate-limiting step using QM/MM calculations. Next, we sample the conformational space of the most important reaction intermediates for both enantiomers by classical molecular dynamics simulations and characterize the productive binding modes. The gained molecular level insight will help to understand the puzzling dependence of enantioselectivity on solvent properties.

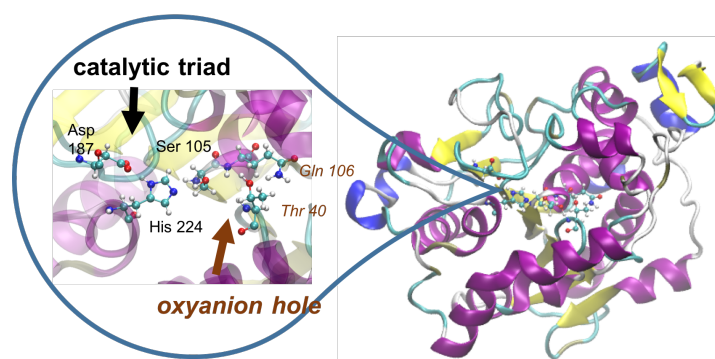


Figure 1: *Candida antarctica* lipase B with highlighted active site

[1] A. M. Klibanov, *Nature* **409** (2001), 241.

[2] S. Tawaki, A. M. Klibanov, *J. Am. Chem. Soc.* **114** (1992), 1882.

[3] Y. Kitamoto, Y. Kuruma, K. Suzuki, T Hattori, *J. Org. Chem.* **80** (2015), 521.

Theoretical studies on ground state and excited states of the NaLi molecule

Marcin Stachowiak

Faculty of Chemistry, Nicolaus Copernicus University, Jurija Gagarina 7, 87-100 Toru, Polandy

In my studies I examined electronic structure and properties of ground and excited states of the NaLi molecule.

I showed that CASSCF/CASPT2 method is suitable to that kind of calculations. It's important conclusion, because examination of excited states is not an easy task. Use of CASSCF/CASPT2 method enabled me to obtain full potential energy surfaces of ground state and multiple excited states as well as spectroscopic parameters.

All calculations were carried out with relativistic version of CASSCF/CASPT2 using IOTC method. I showed that method based on relativistic quantum mechanics smoothly converges to nonrelativistic limit, when relativistic effects are insignificant. My studies prove correctness of IOTC method and validity of application IOTC method in MOL-CAS 7.3 computational package. It shows that division to relativistic and non-relativistic methods is no longer necessary. Correctly defined relativistic method is universal.

Model study of the anticancer drug camptothecin

Marek Štekláč, Martin Breza

Department of Physical Chemistry STU, Radlinskeho 9, SK-81237 Bratislava, Slovakia

Camptothecin (CPT), (S)-4-ethyl-4-hydroxy-1H-pyrano [3',4':6,7]-indolizino-[1,2-b]-quinoline-3,14-(4H,12H)-dione, inhibits enzyme topoisomerase I and its derivatives are used in the pharmaceutical industry as anticancer drugs. It naturally occurs in two forms, which are both stable at different pH ranges. The lactone form (Fig. 1), which is biologically active, is stable at pH<5.5 and the biologically inactive carboxylic form is stable at pH>9. The structures of both camptothecin (CPT) forms and their complexes with Cu(II) were optimized at B3LYP/6-311G* level of theory using the Gaussian09 program [1]. Their electronic structures were evaluated via QTAIM (Quantum Theory of Atoms-in-Molecule) topological analysis of electron density [2] and Mulliken population analysis.

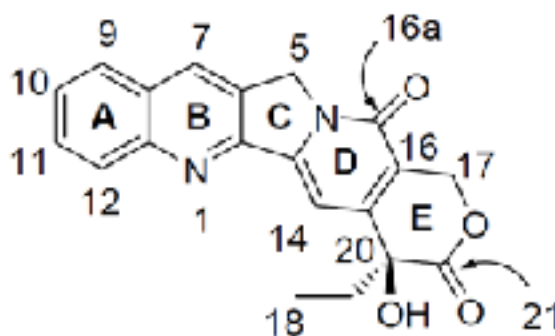


Figure 1: Atom numbering of camptothecin in a neutral lactone form

This study is aimed to compare the toxicity of possible reaction sites, i.e. the heteroatoms in camptothecin based on their ability to form bonds with copper(II) ion. This method is used to quantify the electron density transfer and spin density transfer from CPT molecule to Cu(II) ion.

This study is supported by the Slovak Grant Agency VEGA (contract no. 1/0598/16).

[1] M. J. Frisch *et al.*, Gaussian09 (Revision D.0.1), Gaussian, Inc., Wallingford CT (USA), 2013

[2] R. F. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, 1994

Quantum Chemical Studies of Acetylene Bromoboration

Jakub Stošek, Markéta L. Munzarová, and Ctibor Mazal

Department of Chemistry, Faculty of Science, Masaryk University. Kotlářská 2, 611 37 Brno, Czech Republic, email: jakub.stosek@mail.muni.cz

An interesting feature of alkyne bromoboration is that the reaction of BBr_3 with acetylene provides a *trans*-adduct whereas reactions of BBr_3 with all other alkynes tested provide *cis*-adducts. Recent investigations [1] of the reaction do not correspond with a generally accepted assumption that such outcome is a result of a consecutive isomerization of an initially formed *cis*-(2-bromovinyl)dibromoborane in presence of BBr_3 . It has been actually proven that the *cis*-adduct that was indeed found besides the *trans*-one in the crude reaction mixtures is stable even in neat BBr_3 . In addition, it was also noticed that in some conditions, the *trans*-adduct can be obtained almost exclusively in a much faster reaction that would correspond to its formation by the consecutive isomerization of the *cis*-adduct. To rationalize these observations, these possibilities were investigated throughout our study: BBr_3 addition on acetylene, both polar and radical, as well as a *cis*-to-*trans* isomerization [2], both polar and radical. The radical mechanism of BBr_3 addition on acetylene involves a very interesting solvent-stabilized radical intermediate involving bridging bromine atom. All these mechanisms could compete with the “traditional” concerted mechanism of a *syn*-addition of BBr_3 to acetylene with consecutive *cis*-to-*trans* isomerization. By means of *ab initio* calculations, we model the interaction between BBr_3 and acetylene in the presence as well as absence of an additional Br^- anion, the interaction of BBr_3 and vinyl bromide or vinyl bromide radical. We model as well the interaction of *cis*-adduct with HBr and the interaction of *cis*-adduct with bromine radical in the presence as well as absence of BBr_3 . Calculations for BBr_3 addition on acetylene and on vinyl bromide radical are performed for the cases of acetylene bromo-, chloro- and iodoboration. The guesses of all transition states are estimated using the single coordinate driving method. These guesses are then optimized and followed by the frequency analysis to verify the optimized transition states. All calculations are carried out at the B3LYP or MP2 level of theory as implemented in the Gaussian09 quantum chemical software. The mechanism is studied in vacuum or in the presence of CH_2Cl_2 using SCRF model of implicit solvent.

[1] Polášek, J. *Diploma Thesis*. Masaryk University, **2017**, Brno.

[2] Semrád, H; Stošek, J.; Munzarová, M. L. *Ab initio studies of the acetylene bromoboration mechanism. Conference abstract, 52nd Symposium on Theoretical Chemistry – Chemistry in Solution, Bochum, Germany, 2016.*

Reaction of CH₂IOH with OH radical

S. Suliman¹, C. Fortin^{2,3,4}, D. Khiri^{2,4}, F. Louis^{2,4}, V. Fevre-Nollet^{2,4}, F. Cousin^{3,4}, I. Černušák¹

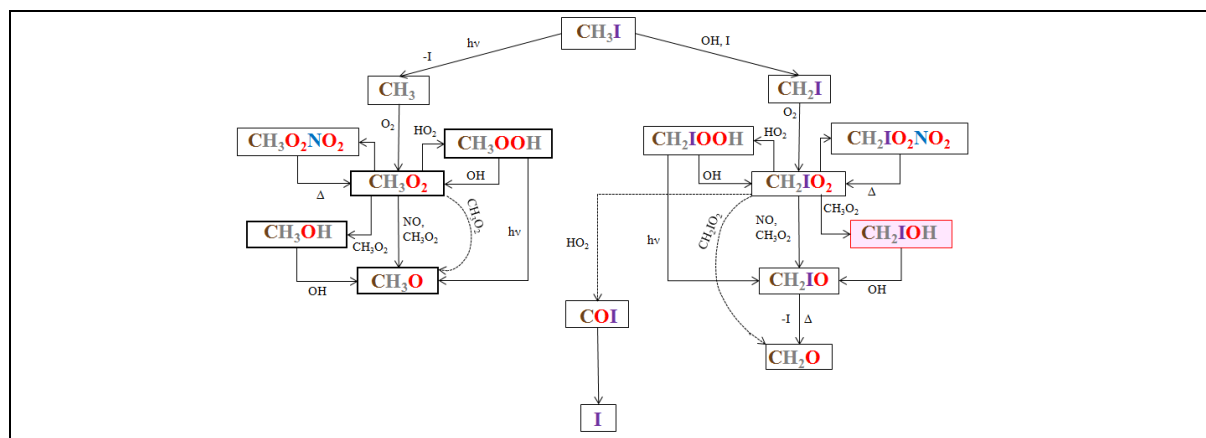
¹ Department of Physical & Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Ilkovičova 6, 84215 Bratislava, Slovakia, e-mail: siba.sul1987@gmail.com

² Univ. Lille, CNRS, UMR 8522-PC2A, PhysicoChimie des Processus de Combustion et de l'Atmosphère, F-59000 Lille, France

³ Institut de Radioprotection et de Sûreté Nucléaire, PSN-RES, Cadarache, Saint-Paul Lez Durance, F-13115, France

⁴ Laboratoire de recherche commun IRSN-CNRS-Lille, "Cinétique Chimique, Combustion, Réactivité" (C3R), Cadarache, Saint-Paul Lez Durance, F-13115, France

CH₃I is the dominant organoiodine species with the highest mixing ratio in the atmosphere. One of the atmospheric degradation product of CH₃I is the iodomethanol. The possible reactions leading to CH₂IOH are depicted in the following scheme:



The atmospheric fate of CH₂IOH has not yet been studied either experimentally or theoretically. Our main objective is to provide reliable kinetic and thermodynamic data for reaction CH₂IOH + OH based on *ab initio* calculations. The following reaction pathways are studied for OH attacking CH₂IOH: a) H or b) I atoms abstraction and c) HI elimination. MP2/cc-pVTZ optimized geometries (including the vibrational frequencies check) for all stationary points on the potential energy surface are used to calculate the single-point energies at the CCSD(T)/aug-cc-pwCVnZ (n = D, T, Q) levels of theory. The core-valence correction is computed at the CCSD(T)/aug-cc-pwCVTZ level of theory. The scalar relativist effects are added with the CISD/aug-cc-pVTZ level of theory. Spin-orbit corrections (SOC) are calculated for all the stationary points considered and for the extended part of intrinsic reaction coordinate(s) to explore: a) the effect of SOC at stationary points; b) the changes of SO corrections along the reaction coordinate(s). In addition, we report standard heats of formation ($\Delta_f H^\circ_{298K}$ in kJ/mol) for CH₂IOH (-132.71 ± 0.37), *gauche*-CHIOH (49.62 ± 0.35), *cis*-CHIOH (60.81 ± 0.35) and CH₂IO (94.22 ± 0.35) not published so far.

Acknowledgments: This study takes part in the commun laboratory C³R (CNRS/IRSN/Lille). This work was part of the CaPPA project. Computer time for part of the theoretical calculations was kindly provided by Informatiques CRI Lille and the CRIANN. This work was supported by the Slovak Research and Development Agency (APVV-15-0105).

A new method of evaluating the photoionization cross section for many-electron atoms and molecules

Mateusz S. Szczygieł¹, Michał Lesiuk¹, Robert Moszyński¹

¹*Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*

We report results of the calculations of the photoionization cross sections for two-electron molecules. We assume that the final state Ψ_f wavefunction is a Slater determinant

$$\Psi_f(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} (\phi_b(\vec{r}_1)\phi_c(\vec{r}_2) + \phi_b(\vec{r}_2)\phi_c(\vec{r}_1)), \quad (1)$$

where ϕ_b is an occupied orbital and ϕ_c describes the electron ejected to the continuum. For simplicity we omit the spin part of Ψ_f . To find Ψ_f we solve the eigenvalue problem $H\Psi_f = E\Psi_f$, with the Hamiltonian in the standard form $H = h_1 + h_2 + V_{12}$. By inserting Eq. (1) into the eigenvalue problem we get a set of coupled equations [1], which we can solve in an appropriate finite basis set, obtaining matrix equations

$$A_b[\phi_c] \phi_b = E S_b[\phi_c] \phi_b, \quad A_c[\phi_b] \phi_c = E S_c[\phi_b] \phi_c. \quad (2)$$

These can be solved iteratively.

To assert proper asymptotic behavior of ϕ_c we assume it has the form $\phi_c = \chi + \phi_{cor}$, where χ gives the asymptotic of the Coulomb wavefunction and ϕ_{cor} is a linear combination of GTO's. The orbital ϕ_{cor} is added to take into account the spatial ion structure and the phase shift. To achieve a proper behavior of χ we set it to be a Coulomb wavefunction expanded as a fixed contraction of plane waves times GTO's (PW-GTO's)

$$\phi_{p_x, p_y, p_z}(\alpha, \mathbf{k}, \mathbf{A}) = x_A^{p_x} y_A^{p_y} z_A^{p_z} e^{-\alpha r_A^2} e^{i\mathbf{k} \cdot \mathbf{r}_A},$$

where p_x , p_y and p_z are non-negative integers, α and \mathbf{k} are free parameters, and \mathbf{r}_A is the position vector in the coordinate system with the origin at the atom \mathbf{A} . All types of integrals can be evaluated in this basis set [2].

To complete calculations we set Ψ_f containing iterative solutions of Eq. (2). For the initial state Ψ_i we choose as a ground state obtained from the standard Hartree-Fock or CI calculations. To get the desired observable we insert Ψ_i and Ψ_f computed as described above into the Fermi Golden rule expression, obtaining the transition probability and hence the cross section.

[1] A. L. Stewart, W. J. Wilkinson, Proc. Phys. Soc. **75** (1960) 796.

[2] S. Reine, T. Helgaker, R. Lindh, WIREs Comput. Mol. **2** (2012) 290.

Thermochemistry of HIO₂ Species and Reactivity of Iodous Acid with Chlorine atom: A Computational Approach

S. Taamali¹, D. Khiri¹, L. Cantrel^{2,3}, F. Louis^{1,3}, and I. Černušák⁴

¹Univ. Lille, CNRS, UMR 8522-PC2A, PhysicoChimie des Processus de Combustion et de l'Atmosphère, F-59000 Lille, France

²Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PSN-RES, Cadarache, Saint-Paul Lez Durance 13115, France

³Laboratoire de Recherche Commun IRSN-CNRS-Lille "Cinétique Chimique, Combustion, Réactivité" (C3R), Cadarache, Saint-Paul Lez Durance, 13115, France

⁴Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Mlynská dolina CH1,84215 Bratislava, Slovakia

Chlorine gas is recognized to be an efficient ozone destroyer in the stratosphere. Its efficiency strongly depends on the chlorine partitioning between its active forms (Cl, ClO) and inactive reservoir species (e.g. HCl). Because of their possible implications in the destruction of the stratospheric ozone layer, chlorine oxides have drawn the attention of atmospheric chemists. For instance the reaction of HOIO, HOOI with Cl led to the formation of HCl, HOCl, ClO, HOI, IO and OIO species. Despite the importance of iodous acid (HOIO) in atmospheric and nuclear chemistry, computational studies on HOIO species are scarce and it is only very recently that experimental evidence of iodous acid in the gas phase [1].

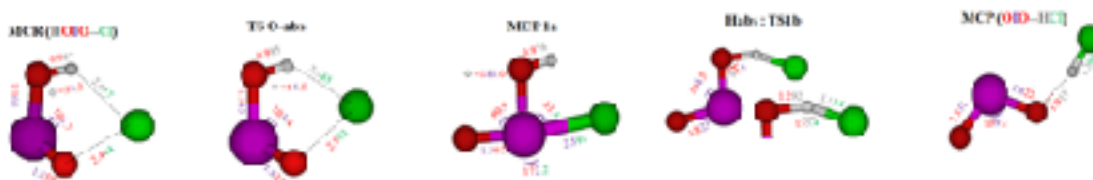


Figure 1: Schematic drawing of the structures optimized at the B3LYP/cc-pVTZ level of theory for the H-abstraction reaction pathway. Bond lengths, bond and dihedral angles are in angstroms and degrees, respectively

The main objective of this work to provide reliable kinetic and thermodynamic data for the gas phase reaction of iodous acid isomers (HOIO and HOOI) with chlorine atoms. Several reaction pathways are studied in order to assess their branching ratios: H-abstraction, I-abstraction, OH-abstraction, IO-abstraction. The reaction mechanism involves many stationary points on the potential energy surface and reveals some unusual features for the H-abstraction (Fig. 1). The theoretical calculations were performed with the augmented correlation consistent basis sets aug-cc-pVTZ for H and O atoms, the aug-cc-pV(T+d)Z for Cl atom, and aug-cc-pVTZ-PP that incorporates a small-core (28 electrons) relativistic pseudo-potential for iodine. Then, the single-point energies at the DFT structures were calculated using coupled cluster theory (CCSD(T)) and the weighted core-valence basis sets aug-cc-pwCVnZ (n = D, T, Q). Core-valence calculations were carried out at the CCSD(T)/aug-cc-pwCVTZ level of theory. The scalar relativistic corrections were computed at the CISD/aug-cc-pVTZ level of theory.

Acknowledgments: We appreciate the support from the French ANR agency under Contract No.ANR-11-LAB-0005"Chemical and Physical Properties of the Atmosphere" (CaPPA), "ANR-11-RSNR-0013-01" (MiRE). Computer time for part of the theoretical calculations was kindly provided by CRI Lille and CRIANN. We thank the Slovak Research and Development Agency (Project APVV-15-0105) for support.

[1] M. Sipila *et al.*, Nature **537** (2016), pp. 532 – 534 .

Electron-Molecule Scattering in Context of Long-Range Rydberg Molecules

Michal Tarana¹

¹*J. Heyrovský Institute of Physical Chemistry of the ASCR, v.v.i., Dolejškova 2155/3, 182 23 Prague 8, Czech Republic*

The ultra-long-range Rydberg molecules, for the first time theoretically predicted by Greene et al. [1], are very exotic systems in which one atom in its ground state (perturber) interacts with another atom in its highly excited Rydberg state with the distance of the nuclei varying between 10^2 and 10^4 a.u. [1, 2, 3]. The existence and character of the electronic bound states of these molecules is determined by the low-energy interaction between the Rydberg electron and the neutral perturber. Typically, this interaction is approximated by the s -wave zero-range Fermi pseudopotential [4] and its p -wave extension [3] or by the finite-range model potential [2]. Both models are constructed using the s -wave and p -wave phase shifts of the corresponding electron-atom scattering process at energies below the lowest threshold of the electronic excitation [6].

In the two-electron computational method presented here [5], the perturber (typically an alkali metal atom) is represented by a single valence electron in a potential that models the atomic core. As a result, the interaction of the Rydberg electron with the neutral perturber is treated as true electron-electron repulsion. Since the two-electron physics is relevant only in the region around the perturber, the R -matrix method is utilized and the two-electron wave function is smoothly matched to the one-electron wave function of the Rydberg electron on a sphere centered at the core of the perturber. Outside this sphere where the positively charged core of the Rydberg electron is located, the electronic wave function is treated in terms of the Green's function.

The potential energy curves for the long-range Rydberg states of H_2 and Rb_2 calculated using the two-electron method are presented and compared with more approximative models of the long-range Rydberg molecules.

- [1] C. H. Greene, A. S. Dickinson, H. R. Sadeghpour, *Phys. Rev. Lett.* **85** (2000) 2458.
- [2] A. A. Khuskivadze, M. I. Chibisov, I. I. Fabrikant, *Phys. Rev. A* **66** (2002) 042709.
- [3] E. L. Hamilton, C. H. Greene, H. R. Sadeghpour, *J. Phys. B* **35** (2002) L199.
- [4] E. Fermi, *Nuovo Cimento* **11** (1934) 157.
- [5] M. Tarana, R. Čurík, *Phys. Rev. A* **93** (2016) 012515.
- [6] M. Tarana, R. Čurík, arXiv:1807.07862 [physics.atom-ph]

Crosslinking in polyethylene by Au and dispersion attractions

Miroslav Urban¹, Martin Blaško¹, Andrej Antušek², Pavel Mach³

¹Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Ilkovičova 6, 84215 Bratislava, Slovakia

²Slovak University of Technology in Bratislava, ATRI, Faculty of Materials Science and Technology, Bottova 25, 91724 Trnava, Slovakia

³Department of Nuclear Physics and Biophysics, Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina, 84248 Bratislava, Slovakia

We propose [1-4], the concerted action of gold atoms and dispersion interactions in crosslinking the polyethylene. Our DFT models consist of two oligomer chains (PEn) with 7, 11, 15, 19 or 23 carbon atoms in each oligomer crosslinked with one to three Au atoms through C-Au-C bonds. Binding energies (BEs) with respect to two oligomer radical fragments and Au are as high as 327 to 385 kJ/mol depending on the length of the oligomer chain. When the dispersion contribution in PEn-Au-PEn oligomers is omitted, BE is almost independent on the number of carbon atoms, lying between 293 to 296 kJ/mol. With three crosslinking Au atoms BE rises to 966 kJ/mol. The dispersion energy contributions to BEs in PEn-Au-PEn depend nearly linearly on the number of C atoms in the PEn chain. BEs of pure saturated closed shell PEn-PEn oligomers are 25 to 90 kJ/mol. With Au acting as a cross-linking agent and dispersion interactions included, BEs are reasonably high, the well-organized parallel structure of oligomers is reconstructed, and the parallelism extends far from the C-Au-C cross-linking bond. For oligomers cross-linked via the common radical mechanism with short and strong interchain C-C bonds our attempts in obtaining parallel oligomer structures failed (Figure 1).

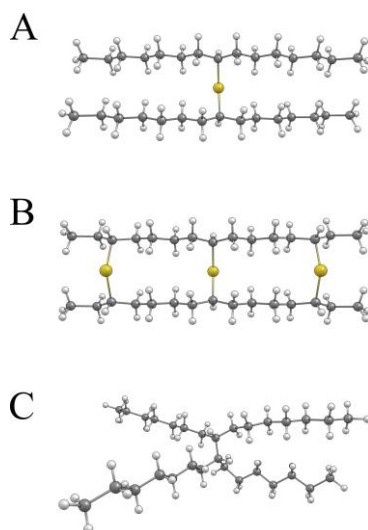


Figure 1: Crosslinked PEn with gold atoms (A, B) and via a common radical mechanism (C)

[1] M. Blaško, P. Mach, A. Antušek, M. Urban, J. Phys. Chem. A **122** (2018) 1496.

[2] A. Antušek, M. Blaško, M. Urban, et al., Phys. Chem. Chem. Phys. **19** (2017) 28897.

[3] L. F. Pašteka T. Rajský, M. Urban, J. Phys. Chem. A **117** (2013) 4472.

[4] T. Rajský, M. Urban, J. Phys. Chem. A, **120** (2016) 3938.

Variational quantum algorithms for strongly correlated quantum chemistry

Libor Veis¹, Pierre-Luc Dallaire-Demers², Alán Aspuru-Guzik^{3,4}

¹*J. Heyrovský Institute of Physical Chemistry, ASCR, 18223 Prague, Czech Republic*

²*Xanadu, 372 Richmond Street W, Toronto, Ontario M5V 1X6, Canada*

³*Department of Chemistry and Chemical Biology, Harvard University, Cambridge MA, 02138*

⁴*Senior Fellow, Canadian Institute for Advanced Research, Toronto, Ontario M5G 1Z8, Canada*

Variational quantum eigenvalue solver (VQE) [1, 2] is a hybrid quantum-classical algorithm whose coherence requirements (when compared to phase-estimation-based approaches) makes it very attractive for current and near-future quantum devices with tens of qubits. In quantum chemical applications, its *efficient* combination with unitary coupled cluster (UCC) wave function parameterization has been proposed [1, 2] and also experimentally verified [4].

It is well known that UCC performs better than conventional CC, however, it is still a single-reference theory which may fail in multireference cases [3]. In order to adapt UCC-VQE for multireference problems, we present its generalization, which is based on the quasiparticle formulation [5, 6] and effectively transforms a multireference problem into a single reference one. We propose its use in combination with matrix product state (MPS) wave functions which can be *efficiently* prepared on a quantum register.

- [1] A. Peruzzo et al., *Nat. Commun.* **5**, 4213 (2014).
- [2] J. McClean, J. Romero, R. Babbush, and A. Aspuru-Guzik, *New J. Phys.* **18**, 023023 (2016).
- [3] F. A. Evangelista, *J. Chem. Phys.* **134**, 224102 (2011).
- [4] P. J. J. OMalley et al., *Phys. Rev. X* **6**, 031007 (2016).
- [5] A. Y. Sokolov, G. Chan, *J. Chem. Phys.* **142**, 124107 (2015).
- [6] P.-L. Dallaire-Demers, J. Romero, L. Veis, S. Sim, A. Aspuru-Guzik, *arXiv:1801.01053*.

A comparison of theoretical and experimental electronic structures. A N-O bond precedence in 3-alkoxy-4-methylthiazole-2(3H)-thione derivatives

Barbrbora Vénosová¹, Lukáš Bučinský¹, Jozef Kožíšek¹, Júlia Kožíšková¹, Jens Hartung²

¹ Institute of Physical Chemistry and Chemical Physics, Slovak University of Technology, Bratislava, Slovakia, 812 37

² Technische Universität Kaiserslautern, Fachbereich Chemie, Organische Chemie, Kaiserslautern, Germany, 676 63

Keywords: theoretical calculation, Hirshfeld atom refinement, Domain averaged Fermi holes

The investigated compound is an O-ester structurally deriving from heterocyclic thiohydroxamic acid 3-hydroxy-4-methylthiazole-2(3H)-thione (see Figure 1). The theoretical calculations have been performed using the B₃LYP functional utilizing different software packages and basis sets. Hirshfeld Atom Refinement (HAR) [1] of the structure was used with three different setups for the refinement of position and thermal smearing parameters. The electronic structure has been analysed by means of Quantum Theory of Atoms in Molecules (QTAIM) [2], localized orbitals and the analysis of Domain averaged Fermi holes (DAFH) [3]. The theoretical assessment of the electronic structure yields a negative value of the Laplacian of the N-O bond, in contradiction to the experimentally determined (positive) value. Nevertheless, the Hessian eigenvalues themselves agree well with each other. Further common features as well as the differences between the theoretical and multipolar refinement based charge densities shall be critically highlighted.

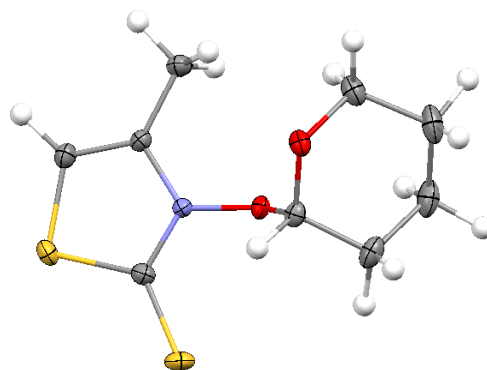


Figure 1: Structure of the molecule studied

Acknowledgement

Financial support was obtained from APVV (Project No. APPV-15-0079) and VEGA (Project No. 1/0416/17). We thank the HPC Center at the Slovak University of Technology in Bratislava, which is a part of the Slovak Infrastructure of High Performance Computing (SIVVP Project 26230120002, funded by the European Region Development Funds), for computing facilities.

[1] Capelli, S. C. et al., *IUCrJ* **1**, 361–379 (2014).

[2] R. F. W. Bader, *Atoms in Molecules*, Oxford University Press, Oxford (1990).

[3] Ponec, R. & Duben, A. J. *J. Comput. Chem.* **20**, 760–771 (1999).

Quantum chemical study of intersystem crossing between singlets and triplets of 6,7-dibromo-2-ethyl-1,3-dimethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene

Mirza Wasif Baig¹, Marek Pederzoli¹, Lukasz Cwiklik¹, Jiri Pittner¹

¹J. Heyrovsky Institute of Physical Chemistry, Dolejskova 2155/3 182 23 Prague 8, Czech Republic

6,7-dibromo-2-ethyl-1,3-dimethyl-4,4-Difluoro-4-bora-3a, 4a-diaza-s-indacene is a BODIPY derivative that has been reported as an important candidate for its use as a photosensitizer in photodynamic therapy of cancer cells due to its high singlet oxygen quantum yield [1]. Unsubstituted BODIPY has no phosphorescence activity 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 perform surface hopping molecular dynamics simulations on potential energy surfaces resulting from the eigenstates of the total electronic Hamiltonian including the spin-orbit coupling. A subset of 30 initial conditions starting in S_2 state was used for gas phase simulations with spin-orbit coupling utilizing implementation of the three-step propagator in the Newton-X software suit as well as two novel “one-step” approaches [2]

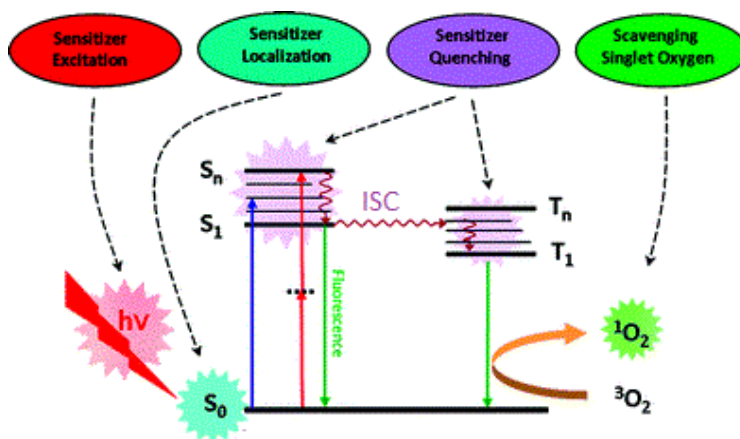


Figure 1: Mechanism of intersystem crossing between singlets and triplets of photosensitizer effective in triggering production of singlet oxygen

[1] A.J.S. Arroyo and E. Palao, *et al.*, PCCP 19 (2017) 69

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

An MS-CASPT2 Calculation of the Excited Electronic States of an Axial BODIPY Dimer

Jin Wen¹, Bowen Han,² Zdeněk Havlas,¹ and Josef Michl^{1,2}

¹*Institute of Organic Chemistry and Biochemistry AS CR, Flemingovo nm. 2, 16610 Prague 6, Czech Republic*

²*Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215, U.S.A.*

The previously reported[1] calculated state energies of monomeric BODIPY and its axial dimer suggest that they are promising candidates for singlet fission, and that the dimer has an unusual low-lying doubly excited state. We find that these results were affected by the use of an imbalanced active space in multireference calculations and are not correct. Multi-state complete-active-space second-order perturbation theory (MS-CASPT2/cc-pVDZ) calculations using an [8,8] (8 electrons in 8 orbitals) active space for the monomer and a [16,16] active space for the dimer reproduce quite well the observed excitation energies of the S₁ states of both, and yield T₁ excitation energies well in excess of half of the S₁ excitation energies. We conclude that neither BODIPY monomer nor its axial dimer would permit exothermic singlet fission and are not worthy of investigation as potentially useful candidates, and that the unusual doubly excited states of the dimer were artifacts.

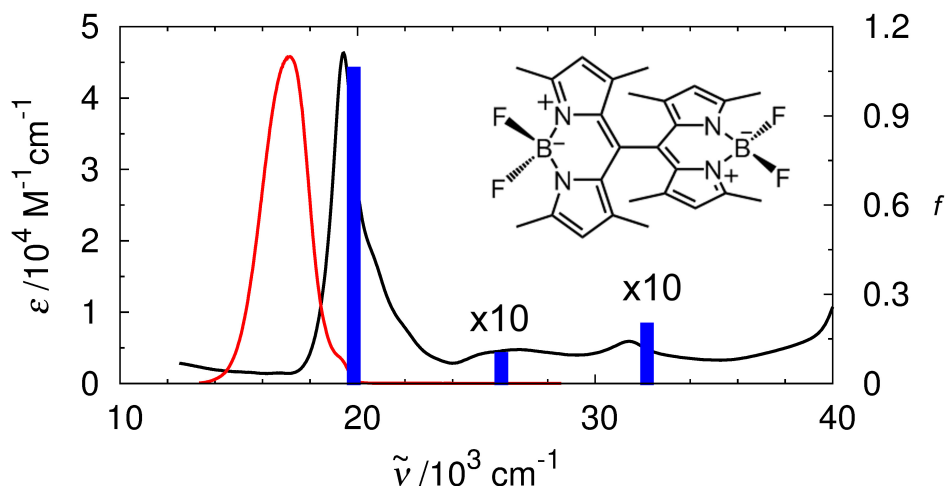


Figure 1: Absorption (black) and fluorescence (red) spectra of **2** in CH₂Cl₂, and MS-(16,16)-CASPT2 excitation energies and oscillator strengths (blue bars).

[1] Duman, S.; Cakmak, Y.; Kolemen, S.; Akkaya, E. U.; Dede, Y. Heavy Atom Free Singlet Oxygen Generation: Doubly Substituted Configurations Dominate S₁ States of Bis-BODIPYs. *J. Org. Chem.* vol **77** (2012) 4516.

Interactions between dodecamers of hyaluronan and hyaluronan-like molecules with TSG-6 protein

Roman Witasek¹, Eva Kutalkova¹, Josef Hrnčirik¹, and Marek Ingr^{1,2}

¹*Tomas Bata University in Zlin, Faculty of Technology, Department of Physics and Materials Engineering, Nam. T.G. Masaryka 5555, 76001 Zlin, Czech Republic*

²*Charles University, Faculty of Science, Department of Biochemistry, Hlavova 8/2030, 12843 Praha 2, Czech Republic*

Hyaluronan (HA) is a linear non-sulfated polysaccharide of natural origin, which contains disaccharide repeats of D-glucuronic acid and N-acetyl-D-glucosamine. HA is found pervasively in the extracellular matrix (ECM), where it can noncovalently bind to a variety of proteins and influence their functions. The biological functions of HA depend on the molecular weight of its chain [1].

One of the modified HA, hyaluronan neutral analog (GlcHA), where monosaccharide units of D-glucuronic acid were substituted by D-glucose, can be promising biocompatible material for the design of drugs [2].

Tumor necrosis factor stimulated gene-6 (TSG-6) is a hyaluronan-binding protein (hyaladherin) that is essential for stabilizing and remodeling the ECM. This protein consists mainly contiguous N-terminal Link and C-terminal CUB domains, it is a potential biomarker of diseases associated with carcinogenesis, which is a possible target for drug delivery [3].

In this study, we simulated the binding of hyaluronan dodecamer (HA₁₂) and its neutral analog (GlcHA₁₂) to the Link domain of TSG-6 protein by using a molecular dynamics method.

All simulations were performed in GROMACS software package (version 5.1.2) using the CHARMM36 all-atom force field at two different concentrations of NaCl solutions at 300 K under NVT conditions.

Both oligomers HA₁₂ and GlcHA₁₂ can bind the Link domain within two topologically different binding modes. The formation and stability of the complexes is affected by the concentration of aqueous NaCl solution. The ability of binding both HA₁₂ and GlcHA₁₂ seems to be facilitated by the high occurrence of the amino acids capable of hydrogen-bond formation, especially lysines and arginines, and the flexibility of the Link-domain structure allowing the protein to adapt to the ligand shape. It suggested the potentiality of designing synthetic ligands of protein receptors with regard to their possible pharmaceutical applications.

Acknowledgments:

This work was supported by The Ministry of Education, Youth and Sports from the Large Infrastructures for Research, Experimental Development and Innovations project „IT4Innovations National Supercomputing Center – LM2015070“.

This contribution was supported by Internal Funding Agency of Tomas Bata University in Zlin, projects IGA/FT/2016/011, IGA/FT/2017/009 and IGA/FT/2018/010.

[1] Dicker, K. T., et al., *Acta biomaterialia* **10** (2014) 1558-1570.

[2] Ponedel'kina, I. Y., et al., *Russian Journal of Bioorganic Chemistry* **31** (2005) 82-86.

[3] Blundell, C. D., et al., *Journal of Biological Chemistry* **280** (2005) 18189-18201.