

CONNECTIONS 2000 KFT.

BOOK OF ABSTRACTS

CESTC 2014, NAGYBÖRZSÖNY

2014.09.21-25.

ISBN 978-963-313-132-9

CONNECTIONS2000 KFT.

PRESENTATION ABSTRACTS

CESTC 2014, Nagybörzsöny

2014.09.21-25

Unraveling the complex nature of the hydrated electron

Pavel Jungwirth

*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic,
Flemingovo nám. 2, 16610 Prague 6, Czech Republic,
e-mail: pavel.jungwirth@uochb.cas.cz*

Interaction of water with ionizing radiation is, in addition to direct DNA damage, causing radiation damage in living organisms and it is also important for nuclear waste treatment. Upon photoionization in water an electron and a cationic hole are formed, and we have followed the fate of both. In the talk, I focus on the structure and dynamics of the hydrated electron which, despite its key role in radiative processes in water, has remained elusive. The traditional cavity model has been questioned recently, but the newly suggested picture of an electron delocalized over a region of enhanced water density is controversial. Here, we present results from ab initio molecular dynamics simulations, where not only the excess electron but also the valence electrons of the surrounding water molecules are described quantum mechanically. Unlike in previous one-electron pseudopotential calculations, many-electron interactions are explicitly accounted for. The present approach allows for partitioning of the electron solvated in liquid water into contributions from an inner cavity, neighboring water molecules, and a diffuse tail. We demonstrate that all three of these contributions are sizable and, consequently, important, which underlines the complex nature of the hydrated electron and warns against oversimplified interpretations based on pseudopotential models. We also investigate the electron solvated at the water surface. The present results clearly demonstrate that the surface electron is mostly buried in the interfacial water layer, with only about ten percent of its density protruding into the vapor phase. Consequently, it has structure which is very similar to that of an electron solvated in the aqueous bulk.

A theoretical study of the microhydration processes of nitrogen iodine oxides: implications for atmospheric chemistry and nuclear safety

Florent Louis^{1,4*}, Camille Fortin^{1,4}, Ján Škoviera^{1,2}, Laurent Cantrel^{3,4}, Ivan Černušák²

¹*PhysicoChimie des Processus de Combustion et de l'Atmosphère (PC2A), UMR CNRS 8522, Université Lille1 Sciences et Technologies, 59655 Villeneuve d'Ascq Cedex, France,*

florent.louis@univ-lille1.fr

²*Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina CHI, Bratislava, Slovakia*

³*Institut de Radioprotection et de Sûreté Nucléaire, PSN-RES, SAG, LETR, Centre de Cadarache, BP3, 13115 St Paul Lez Durance Cedex, France*

⁴*Laboratoire Commun IRSN-CNRS-Lille1 "Cinétique Chimique, Combustion, Réactivité" (C3R), Centre de Cadarache, BP3, 13115 St Paul Lez Durance Cedex, France*

Reactions involving iodine compounds have the potential to affect a number of aspects of the chemistry and composition of the atmosphere. In parallel to the relatively well characterised processes involving chlorine and bromine species, reactions of inorganic iodine have the potential to lead to catalytic ozone destruction, and to amplify the ozone destruction from other halogens, notably bromine, through coupling between the halogen families [1-2]. They may also perturb atmospheric oxidizing capacity, by affecting the abundance and partitioning of HO_x and NO_x [3]. A further potential impact of iodine chemistry is the formation of new particles, documented in coastal regions [4]. It is supposed that these processes are responsible for the widespread distribution of iodine species over the oceans having the potential to affect marine boundary layer cloud condensation nuclei populations and hence climate [5].

The formation of nitrogen iodine oxides species INO_y (i.e., INO, INO₂, INO₃) is especially relevant under high NO_x conditions. These species decompose, selfreact and photolyse, but they also undergo uptake onto aerosol providing an important route for the removal of iodine from the gas-phase.

Behaviour of iodine and iodine compounds in the reactor coolant system (RCS) as well as in the containment of a pressurised water reactor (PWR) during a severe accident has been a subject of several experimental programmes and modelling studies [6] because ¹³¹I is one of the most important radiotoxic fission products that may be released through the RCS and next in the nuclear containment building and further possibly into the environment by the leakages. A detailed understanding of the evolution of the chemical speciation of all iodine compounds formed is necessary to assess the radiological consequences during the accident progress for a wide range of accidental scenarios.

Our focus is mainly directed to the use of computationally methods that could be used so that a reliable quantitative picture of thermodynamic properties ($\Delta_f H^\circ_{298K}$, S°_{298K} , $C_p = f(T)$) for INO_y can be obtained. Their microhydration processes have been studied to elucidate the role of hydrating water molecule(s). Implications for atmospheric chemistry and nuclear safety will be discussed.

[1] D. Davis, J. Crawford, *et al.*, *J. Geophys. Res.*, **1996**, 101, 2135-2147.

[2] A. Saiz-Lopez, J.A. Shillito, *et al.*, *Atm. Chem. Phys.*, **2006**, 6, 1513-1528.

[3] W.J. Bloss, M. Camredon, *et al.*, *Atm. Chem. Phys.*, **2010**, 10, 1018710209.

[4] G. McFiggans, H. Coe, *et al.*, *Atm. Chem. Phys.*, **2004**, 4, 701-713.

[5] C.D. O'Dowd, K. Hämeri, *et al.*, *J. Geophys. Res.*, **2002**, 107, 8107.

[6] See references therein M. Sudolská, L. Cantrel, *et al.*, *J. Nucl. Mat.*, **2014**, 446, 73-80.

Phase transitions in free water nanoparticles. Theoretical modeling of $[\text{H}_2\text{O}]_{48}$ and $[\text{H}_2\text{O}]_{118}$.

Aleš Vitek^{1*}, René Kalus²

¹*IT4Innovatins, VSB-Technical University Ostrava 17. listopadu 15/2172, 708 33 Ostrava - Poruba, Czech Republic, ales.vitek@vsb.cz*

²*IT4Innovatins & Department of Applied Mathematics, VSB-Technical University Ostrava 17. listopadu 15/2172, 708 33 Ostrava - Poruba, Czech Republic*

Constant-pressure heat capacities and caloric curves of medium-sized water clusters $[\text{H}_2\text{O}]_{48}$ and $[\text{H}_2\text{O}]_{118}$ have been calculated via classical parallel-tempering Monte Carlo approach together with subsequent multiple-histogram method using flexible TIP4P potential for water-water interaction. For a low temperatures, quantum effects have been included in harmonic approximation. Theoretical results have been compared with recent experimental data^[1] (see Fig. 1).

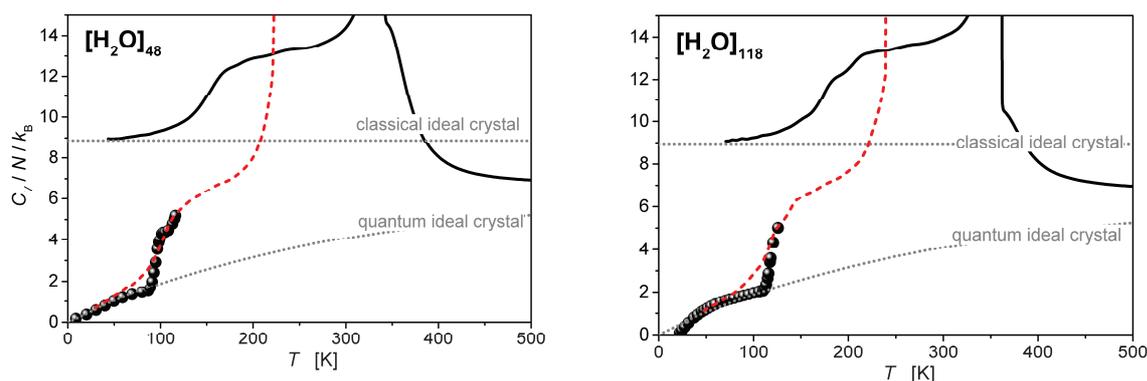


Figure 1: Heat capacities of water cluster $[\text{H}_2\text{O}]_{48}$ and $[\text{H}_2\text{O}]_{118}$: big black dots shows experimental curves, small gray dots figures heat capacities of quantum and classical ideal crystal, black curves shows classical heat capacity curves calculated via parallel-tempering Monte Carlo and red dashed lines figures quantum ideal crystal heat capacity with added classical anharmonicity effects.

[1] C. Hock, M. Schmidt, et al., Phys. Rev. Lett., **2009**, 103, Art. No. 073401 1-4.

Excess electrons in aqueous solutions: quantum molecular dynamics simulations of ultrafast events in condensed phases

László Turi^{1*}

¹*Eötvös Loránd University, Department of Physical Chemistry, Budapest 112, P. O. Box 32, H-1518, Hungary, turi@chem.elte.hu*

Excess electrons in aqueous environment are known as hydrated electrons. Excess electron hydration in bulk water and finite size water clusters is a process of fundamental importance with wide-ranging implications in various physical, chemical and biological areas. The scientific relevance of the hydrated electron stems equally importantly from its high chemical reactivity, and from its significance as a simple, nevertheless instructive model system. In particular, the hydrated electron can be thought of as the simplest possible solute having only a single electronic degree of freedom. Due to this fact elementary quantum mechanical phenomena, such as quantum decoherence, quantum and classical relaxation events, non-adiabatic electronic transitions and solvent relaxation, and their intertwined couplings can be studied without the interference of more complex condensed phase processes. For these reasons the hydrated electron and its finite size analogues, water cluster anions, are popular targets for the most sophisticated ultrafast spectroscopic [1] and theoretical investigations [2]. In the present work we will overview the results of a series of molecular dynamics simulations of excess electrons in various size water clusters and in bulk water. The results will illustrate the use and the applicability of a simple, mixed quantum-classical molecular dynamics simulation technique for the present, non-trivial physical system. Furthermore, during our discussion we also demonstrate and develop an understanding of important quantum mechanical and quantum statistical mechanical concepts, such as quantum decoherence and quantum correlation functions, playing a key role in condensed phase quantum dynamics. At last, the physical properties of excess electrons in various size water clusters will be examined, and compared to available experimental data. The discussion will focus on the most critical issues and still unresolved questions about the basic aspects of the physics of these systems. In particular, the localization modes of the excess electron in water clusters (i.e. surface states vs. interior states) will be characterized [3]. The performed quantum dynamics simulations and the subsequent analysis provide general insight in the microscopic details of the combined solvent and electronic relaxation phenomena [4].

The work was supported by a grant to L. T. from the National Research Fund of Hungary (OTKA) under Contract K104237.

[1] M. H. Elkins, H. L. Williams, *et al.*, *Science* **2013**, 342, 1496-1499.

[2] L. Turi, P. J. Rossky, *Chem. Rev.* **2012**, 112, 5641-5674.

[3] L. Turi, W.-S. Sheu, *et al.*, *Science* **2005**, 309, 914-917.

[4] L. Turi, *J. Chem. Phys.*, **2014**, 140, 204317.

Combining First Principles MD and NMR to Understand the Hofmeister Series

Christoph Allolio^{1,2*}, Gül Bekçioğlu², Nora Illanes², Michael Ryan-Hansen³, Daniel Sebastiani²

¹*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, v.v.i., Flemingovo nám. 2, 166 10 Prague 6, Czech Republic, christoph.allolio@marge.uochb.cas.cz*

²*Department of Chemistry, Martin-Luther-Universität Halle-Wittenberg, von Danckelmannplatz 4, 06120 Halle(Saale), Germany*

³*Department of Chemistry, Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark*

The Hofmeister series, first described in 1888, ranks the influence of ions on many phenomena such as protein precipitation or folding. The underlying ion-specific effects are of fundamental importance for chemistry, liquid state physics and biology. Until recently they were typically discussed in terms of enhancing or breaking bulk water structure.^[1] Recently, a new picture has emerged which incorporates the crucial role of ion protein interactions.^[2] Nevertheless, direct effects of ions on water become important at intermediate concentrations. Long range cooperative effects on water dynamics have also been observed experimentally.^[3] Using *ab initio* molecular dynamics we computed ¹H NMR shifts of aqueous salt solutions at high to very high concentrations and find them to be in good agreement with experimental measurements.^[4,5] In addition, we calculated structural and dynamic observables based on the hydrogen bond network. Analysis of the hydrogen bond network reveals cooperative effects on hydrogen bond stability beyond the first solvation shell as well as cluster formation at high concentrations.^[4]

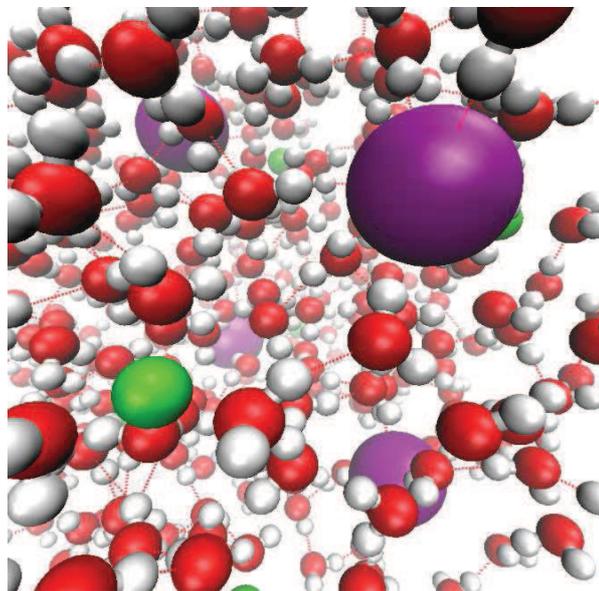


Figure 1: Snapshot from an AIMD simulation of LiI at 1 M concentration.

[1] Y Marcus, *Chem. Rev.* **2009**, 109, 1346.

[2] P. S. Cremer, P. Jungwirth, *Nature* **2014**, 6, 261.

[3] K.J. Tielrooij, N. Garcia-Araez, M. Bonn and H.J. Bakker, *Science* **2010**, 328, 1006

[4] C. Allolio, N. S. Illanes *et al.*, *J. Phys. Chem. B* **2013**, 177, 9939.

[5] G. Bekçioğlu, C. Allolio *et al.*, *in preparation*

Analysis of Hydrogen bond networks in water cluster (2-30) and liquid

Imre Bakó

a) Institute of Organic Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar tudósok körútja 2, H-1117 Budapest, Hungary

Abstract

The properties of hydrogen bonded networks in water cluster and liquid water have been studied experimentally and theoretically. We have already calculated several electronic and structural properties of liquid water using ab initio molecular dynamics simulation. In this lecture we showed how these properties (dipole, charge, bond order) change as a function of cluster size. These studies revealed the importance of the cooperative effects in these clusters. We explore also the size and the properties of the ring in the liquid water and water cluster. The size of two and three bodies interaction in the water cluster (2-30) has been also discussed using two different BSSE scheme.

Theoretical and Experimental Study on Europium and Neodymium Trivalent Ions in the Crystal Field of Water

Anne-Marie Kelterer*, Anna M. Wernbacher, Christof Holzer, Jan M. Senekowitsch, Karl Gatterer

Physical and Theoretical Chemistry, Graz University of Technology, Graz, Austria, kelterer@tugraz.at

The two trivalent lanthanide ions exhibit hypersensitive transitions in their optical spectra when placed in a crystal field of solvent molecules or in a crystalline surrounding. The hypersensitivity may depend on the symmetry of the field, the polarizability of the cluster as well as other effects, which will be discussed briefly.

The energy level structure of Eu^{3+} and Nd^{3+} placed in the crystal field of water is considered. The basic theory of f-f transitions will be presented including the role of symmetry and selection rules^[1]. The derivation of irreducible representations and degeneracies of the free ion and of the crystal field levels will be shown in detail in this presentation.

Experimental absorption and emission spectra have been measured in water, water-acetone and water-methanol mixtures^[2]. The intensities of the f-f transitions were assigned by means of the Judd-Ofelt theory.

Theoretical SOC-CASSCF as well as relativistic KRCI and COSCI calculations were performed for the free Nd^{3+} and Eu^{3+} ions and for Eu^{3+} and Nd^{3+} in water complexes of different coordination numbers and with different symmetries.

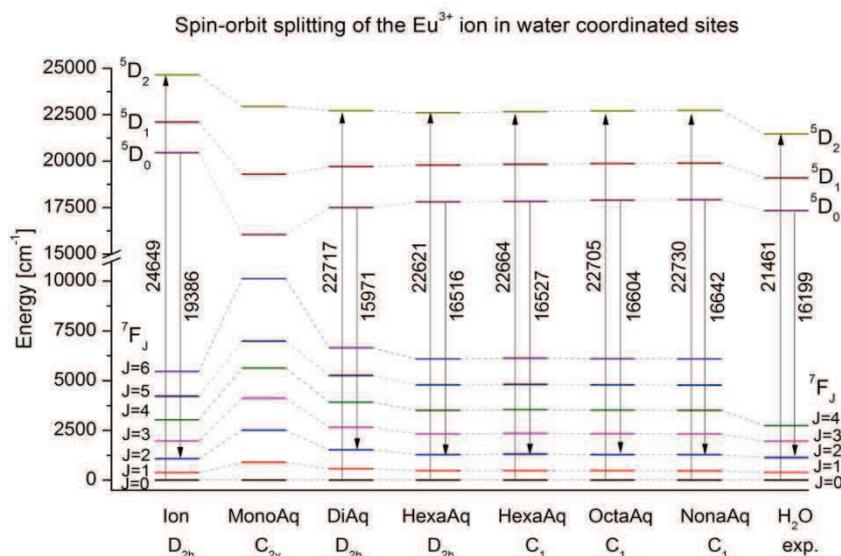


Figure 1: COSCI energy levels of the Eu^{3+} ion in the crystal field of water with with different coordination numbers and symmetries.

The resulting energy levels of Eu^{3+} (Fig.1) and Nd^{3+} will be discussed in terms of computational method, correlation space, coordination number as well as symmetry. The results are compared to the available experimental data.

[1] P. Tanner, *Chem. Soc. Rev.* **2013**, 42, 5090.

[2] A.M. Wernbacher, Master's Thesis, 2014, TU Graz.

Structural and optical properties of lithium and copper cation complexes with dimethyl sulfoxide

Michal Ilčin^{1a*}, Vladimír Sládek^{2a}, Martin Breza^{3b}, Vladimír Lukeš^{4a}

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

^aDepartment of Chemical Physics

^bDepartment of Physical Chemistry

DFT and ab initio MP2 studies of optimal geometries and electron spectra of $[\text{Li}(\text{DMSO})_n]^+$ ^[1,2] and $[\text{Cu}(\text{DMSO})_n]^{2+}$ complexes ($n = 1-6$) were studied. For both systems the coordination to the metal atom via oxygen atom of DMSO is more stable than through sulfur atom (this is also due to steric reasons). For $[\text{Li}(\text{DMSO})_n]^+$ complex the Li–O bond elongation and decreasing electron density transfer from oxygen to lithium were observed with coordination number increase^[2]. This is connected with the exponential decrease of the complex formation energy per DMSO ligand with increasing coordination number. Also the DMSO structure deformation is lowering with increasing coordination number^[2]. Most stable coordination number for $[\text{Li}(\text{DMSO})_n]^+$ and $[\text{Cu}(\text{DMSO})_n]^{2+}$ complexes are discussed and these two systems are compared from several points of view. TD-DFT calculations of vertical electronic transitions for IEFPCM polarizable continuum model in DMSO solutions were performed. UV spectra of $[\text{Li}(\text{DMSO})_n]^+$ and $[\text{Cu}(\text{DMSO})_n]^{2+}$ complexes are discussed. In calculated spectra of DMSO and $[\text{Li}(\text{DMSO})_n]^+$ blue shift is obvious (for comparison of DMSO and $[\text{Li}(\text{DMSO})_n]^+$ UV spectra see Figure 1). For the observed blue shift of the original DMSO excitation energy the Li–DMSO bonding is responsible^[2].

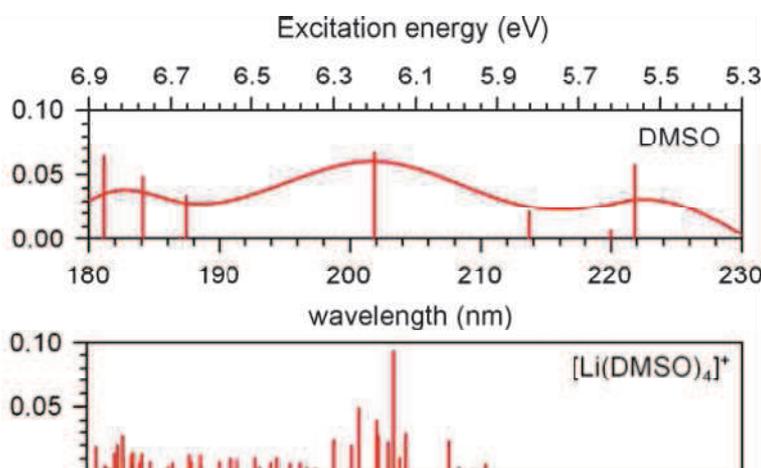


Figure 2: Comparison of DMSO UV spectrum with $[\text{Li}(\text{DMSO})_4]^+$ spectrum

In order to obtain band UV spectrum instead of line spectrum the molecular dynamics were applied. Molecular dynamics can be also used for ligand bonding dynamics study, but for the obtaining of credible results QM molecular dynamics should be used while for UV spectrum lines broadening molecular mechanics description can be satisfactory.

Acknowledgment

This work was supported by Slovak Grant Agency VEGA (Project No. 1/0735/13).

[1] Yu.L. Frolov, I.V. Guchik, *et al.*, *J. Struct. Chem.* **2003**, 44, 927-931.

[2] V. Sládek, V. Lukeš, *et al.*, *Comp. Theor. Chem.* **2011**, 963, 503-509.

Modeling of Water Dissociation on Zero-Valent Iron Nanoparticles

František Karlický, Petr Lazar, Michal Otyepka

Regional Centre of Advanced Technologies and Materials, Department of Physical Chemistry,
Faculty of Science, Palacký University, 17. listopadu 15, 771 46 Olomouc, Czech Republic,
frantisek.karlicky@upol.cz

The reactivity of nano zero-valent iron (nZVI) nanoparticles is of increasing interest owing to their important practical applications, ranging from the steel industry to water remediation technologies. Despite recent progress, the theoretical description of nZVI and its reactivity is still challenging.^[1]

We decipher mechanism and kinetics of the reaction of water molecule with an iron atom^[2] and Fe(100) or Fe(111) surfaces^[3] and evaluate various computational methods for both models.^[4] Rate-limiting activation barriers of 31.6 and 18.0 kcal/mol for water reacting with the iron atom and infinite iron surface, respectively, are, however, quite different. Finally, iron clusters may be considered a most logical and quite realistic model of nZVI. We therefore discuss reactivity of iron clusters depending on the cluster size and the local geometrical structure and we compare theoretical results with our recent experimental reaction kinetics of 60 nm sized nZVI nanoparticles as monitored by ⁵⁷Fe Mössbauer spectroscopy.^[5]

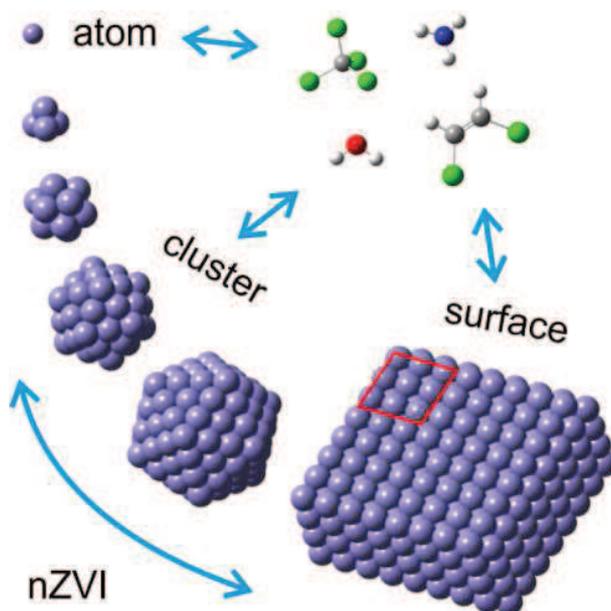


Figure 1: Reactions of small molecules with nZVI nanoparticles modeled by atoms, clusters or surfaces.

- [1] F. Karlický, M. Otyepka, *Int. J. Quantum Chem.* **2014**, 114, 987-992
- [2] F. Karlický, M. Otyepka, *J. Chem. Theory Comput.* **2011**, 7, 2876-2885
- [3] P. Lazar, M. Otyepka, *J. Phys. Chem. C* **2014**, 116, 25470-25477
- [4] F. Karlický, P. Lazar, *et al.*, *J. Chem. Theory Comput.* **2013**, 9, 3670-3676
- [5] J. Filip, F. Karlický, *et al.*, *J. Phys. Chem. C* **2014**, 118, 13817-13825

Sodium phosphoethynolate as a building block. Theory and experiment

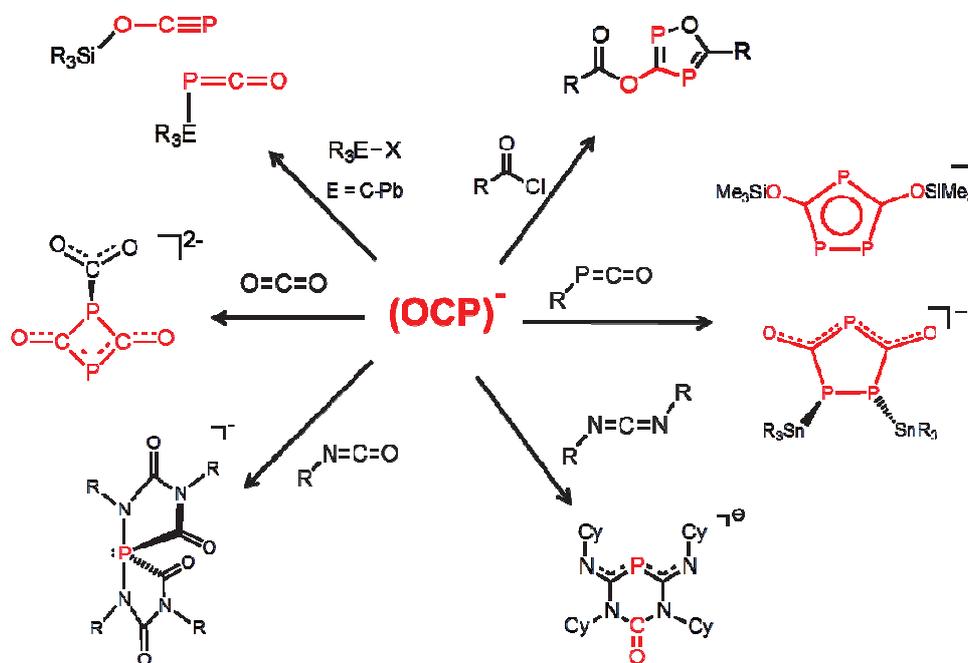
Zoltán Benkő^{1,2,*}, Dominikus Heift², Hansjörg Grützmacher^{2,*}

¹ *Budapest University of Technology and Economics, Szent Gellért tér 4, H-1111 Budapest, Hungary, zbenko@mail.bme.hu*

² *Institution, ETH-Zurich, Vladimir-Prelog-Weg 1, CH-8093 Zurich, Switzerland, hgruetzmacher@ethz.ch*

The phosphoethynolate anion (PCO^-) is a sparsely investigated representative of chemical species having carbon-phosphorus multiple bonds. In contrast to its lighter analogue, the cyanate ion, the phosphoethynolate anion can take part in (see also figure below):

- a) cycloadditions^[1]
- b) nucleophilic substitutions^[2]
- c) P^- transfer reactions, either with or without the release of carbon monoxide.^[3]



Herein the versatile reactivity of the phosphoethynolate anion as a simple building block will be presented. To elucidate the reaction mechanisms leading to these remarkably different products, low temperature NMR investigations and theoretical computations have been carried out, which will also be discussed.

[1] (a) D. Heift, Z. Benkő and H. Grützmacher, *Dalton Trans.* **2014**, 43, 831. (b) A. R. Jupp, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2013**, 52, 10064.

[2] (a) S. Alidori, D. Heift, G. Santiso-Quinones, Z. Benkő, H. Grützmacher, M. Caporali, L. Gonsalvi, A. Rossin and M. Peruzzini, *Chem. Eur. J.*, **2012**, 18, 14805. (b) D. Heift, Z. Benkő and H. Grützmacher, *Dalton Trans.* **2014**, 43, 5920.

[3] D. Heift, Z. Benkő and H. Grützmacher, *Angew. Chem. Int. Ed.*, **2014**, DOI: 10.1002/anie.201402884

Can low-valent silicon compounds be better transition metal ligands than phosphines and NHC?

Tibor Szilvási^{1*}, Zsolt Benedek¹

¹ *Budapest University of Technology and Economics (BUTE), Department of Inorganic and Analytical Chemistry, Szent Gellért tér 4, 1111, Budapest, Hungary, szilvasitibor@ch.bme.hu*

Transition metal catalysts make possible an enormous amount of selective and atom-economical transformations and are being used in almost every field of chemistry, and their applications in industry are on the increase, even at the production level. Traditionally, phosphines were used, later, the successful application of carbenes, especially N-heterocyclic carbenes (NHC), broadened the list of potential transition metal ligands. This raises the question whether other low-valent group 14 compounds, especially silylenes, can be used for the same purpose. Thus, we gathered all synthesized low-valent silicon compounds and investigate them with quantum chemical methods for their possible effects on the catalytic activity of transition metals catalysis. In this theoretical study, we considered all important features of a ligand that can influence the reaction rate: σ -donating and π -accepting abilities, ligand-to-metal charge transfer (LMCT) and steric properties, and compared to regularly applied phosphines and carbenes in order to examine whether low-valent silicon compounds can serve as better alternatives of conventional ligands in practice. We show that there are low-valent silicon compounds which can easily outperform conventional ligands even in all categories. We also show the principle behind the enhanced properties and how to design even better transition metal ligands.

To Be or Not to Be Covalent in Clays?

Robert K. Szilagy

*Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT, 59717, U.S.A.
szilagy@montana.edu*

Understanding the chemical bonding in clays among the high-valent Al(III), Si(IV) centres and the oxide and hydroxide groups is essential for designing theoretical methods for modelling clay structure and reactivity. A common approach in literature is to assume ionic interactions only. Thus, the chemical interactions not captured by Coulomb forces get described by empirical parameterization of Lenard-Jones potentials toward achieving reasonable accuracy with respect of experimental equilibrium structures. It is then assumed that the energetics will fall into place due to the convergence of parameter optimization (ClayFF^[1]). A more holistic approach is to consider bond stretching and angle bending parameters that become the empirical representations for the covalent interactions between the atomic components of clays (INTERFACE^[2]).

The presentation will discuss a rigorous approach to determine the importance of covalent and magnitude of ionic interactions within kaolinite^[3] among the two different electrophilic and the four different nucleophilic centres (Figure 1). A systematic investigation was carried out for calculated electron densities obtained for pure ionic electronic structure,^[4a] at the Hartree-Fock^[4b] level, and with density functional PW91.^[4c] The use of triple- ζ quality basis set with polarization was required to approach basis set saturation. The electron density was analysed by means of Mulliken,^[5a] Weinhold,^[5b] and Bader^[4c] population analysis methods. The estimates for atomic point charges, the magnitude of covalent interactions between the nucleophilic and electrophilic centres suggest the need for rethinking both semi-empirical Hamiltonians and the molecular mechanical parameterization strategies.

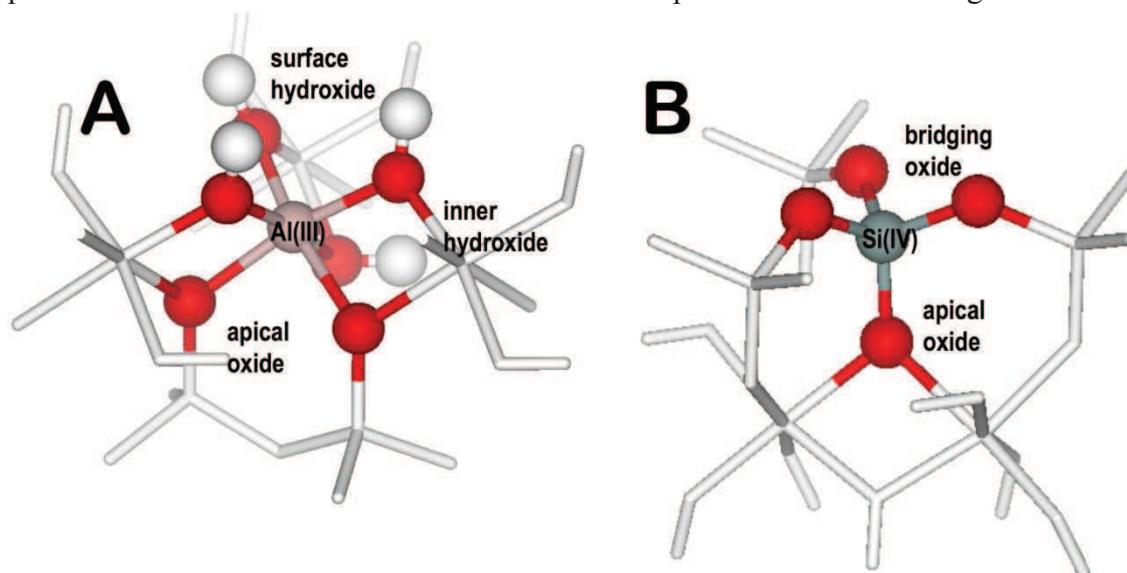


Figure 1: Coordination chemical models for the Al (A) and Si (B) sites of kaolinite

[1] R.T. Cygan, J.-J. Liang, A.G. Kalinichev, *J.Phys.Chem. B* **2004**, 108, 1255–1266.

[2] H. Heinz, T.-J. Lin, R.K. Mishra, F.S. Emami, *Langmuir* **2013**, 29, 1754–1765.

[3] L. Smrcok, D. Tunega, A.J. Ramirez-Cuesta, E. Scholtzova, *Phys.Chem.Minerals* **2010**, 37, 571–579.

[4] a) R.K. Szilagy, M. Winslow, *J. Comp. Chem.* **2006**, 27, 1385–1397. b) D.R. Hartree, *Proc. Cambridge Phil.Soc.* **1928**, 24, 89-110 and 111-132. V. Fock, *Zeitsch. Phys.* **1930**, 61, 126-148. c) J.P. Perdew, Y. Wang, *Phys.Rev.B* **1992**, 45, 13244–13249.

[5] a) R.S. Mulliken, *J.Chem.Phys.* **1955**, 23, 1833–1840. b) A.E. Reed, L.A. Curtiss, F. Weinhold, *Chem.Rev.* **1988**, 88, 899-926. c) R.F.W. Bader, *Chem.Rev.* **1991**, 91, 893-928.

Adhesive Forces Between Aromatic Molecules and Graphene

Christoph Lechner¹, Alexander F. Sax^{2*}

¹*University of Graz, Heinrichstraße 28, 8010 Graz, Austria*

²*University of Graz, Heinrichstraße 28, 8010 Graz, Austria, alexander.sax@uni-graz.at*

Adhesive forces were investigated in a computational study for the complexes of graphene with each of the four adsorbates, benzene, anthracene, pyrene and tetracene, by using the DFT method B3LYP and the semiempirical method DFTB, together with empirical dispersion corrections. The four aromatic molecules differ in size and flexibility. Whereas the adhesion energy (for complete separation) is independent of the way an adsorbed molecule is separated from graphene, the maximum adhesive forces depend strongly on the way the adsorbate is lifted. We investigated, therefore, four lifting modes that differ by i) the pull-off points at which an external detachment force acts on the adsorbate and ii) whether the adsorbed molecule is rigid or flexible. In rigid vertical lifting, all atoms of the adsorbate are pull-off points; in flexible central lifting, the pull-off points are in the middle of the adsorbate; in both rigid and flexible terminal lifting, the pull-off points are at one end and the adsorbate is regarded as being either rigid or flexible. We find that, for both the adhesion energies and the maximum adhesive forces, the DFTB results are at most 10 percent lower than the corresponding DFT results. For small or rigid molecules like benzene and pyrene, there is no significant difference between rigid vertical and flexible central lifting. For a flexible molecule like tetracene, the difference of the maximum adhesive force can be up to 70 percent. Terminal lifting consists of two subprocesses. For the second subprocess, both the adhesion energy and the maximum adhesive force are essentially unchanged across all four adsorbates; for the first subprocess, however, we find a pronounced size dependence of the adhesion energy.

THEORETICAL STUDY OF THE HOMOLYTIC AND HETEROLYTIC O–H BOND CLEAVAGE IN VITAMIN B6

Peter ŠKORŇA, Ján RIMARČÍK, Michaela KLENOVIČOVÁ, Erik KLEIN*

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, Slovakia

[*erik.klein@stuba.sk](mailto:erik.klein@stuba.sk)

Abstract

This work is focused on the thermodynamic study of the reaction enthalpies related to the three mechanisms of primary antioxidants action of the three vitamin B6 components, as well as 4-pyridoxic acid that represents their metabolite.

1. INTRODUCTION

Current experimental research results indicate that vitamin B6, Fig. 1, shows an antioxidant activity in plants [1]. It is more powerful singlet oxygen, $^1\text{O}_2$, scavenger than vitamins C and E [2]. In blood, it shows higher antioxidant activity than vitamin C [3], too.

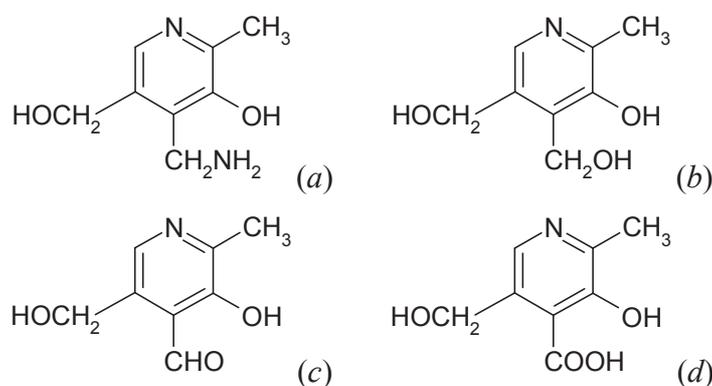


Figure 1: Vitamin B6: pyridoxamine (a), pyridoxine (b), pyridoxal (c); 4-pyridoxic acid (d).

In this work we decided to study the reaction enthalpies related to the three mechanisms of primary antioxidants action for pyridoxamine, pyridoxine, pyridoxal, and 4-pyridoxic acid in three environments: gas-phase, benzene, and water. Antioxidant action of investigated compounds can be ascribed to the OH group attached directly to the aromatic ring, placed in the *meta* position to nitrogen. One of the aims of the work is to compare calculated reaction

enthalpies with data available for typical primary phenolic antioxidants, such as tocopherols or flavonoids.

2. COMPUTATIONAL DETAILS

All calculations were performed using Gaussian 09 program package [4]. The geometries of all studied species were optimized using DFT method with B3LYP [5] functional without any constraints (energy cut-off of 10^{-5} kJ mol⁻¹, final RMS energy gradient under 0.01 kJ mol⁻¹ Å⁻¹). Calculations were performed in 6-311++G** basis set [6]. Solvent contribution to the total enthalpies was computed using integral equation formalism IEF-PCM method [7, 8]. From the total enthalpies, following reaction enthalpies were calculated for the above mentioned reaction centre: (i) O–H bond dissociation enthalpies; (ii) ionization potentials and (iii) proton dissociation enthalpies; (iv) proton affinities of anions formed by OH group deprotonation and (v) electron transfer enthalpies (for the definitions, see ref. [9]) at $T = 298$ K.

3. RESULTS AND DISCUSSION

In all environments, bond dissociation enthalpies, BDE, reached similar values. In the gas-phase, they lie in the 346–400 kJ mol⁻¹ range. The lowest value was found for pyridoxamine and pyridoxine (difference between the corresponding values only 1 kJ mol⁻¹). The highest BDEs were found for 4-pyridoxic acid (390 kJ mol⁻¹) and pyridoxal (400 kJ mol⁻¹), because CHO and COOH groups form strong intramolecular hydrogen bonds with the OH group representing the reaction center. The lowest ionization potential and electron transfer enthalpy values were found for pyridoxamine. On the contrary, lowest proton dissociation enthalpies in all studied environments were obtained for 4-pyridoxic acid. Lowest proton affinities were found for pyridoxine. In solution-phase, reaction enthalpies for processes including charged species are significantly lower than corresponding gas-phase values. In general, found reaction enthalpies are similar to those found for phenolic antioxidants – tocopherols or flavonoids [9].

Currently, obtained results are analyzed in order to (i) identify the effect of –CH₂NH₂, –CH₂OH, –CHO, and –COOH groups in the *para* position to nitrogen atom (Fig. 1) on the studied reaction enthalpies, and (ii) to assess the role of the environment.

4. CONCLUSION

In this ongoing theoretical work, we study pyridoxamine, pyridoxine, pyridoxal, and 4-pyridoxic acid in the various environments with the focus on the thermodynamics of aromatic OH group homolytic and heterolytic splitting-off. Calculated reaction enthalpies are analyzed to shed light on the effect of the substituent located in the *para* position to nitrogen atom.

5. ACKNOWLEDGEMENT

This work has been supported by the Slovak Grant Agency (VEGA 1/0735/13 and 1/0307/14).

6. REFERENCES

- [1] Denslow A S, Walls AA, Daub EM: *Physiol. Mol. Plant. P.* 66 (2005), 248–249
- [2] Bilski P, Li YM, Ehrenshaft M, Daub EM, Chignell FC: *Photochem. Photobiol.* 71 (2000), 129–134
- [3] Stocker P, Lesgards J-F, Vidal N, Chalier F, Prost M: *Biochim. Biophys. Acta* 1621 (2003), 1–8
- [4] Frisch MJ, et al. *Gaussian 09, Revision C.01*, Gaussian, Inc., Wallingford, CT, 2010
- [5] Becke A: *J. Chem. Phys.* 98 (1993), 5648–5652
- [6] Binkley JS, Pople JA, Hehre WJ: *J. Am. Chem. Soc.* 102 (1980), 939–947
- [7] Cancès E, Mennucci B, Tomasi J: *J. Chem. Phys.* 107 (1997), 3032–3041
- [8] Cancès E, Mennucci B: *J. Math. Chem.* 23 (1998), 309–326
- [9] Vagánek A, Rimarčík J, Lukeš V, Klein E: *Comput. Theor. Chem.* 991 (2012), 192–200

Precise calculations of NMR constants and determination of nuclear magnetic dipole moments

Andrej Antušek¹, Michal Jaszuński², Karol Jackowski³

¹*Slovak University of Technology, Faculty of Materials Science and Technology, Paulinska 16, 917 24 Trnava, Slovakia*

²*Polish Academy of Sciences, Institute of Organic Chemistry, Kasprzaka 44, 01-224 Warsaw, Poland*

³*Warsaw University, Department of Chemistry, Laboratory of NMR Spectroscopy, Pasteura 1, 02-093 Warsaw, Poland*

andrej.antusek@stuba.sk

The NMR shielding was a significant obstacle for measurement of precise values of nuclear dipole moments. Rough approximation of NMR shielding constants in original measurements of nuclear magnetic dipole moments led to inaccurate values of nuclear magnetic dipole moments and significant internal discrepancy in NMR data of distinct isotopes. Development of precise quantum chemical methods for NMR properties of molecules allows re-measurement of nuclear magnetic dipole moments and significantly reduces discrepancies [1]. In the lecture, results of NMR shielding calculations incorporating correlation and relativistic effects and vibrational corrections will be presented. Theoretical values of NMR shielding constants combined with gas-phase NMR experiments define new values of nuclear magnetic dipole moments and open possibility to define single NMR standard [2]. However, number of isotopes which can be measured in gas-phase NMR spectroscopy is limited and the study was extended for nuclear magnetic dipole moments of isotopes which creates closed shell ions in water. In this case, calculations of NMR constants in ion-water clusters combined with standard liquid-phase NMR measurements bring very satisfactory results [3].

[1] A. Antušek, K. Jackowski, *et al.*, *Chem. Phys. Lett.* **2005**, 411, 111-116.

[2] M. Jaszuński, A. Antušek, *et al.*, *Progress in NMR Spectroscopy* **2012**, 67, 49-63.

[3] A. Antušek, P. Rodziewicz, *et al.*, *Chem. Phys. Lett.* **2013**, 588, 57-62.

Exchange energy of one- and two-active-electron molecules

Piotr Gniewek^{1*}

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

*pgniewek@tiger.chem.uw.edu.pl

Exchange energy is one of the most important concepts of molecular interactions, yet it is very difficult to calculate this effect accurately. For one and two active electron diatomic molecules the exchange energy J can be defined as

$$J = \frac{1}{2}(E_g - E_u),$$

where E_g and E_u are the Born-Oppenheimer energies of the two lowest lying gerade and ungerade states, respectively. We show that J can be calculated directly from three different formulas: a surface integral formula of Herring and Holstein,

$$J_{surf}[\varphi] = \frac{-\int \varphi \nabla \varphi dS}{\langle \varphi | \varphi \rangle - \int_{right} \varphi^2 dV},$$

a volume integral formula of Symmetry-Adapted Perturbation Theory (SAPT),

$$J_{SAPT}[\varphi] = \frac{\langle \varphi_0 | VP\varphi \rangle - \langle \varphi_0 | V\varphi \rangle \langle \varphi_0 | P\varphi \rangle}{1 - \langle \varphi_0 | P\varphi \rangle^2},$$

and a variational volume integral formula,

$$J_{var}[\varphi] = \frac{\langle \varphi | HP\varphi \rangle - \langle \varphi | H\varphi \rangle \langle \varphi | P\varphi \rangle}{1 - \langle \varphi | P\varphi \rangle^2}.$$

In the above formulas H is the hamiltonian of the system, V is the interaction operator, and P is the symmetry operator (in the case of one-electron systems it is the operator of the spatial reflection in the median plane M , and in the case of two-electron molecules it is the operator of electron exchange).

The so-called primitive function^[1] φ can be approximated in several ways^[2]:

- (a) the Hirschfelder-Silbey perturbation theory^[3],
- (b) polarization approximation^[4],
- (c) multipole expansion^[5],
- (d) variational calculation in the basis of localized functions.

The variational formula provides the best description of the exchange energy for the hydrogen molecular ion, which is a model system with exact solution^[6].

[1] W. Kutzelnigg, *J. Chem. Phys.* **1980**, 73, 343-359.

[2] B. Jeziorski, R. Moszyński, *et al.*, *Chem. Rev.* **1994**, 94, 1887-1930.

[3] J. O. Hirschfelder, R. Silbey, *J. Chem. Phys.*, **1966**, 45, 2188-2192.

[4] J. O. Hirschfelder, *Chem. Phys. Lett.*, **1967**, 1, 325-329.

[5] R. Ahlrichs, *Theor. Chim. Acta* **1976**, 41, 7-15.

[6] P. Gniewek, B. Jeziorski, *submitted to Phys. Rev. A*, **2014**

Multireference equation of motion coupled cluster method

Ondrej Demel¹, Marcel Nooijen^{2*}

¹*J. Heyrovský Institute of Physical Chemistry of ASCR, Dolejškova 3, 18223. Prague, Czech Republic*

²*University of Waterloo, 200 University Avenue West, N2L 3G1, Waterloo, Canada*

nooijen@uwaterloo.ca

The multireference equation of motion coupled cluster method^[1] is a quantum chemistry approach designed to describe a number of electronic states that can all be described qualitatively by the same active space. MR-EOMCC follows a transform then diagonalize strategy, in which an exponential cluster operator is obtained based on a parent reference manifold. The final target states are defined by a fairly compact diagonalization of the transformed Hamiltonian as in single reference EOMCC. Here, excitations involving two external orbitals are described in a global, internally contracted fashion using the cluster operator. Remaining excitations, in particular the 1h, 1p, 1h1p and 2h1p excitations, are obtained in an uncontracted fashion by explicit diagonalization, and they are thus specific for each state of interest, rather than global.

Recently, a hierarchy of MREOM variants have been developed that include additional semi-internal excitations in the cluster operator^[2,3]. In this way, three goals are achieved simultaneously. First, the accuracy of the scheme is significantly improved. Second, the diagonalization manifold can be greatly reduced, eliminating especially the most numerous 2h1p and 1h1p excitations. This leads to considerable savings in computational cost. Finally, the size-consistency error is reduced. The additional transformations can be performed either sequentially or simultaneously with the original transformation.

The MR-EOMCC approach and its extensions are applied to an extensive set of test cases to examine the accuracy and versatility of the approach.

Applications to first row transition metal atoms (Cr, Mn and Fe) yielded results for up to 524 electronic states (for Cr) with an RMS error compared to experiment of about 0.05 eV. The computational costs of the transformation steps in MREOM are comparable to those of closed-shell CCSD.

[1] D.Datta, M. Nooijen, *J. Chem. Phys.* **2012**, 137, 204107.

[1] O. Demel, D.Datta, M. Nooijen, *J. Chem. Phys.* **2013**, 138, 134108.

[2] M. Nooijen, O. Demel, D. Datta, L. Kong, K. R. Shamasundar, V. Lotrich, L. Huntington, and F. Neese, *J. Chem. Phys.* **2014**, 140, 081102.

Interactions of atoms, molecules, and surfaces – pushing the limits of accuracy

Konrad Patkowski

Department of Chemistry and Biochemistry, Auburn University, Auburn, AL 36849, United States, patkowski@auburn.edu

The knowledge of weak interaction energies between atoms or molecules is crucial for understanding the properties of clusters, liquids, crystals, adsorbed species, and biomolecules. The intermolecular interaction energies are small (no more than a few kcal/mol) and extremely sensitive to virtually all details of the quantum-chemical calculation, including the one-electron basis set and the treatment of electron correlation. Several examples from our group's research will be presented in which accurate interaction energies were obtained for complexes ranging from He-H₂^[1] all the way to methane-carbon nanotube^[2]. The requirements for obtaining accurate interaction energies will be illustrated and explored. For small complexes where the CCSD(T) coupled-cluster approach is a good starting point, it will be shown how important (and how hard) it is to converge to the complete basis set limit both the CCSD(T) interaction energy (using basis set extrapolations, midbond functions, and explicitly correlated approaches^[3,4]) and the higher-order coupled-cluster corrections^[5]. For larger complexes where CCSD(T) might not be feasible, the importance of a careful benchmarking and selection of an approximate approach will be illustrated^[2,6-8]. In particular, we will argue that while modern density-functional methods augmented by atom-pairwise dispersion provide a robust and efficient way to compute weak interaction energies, their accuracy across entire potential energy curves is hampered by the limitations of the existing approaches to damp the dispersion at short range.

[1] B. W. Bakr, D. G. A. Smith, K. Patkowski, *J. Chem. Phys.* **2013**, 139, 144305.

[2] D. G. A. Smith, K. Patkowski, *J. Phys. Chem. C* **2014**, 118, 544-550.

[3] K. Patkowski, *J. Chem. Phys.* **2012**, 137, 034103.

[4] K. Patkowski, *J. Chem. Phys.* **2013**, 138, 154101.

[5] D. G. A. Smith, P. Jankowski, M. Slawik, H. A. Witek, K. Patkowski, *J. Chem. Theory Comput.* (in press).

[6] D. G. A. Smith, K. Patkowski, *J. Chem. Theory Comput.* **2013**, 9, 370-389.

[7] D. G. A. Smith, K. Patkowski, manuscript in preparation.

[8] S. Li, D. G. A. Smith, K. Patkowski, manuscript in preparation.

Precision calculations for the lithium and beryllium dimers with Slater-type orbitals

Michał Lesiuk

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

Slater-type orbitals (STO)^[1] have recently become of interest in our laboratory because of increasing demand for spectroscopically accurate calculations for diatomic systems. The main obstacles in using STO in such calculations are very complicated analytical expressions for the molecular two-electron integrals and severe numerical instabilities occurring during their evaluation. We have managed to derive several new expressions for the difficult cases and introduced numerous improvements which allow to efficiently compute two-electron integrals with sufficient precision. All the advances in this field were implemented in our two-centre STO integral program^[2] which is a building block of the quantum chemistry program *KOŁOS* developed by our group.

In this presentation we show the first applications of the newly developed methods - *ab-initio* calculations for the lithium and beryllium dimers. Both systems are of interest from the spectroscopic point of view. For these atoms STO basis sets of quality ranging from *double-zeta* to *sextuple-zeta* were developed. Basis sets are constructed to obey the so-called *correlation consistency* principle^[3] and are augmented with proper suite of diffuse functions. In order to reach the desired level of accuracy high-order coupled-cluster methods^[4] were utilised, CCSD(TQ) and CCSDT, combined with full CI calculations to account for higher excitations. We also include minor corrections for relativistic and adiabatic effects. In order to examine the advantages connected with the use of the STO basis set we present analogous calculations with Gaussian orbitals and provide a detailed comparison. The results presented here appear to be the most accurate *ab-initio* calculations for Li₂ and Be₂ available in the literature up to date and one of the most accurate calculations for molecular systems bigger with more than 4 electrons ever performed.

[1] J. C. Slater, Phys. Rev. **31**, 333 (1928).

[2] M. Lesiuk and R. Moszynski, manuscript in preparation.

[3] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).

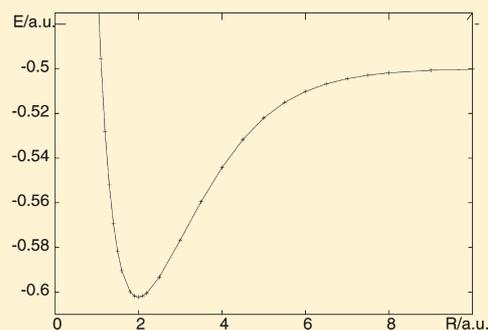
[4] R.J. Bartlett, J. Phys. Chem. **93**, 1697 (1989); K. Raghavachari, G.W. Trucks, J.A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989); J. Noga and R.J. Bartlett, J. Chem. Phys. **86**, 7041 (1987); R.J. Bartlett, J.D. Watts, S.A. Kucharski, and J. Noga, Chem. Phys. Lett. **165**, 513 (1990).

Covalent Bonding: The Role of Exchange Effects

I. Mayer*

Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1519 Budapest, Hungary

ABSTRACT: It is stressed that the two-center exchange energy components lead to a significant lowering of the total molecular energy because of exclusion of self-repulsion, and this is inevitable for covalent bond formation. The success of the two-center bond order index relies on the fact that it gives a qualitative estimate of this important phenomenon.



In a recent paper¹ Bacskay and Nordholm performed a number of calculations of H_2^+ and essentially reiterated and extended the classical results of Ruedenberg^{2–4} concerning the complex role of kinetic energy in the formation of chemical bonds. The results seem to be completely in line with the summary given in the textbook⁵ of the present author: “The problem was investigated in much detail by Ruedenberg on simple examples like H_2^+ . He considered the bond formation as being formally divided into consecutive steps: the first step is a *promotion* with a contraction of the valence orbitals. This leads to a lowering of the potential energy (the electrons in average are closer to the nuclei) but the kinetic energy increases *more* than this potential energy lowering. (This increase of the kinetic energy is an obvious consequence of the uncertainty relation.) Then the delocalization permits a kinetic energy lowering *with respect to the promoted state*; this decrease in the kinetic energy is inevitable to provide the possibility of conserving the lower potential energy that has been a result of the promotion. However, in the final account the bond formation is connected with a decrease of the potential energy and increase of the kinetic energy in accord with the virial theorem.” (The last remark refers to the minimum on the potential energy curve, as the virial theorem is directly applicable only in points where the energy is stationary.)

The importance of the subject, however, deserves repeated attempts to give a proper physical interpretation of the chemical bond formation. In particular, it is desirable to connect the concept of delocalization appearing in the considerations like those of Ruedenberg or Bacskay and Nordholm with the concept of bond order (multiplicity) and the powerful picture of Lewis electron pairs, which are fundamental in chemists’ thinking. For that reason, it is desirable to consider a different simple decomposition of the energy, first for the same H_2^+ model, then for the general case, too.

As the internuclear distance increases, the energy of H_2^+ quickly tends to that of a free hydrogen atom ($-1/2$ atomic

units), as the system dissociates into a hydrogen atom and a free proton. (The energy of a free proton is zero by definition, and it interacts with a neutral H atom.) However, owing to the symmetry of the system, the wave function of H_2^+ becomes the sum of wave functions corresponding to the electron to be “here” or “there”; the energy of such a linear combination for sufficiently large distances equals that of either degenerate localized state. As we are dealing with a single electron system, this linear combination results in an electron orbital delocalized between the two atoms.

For such a wave function each hydrogen atom bears, on average, a positive charge $1/2$. From a global electrostatic point of view that means a rather significant repulsive interaction of $1/(4R_{AB})$ between the atoms, where R_{AB} is the interatomic distance. This electrostatic interaction decays rather slowly with the distance. At the distances about or over 5 atomic units, practically no interactions count except the electrostatic interactions of point charges; the repulsion of $1/(4R_{AB})$ would constitute 0.05 atomic units at $R_{AB} = 5$ au and 0.025 atomic units at $R_{AB} = 10$ au. These are quite considerable numbers on the chemical scale: over 30 and 15 kcal/mol, respectively, but nothing similar can be seen on the actual H_2^+ potential curve; see Figure 1. Why? Obviously there is an effect compensating this electrostatic repulsion. Understanding its nature is instructive for getting a deeper insight into the role of delocalization in chemical bonding.

If one has a proton and a H atom, then there are two global electrostatic effects, which just cancel each other: an internuclear repulsion $1/R_{AB}$ and an electron–nuclear attraction $-1/R_{AB}$. In the delocalized case the global electrostatic effect formally contains, besides the terms present also in the $p + H$ case, an electron–electron repulsion that exactly equals the problematic $1/(4R_{AB})$ term. However, we have in

Received: February 4, 2014

Revised: March 13, 2014

Published: March 13, 2014



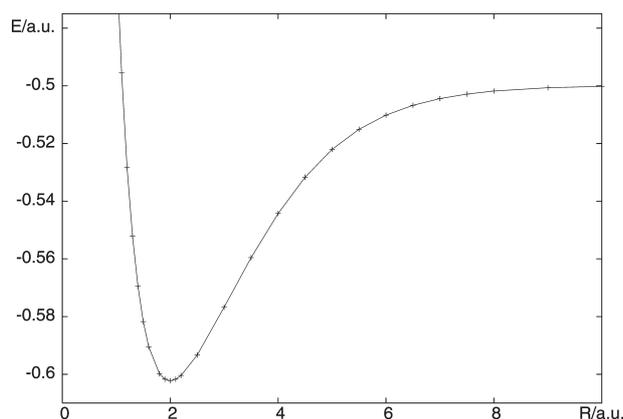


Figure 1. Potential curve of the H_2^+ ion (cc-pVTZ basis).

our system only a single electron, and the electron does not interact with itself in the nonrelativistic quantum theory. So the global electrostatic effect should be corrected for the self-interaction of the electron. After this correction is done, we get zero electrostatic interaction, and the resulting potential energy curve will be determined by other factors, namely, the behavior of the potential and kinetic energies, as discussed in refs 1–5.

Nonetheless, the self-interaction correction discussed is in intimate connection with the concept of chemical bonding. To see this, we turn to the energy partitioning scheme discussed in ref 6. The expressions given there refer to the single determinant (Hartree–Fock) case. However, the Hartree–Fock level is sufficient for understanding the qualitative aspects of bonding: electron correlation usually influences the numbers but not the chemical picture.

In that energy decomposition the leading two-center contribution is the “electrostatic interaction in the point charge approximation.” It represents a sum of two terms: one describes the electrostatic interaction of the resulting atomic point charges, another reflects the interatomic exchange. Now, it is known that in Hartree–Fock theory exchange includes the self-repulsion of electrons and that they cannot be separated out from each other conceptually because self-repulsion alone would not be unitary invariant.

The expressions in ref 6 are given in terms of spin-orbitals; turning to the spatial orbitals, the two-center exchange contribution in the point-charge approximation can be rewritten as

$$\begin{aligned}
 E_{AB}^{\text{exch.point}} &= \varepsilon_{AB}^{\text{exch.point}} + \varepsilon_{BA}^{\text{exch.point}} \\
 &= -\frac{1}{R_{AB}} \sum_{\mu \in A} \sum_{\nu \in B} [(\mathbf{P}^{\alpha} \mathbf{S})_{\mu\nu} (\mathbf{P}^{\alpha} \mathbf{S})_{\nu\mu} + (\mathbf{P}^{\beta} \mathbf{S})_{\mu\nu} \\
 &\quad (\mathbf{P}^{\beta} \mathbf{S})_{\nu\mu}] \\
 &= -\frac{1}{2R_{AB}} \sum_{\mu \in A} \sum_{\nu \in B} [(\mathbf{D} \mathbf{S})_{\mu\nu} (\mathbf{D} \mathbf{S})_{\nu\mu} + (\mathbf{P}^s \mathbf{S})_{\mu\nu} (\mathbf{P}^s \mathbf{S})_{\nu\mu}]
 \end{aligned} \quad (1)$$

Here R_{AB} is the internuclear distance between atoms A and B , \mathbf{P}^{α} and \mathbf{P}^{β} are the usual density matrices for spins α and β , respectively, \mathbf{S} is the overlap matrix of the atomic orbitals, \mathbf{D} is the total density matrix, and \mathbf{P}^s is the spin-density matrix. All matrices are expressed in the basis of atomic orbitals.

Now, comparing with the definition^{7,8} of the bond order index, B_{AB} , we see that⁹

$$E_{AB}^{\text{exch.point}} = -\frac{1}{2R_{AB}} B_{AB} \quad (2)$$

As the bond order B_{AB} for H_2^+ is exactly $1/2$, this result is completely in agreement with the self-interaction term $-1/(4R_{AB})$ discussed above.

Table 1 contains some selected energy values for the H_2^+ system calculated by using cc-pVTZ basis set. As could be

Table 1. Selected Energetic Parameters (in au) of the H_2^+ System, Calculated by Using the cc-pVTZ Basis Set at Different Internuclear Distances

R (au)	2	5	10
electrostatic energy ^a	0.0529	0.0465	0.0249
-point charge approx.	0.1250	0.0500	0.0250
exchange energy	-0.1482	-0.0533	-0.0251
-point charge approx.	-0.1250	-0.0500	-0.0250
total energy	-0.6022	-0.5221	-0.5002

^aIncluding internuclear repulsion.

expected, the point-charge approximation is good at larger internuclear distances, but not at the equilibrium one; there the reduced overall electrostatic repulsion reflects the stabilizing effect of the charge accumulation between the nuclei.

Now, if we add one more electron, then there will be two electrons occupying the bonding molecular orbital, leading to one Lewis electron pair, and the bond order value becomes equal to one. The electron–electron self-interaction, reducing the total energy as compared with the crude electrostatics, would also be twice as large at the same distance R_{AB} , but the increase of bonding interactions reduces R_{AB} , so the effect becomes larger. Note that in this case there are no resulting atomic charges, so the exclusion of the electron self-interaction gives an energy reduction with respect to the vanishing overall electrostatic interaction energy (at the level of point charge approximation), corresponding to the neutral situation.

However, it is also to be realized that in the case with a doubly occupied bonding molecular orbital (MO) there is a price to be paid for the exchange (self-interaction) reduction of the electrostatic energy. That is connected with the appearance of the ionic terms in the wave functions, i.e., those in which both electrons are on the same atom. This gives rise to one-center electron–electron repulsion terms,¹¹ which are absent for a single H atom. They may be very significant, but this effect is an inevitable consequence of electron delocalization, and electron delocalization is necessary in order that other terms usually discussed in connection with bond formation, like accumulation of charge in the bonding region, reduction of the kinetic energy as compared with the atomic promoted states, etc., could contribute to the final energy. Thus, the total binding energy is due to these terms as well as the exchange energy; while the appearance of the ionic terms reduces the energy of the chemical bonding. (Table 2 collects some illustrative numbers for the Hartree–Fock calculations performed for the H_2 molecule by using cc-pVTZ basis set.)

The effects of the charge accumulation, etc., are responsible for the fact that putting the electrons in the antibonding combination of the two hydrogenic orbitals leads to repulsive interaction and no chemical bonding; although, the interatomic bond order and the exchange effects are independent of whether the bonding or the antibonding combination of the hydrogenic orbitals is occupied. This clearly puts some limits

Table 2. Selected Hartree–Fock Energetic Parameters (in a.u.) of the H₂ System, Calculated by Using the cc-pTVZ Basis Set at Different Internuclear Distances

R (au)	1.4	2	3
electrostatic energy ^a	−0.1418	−0.0912	−0.0263
-point charge approx.	0	0	0
exchange energy	−0.3139	−0.2546	−0.1801
-point charge approx.	−0.3571	−0.2500	−0.1667
one-center el.–el. repulsion	0.3420	0.3015	0.2639
total energy	−1.1330	−1.0911	−0.9886

^aIncluding internuclear repulsion.

on the interpretative power of the bond order index, as it does not always permit to distinguish between bonding and antibonding situations. In practice, however, that may influence some nonbonded interactions, only.

It is interesting to follow what happens if further electrons are added to the system, assuming, of course, the appropriate increase of the nuclear charges, too, so the overall neutrality of the system is maintained. The next interesting system is a helium dimer in which, to a good approximation, both the bonding and the antibonding combinations of the atomic 1s orbitals are doubly occupied. In light of the above remark about the antibonding orbitals, at first sight one could expect that the exchange effects of both pairs of electrons will be added up. This is not, however, the case: they destroy the effect of each other. Both the practical calculations and a detailed analytical study⁸ show that such a pair of bonding and antibonding orbitals leads to zero bond order, thus to zero electrostatic exchange effect. This may be understood very easily without much calculation.

It is known that the single determinant wave functions are uniquely determined by the subspace of the occupied orbitals, which means that one can use instead of the original orbitals any of their linear combinations, as far as they are linearly independent and thus span the original occupied subspace. (This may change only the normalization of the many-electron wave function, but that has no physical significance.) In particular, the original atomic orbitals of which the bonding and antibonding MOs are built also represent appropriate linear combinations of the latter,¹⁰ which means that one obtains the same many-electron wave functions also by filling with two electrons each of the original atomic basis orbitals. This wave function does not exhibit any delocalization, so there are no interatomic exchange (electron–electron self-repulsion) effects either. In accord with that, the bond order between two helium atoms is practically zero and no covalent chemical bond appears. (As the atomic orbitals of the two helium atoms slightly overlap, there is some repulsion of closed shells. That is the only effect at the single determinant level of theory. Dispersion, which is a par excellence electron correlation effect, causes a very, very shallow minimum to appear on the He...He potential curve, but that is out of our present scope.)

Of course, if more basis orbitals are involved on the individual atoms, then there can be one or more bonding electron pairs, the effect of which is not compensated by an occupied antibonding counterpart. However, the fact that the core orbitals as well as the lone pairs do not contribute to the bond orders of homonuclear diatomics can be understood exactly in the same manner as the absence of the bonding in helium dimer. Thus, one arrives⁸ to the definition of the well-known “chemist’s bond order”

$$B = \frac{N_{\text{bond}} - N_{\text{antibond}}}{2} \quad (3)$$

where N_{bond} and N_{antibond} are the number of electrons occupying bonding and antibonding orbitals, respectively. This equality is fulfilled⁸ for all first row homonuclear diatomics at the minimal basis level, except C₂.^{12,13} Instead of each pair of occupied bonding and antibonding orbitals, one can always turn to the respective localized core or lone pair orbitals. Thus, one may argue that the localized orbital picture is more adequate for discussing the ground state chemical structure of molecules, while the delocalized picture is better to describe global ionization or excitation processes. The two representations are complementary in that sense.

Double and triple bonds are formed if bonding combinations of atomic basis orbitals of different symmetry, e.g., of σ and π -type, are occupied, and the respective antibonding combinations are not. Then the bond-order will also equal (or, in more general case, be close) to two or three. (Sometimes there are claims concerning of even higher bond orders, but we wish not consider that point here.) Behind every such bond order there is an attractive energy contribution of the electron–electron self-repulsion, representing an inseparable part of exchange. This contribution is of utmost importance for forming the covalent chemical bonds; this connection explains why the bond order index is a successful measure of the bond strengths and a useful quantum chemical counterpart of the number of the valence lines used in a chemical formula.

It is to be noted that the bond order equals some ideal integer or half-integer value only in some very special cases. Thus, independently of the basis set used, the bond order is exactly equal to 1/2 for H₂⁺ and 1 for an RHF calculation of H₂; for other homonuclear diatomics (except C₂) this is true only if the minimal basis set is used.⁸ If one uses larger basis sets or considers heteropolar bonds, then deviations from the ideal integer values are obtained, and the bond orders obtained in the calculations are usually close but slightly lower than the ideal values.^{14,15} The use of integer bond multiplicities in these cases may be considered as a sort of generalization (or simplification), which distinguishes the chemist’s way of thinking from the physicist’s way of description of molecular systems.

The above discussion also indicates that among the large (conceptually infinite) number of different localization procedures the classical Edmiston–Ruedenberg one¹⁶ may be considered the most adequate. Essentially it produces orbitals for which the intraorbital self-repulsion exchange effect is maximal; therefore, they reflect best to the intimate connection between exchange and chemical bonding.

To summarize the message of this short note, we may stress that the two-center exchange energy components lead to a significant lowering of the total molecular energy because of the exclusion of self-repulsion, and this is inevitable for covalent bond formation. The success of the two-center bond order index relies on the fact that it gives a qualitative estimate of this important phenomenon.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: mayer@chemres.hu or mayer.istvan@ttk.mta.hu.
Phone: +36-1-382-6981.

Notes

The authors declare no competing financial interest.

■ REFERENCES

- (1) Bacskay, G. B.; Nordholm, S. Covalent Bonding: The Fundamental Role of the Kinetic Energy. *J. Phys. Chem. A* **2013**, *117*, 7946–7958.
- (2) Ruedenberg, K. The Physical Nature of the Chemical Bond. *Rev. Mod. Phys.* **1962**, *34*, 326–376.
- (3) Ruedenberg, K.; Schmidt, M. W. Physical Understanding through Variational Reasoning: Electron Sharing and Covalent Bonding. *J. Phys. Chem. A* **2009**, *113*, 1954–1968.
- (4) Bitter, T.; Wang, S. G.; Ruedenberg, K.; Schwarz, W. H. E. Toward a Physical Understanding of Electron-Sharing Two-Center Bonds. II. Pseudo-Potential Based Analysis of Diatomic Molecules. *Theor. Chem. Acc.* **2010**, *127*, 237–257.
- (5) Mayer, I. *Simple Theorems, Proofs, and Derivations in Quantum Chemistry*; Kluwer Academic/Plenum Publishers: New York, 2003.
- (6) Mayer, I. Towards a “Chemical” Hamiltonian. *Int. J. Quantum Chem.* **1983**, *23*, 341–363.
- (7) Mayer, I. Charge, Bond Order and Valence in the ab Initio SCF Theory. *Chem. Phys. Lett.* **1983**, *97*, 270–274.
- (8) Mayer, I. Bond Order and Valence Indices: A Personal Account. *J. Comput. Chem.* **2007**, *28*, 204–221.
- (9) In ref 7, the coefficient 1/2 was misprinted as 2.
- (10) If there were no interatomic overlap, then the original atomic orbitals could be recovered simply as the normalized sum and difference of the bonding and antibonding MOs. Owing to the overlap, this procedure does not lead to the atomic orbitals but to their Löwdin-orthogonalized counterparts.⁵ The latter will be the appropriate orthonormalized *equivalent orbitals* for such a system.
- (11) Mayer, I. Improved Chemical Energy Component Analysis. *Phys. Chem. Chem. Phys.* **2012**, *14*, 337–344.
- (12) For C₂ there are occupied bonding and antibonding orbitals that are not counterparts of each other because they are built of different atomic hybrids.¹³
- (13) Jug, K. Personal communication, 1985.
- (14) If one accounts properly for electron correlation, then the making/breaking of the chemical bonds can also be followed:¹⁵ at the equilibrium distance, one obtains a value close to the ideal integer one, which then smoothly decreases and goes to zero as the interatomic distance increases.
- (15) Mayer, I. Improved Definition of Bond Orders for Correlated Wave Functions. *Chem. Phys. Lett.* **2012**, *544*, 83–86.
- (16) Edmiston, C.; Ruedenberg, K. Localized Atomic and Molecular Orbitals. *Rev. Mod. Phys.* **1963**, *35*, 457–465.

How can DFT methods enhance applications of metalloporphyrins?

Dorota Rutkowska-Zbik^{1*}, Agnieszka Drzewiecka-Matuszek¹, T. Korona², Łukasz Orzeł³, Małgorzata Witko¹

¹*Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek 8, 30-239 Kraków, Poland, nczbik@cyf-kr.edu.pl*

²*Faculty of Chemistry, University of Warsaw, ul. Pasteura 1, 02-093 Warszawa, Poland*

³*Faculty of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060 Krakow, Poland*

Metalloporphyrins (heme and its analogues, chlorophylls, corins, etc.) constitute a group of macrocyclic complexes, which find numerous applications as catalysts, drug carriers, therapeutic species and building blocks of photovoltaic cells. Their versatile chemical properties are due to the presence of the extended tetrapyrrolic moiety, which is tunable upon binding of different metal ions, changes in axial metal ligation, or the presence of macrocycle substituents.

The aim of the presentation is to show how DFT-based methods can aid in the explanation of the observed behaviour of the selected metalloporphyrin systems and provide new hints as to their possible applications.

The reactivity of porphyrin-based catalysts is discussed taking as an example catalytic oxidation of alcohol and aldehyde by so-called Compound II analogue, oxoporphyrin iron(IV) ^[1].

The suitability of vitamin B₁₂ core as cisplatin drug carrier ^[2] is invoked to show the contribution of theoretical methods to the design of the novel systems, which may find applications in pharmaceutical industry.

Finally, the effect of the addition of porphyrin to PCBM fullerene on the UV-VIS characteristics of the blend ^[3] is shown.

Acknowledgements: Authors acknowledge support from the National Science Centre, Poland, through projects N N204 439640 and DEC-2012/05/B/ST5/00389. DRZ and ADM received funding from the Marian Smoluchowski Krakow Research Consortium - a Leading National Research Center KNOW supported by the Ministry of Science and Higher Education.

[1] M. Oszajca, A. Drzewiecka-Matuszek, A. Franke, D. Rutkowska-Zbik, M. Brindell, M. Witko, G. Stochel, R. van Eldik, *Chem. Eur. J.* **2014**, 20, 2328-2343.

[2] D. Rutkowska-Zbik, G. Mazur, A. Drzewiecka-Matuszek, Ł. Orzeł, G. Stochel, *J. Phys. Chem. B* **2013**, 117, 9655–9661.

[3] T. Korona, D. Rutkowska-Zbik, *Comput. Theoret. Chem.* **2014**, 1040-1041, 243–258.

Is Tetrachlorocuprate(II) Square-Planar?

Christof Holzer*¹, Anne-Marie Kelterer¹

¹ Institute of Physical and Theoretical Chemistry, Graz University of Technology, Stremayrgasse 9/I, 8010 Graz, Austria, christof.holzer@student.tugraz.at

The tetrachlorocuprate(II) molecule $[\text{CuCl}_4]^{2-}$, is one of the most important benchmark molecules for the calibration of modern density functionals for transition metal spectroscopy.^[1] Therefore a high knowledge of every aspect of this system is desirable.

Various tetrachlorocuprates(II), $[\text{CuCl}_4]^{2-}$, are well studied experimentally. These complexes have a phase transition near room temperature where the coordination geometry changes from square planar to a distorted tetrahedron. The square planar coordination geometry however is often a strongly Jahn-Teller distorted octahedron with another two chloride ligands located at the axial z-axis of the octahedron. There are, to our best knowledge, only two systems containing the $[\text{CuCl}_4]^{2-}$ moieties which can safely be considered as truly square planar.^[2,3]

For this reason high level ab initio wave function theory computations using MR-ACPF were performed for the square planar configuration and compared to the Jahn-Teller distorted octahedral configuration. The influence of bond length of the axial and in-plane ligands on the excitation energies, as well as their influence on the d-orbitals is presented, including aspects of symmetry.

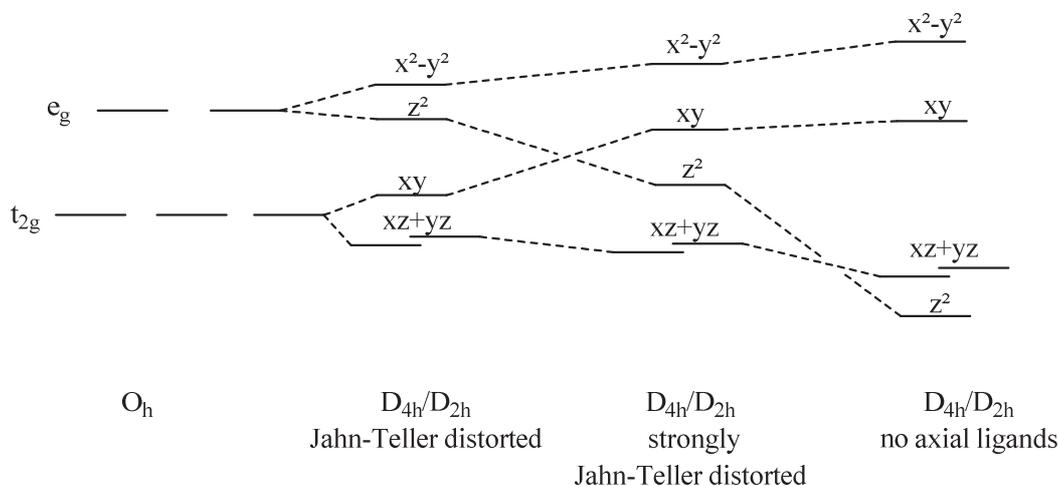


Figure : Crystal field splitting of the Cu^{2+} cation coordinated by Cl^- anions

[1] R.K. Szilalgyi, M. Hetz, E.L. Solomon, *J. Phys. Chem.* **2002**, 106, 2994-3007.

[2] A. Dick, *et al.*, *J. Chem. Phys.* **2008**, 129, 214505.

[3] C. Chow, k. Chang, R.D. Willett, *J. Chem. Phys.*, 1973, 59, 2629-2640.

Domain-Averaged Fermi Hole Analysis: an Interesting Tool for Interesting Bonds

Tamás Kégl^{1*}, László Kollár¹, Tamara Papp¹, Robert Ponec², Bianka Barcs¹

¹Department of Inorganic Chemistry, University of Pécs, and MTA-PTE Research Group for Selective Chemical Syntheses, H-7624 Pécs, P.O. Box 266, Hungary

²Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic v.v.i., Prague 6, Suchbátka 2, 165 02, Czech Republic

The Domain-Averaged Fermi Hole Analysis (DAFH) has been introduced some time ago as a new tool for the visualization and analysis of bonding interactions. It is particularly useful for the interpretation of nontrivial bonding patterns like metal-metal bonding, hypervalence, multicenter bonding, and so on. DAFH analysis provides an appealing, highly visual description of molecular structures including electron pairs like chemical bonds and lone pairs retained in one fragment, as well as dangling valences, created by formal splitting of the bonds resulting in isolation of the given fragment from the rest of the molecule. The DAFH method may especially be useful for the scrutiny of transition metal complexes with complicated bonding situations. A few examples will be discussed where valuable information can be obtained with the analysis of holes associated with ligands of key importance, coordinated to metals.

Figure 1a shows the eigenvector from the DAFH averaged over the fragment CO₂ of the complex Ni(PH₃)₂(η²-CO₂).^[1] Although, this represents a π-bonding interaction, the inspection of the eigenvector depicted using various isovalues reveals, that the lone pair with π symmetry of the coordinating oxygen accounts mainly for the donating interaction.

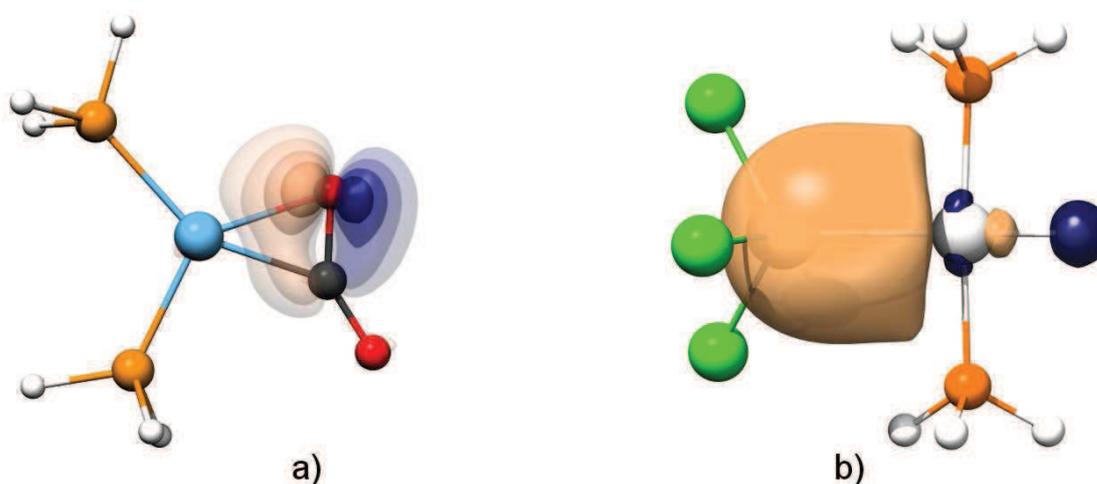


Figure 1: Graphical representation of eigenvectors of the DAFH of the a) CO₂ fragment in Ni(PH₃)₂(CO)₂ and b) that of the SnCl₃ fragment in *trans*-[HPt(PH₃)₂(SnCl₃)]

Figure 1b depicts the eigenvector of the DAFH of the SnCl₃ fragment in complex *trans*-[HPt(PH₃)₂(SnCl₃)] associated with the broken valence of chemical bond corresponding to electron pair almost evenly distributed between the two fragments. Although, the coordination of SnCl₃ to platinum is mainly interpreted in a donor-acceptor manner in the literature, our results reveal that Pt-Sn interaction is much like a σ-bond between the two metals.

[1] T. Kégl, R. Ponec, L. Kollár, *J. Phys. Chem. A* **2011**, 115, 12463-12473.

Application of hybrid quantum mechanics molecular mechanics (QM/MM) calculations in the study of enzymatic reactivity

Julianna Oláh,* Balázs Krámos, Anikó Lábás

Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Szent Gellért tér 4, Budapest H-1111, Hungary

julianna.olah@mail.bme.hu

Enzymes are vital to life. Understanding their reactivity is a key to unraveling the biochemical processes occurring in and around us. However, enzymes are also challenging. Experimental techniques can provide many important details about their functioning and structure, still in many cases the catalytic mechanism of the enzyme cannot be established solely based on experimental data. In these cases computational techniques may help e.g. by giving insight into the structure and energy of potential intermediates and transition states.

Hybrid quantum mechanics molecular mechanics (QM/MM) calculations offer a powerful tool for the study of enzymes at the atomic level. They combine the advantages of quantum chemistry and molecular mechanics: critical part of the system, where bond breaking and forming occurs is treated quantum mechanically, while the rest of the system is described using a molecular mechanics force field (Fig. 1A). However, QM/MM methods also face the difficulties of both methodologies together with the problems arising from the combination of two fundamentally different methodologies.

In the first part of the talk a short overview of the QM/MM method used in our group will be given with an outlook to other available methods. Challenges of QM/MM calculations will be highlighted with an emphasis on the factors that have to be considered when starting a QM/MM study, e.g. preparation of the X-Ray structure for the calculations, importance of the sampling of protein conformations, treatment of the QM/MM boundary, energy vs free energy profiles.

In the second part of the talk some of our results^[1-4] obtained in the study of cytochrome P450 enzymes (see Fig. 1B for the structure of the catalytically active iron porphyrin residue) will be discussed.

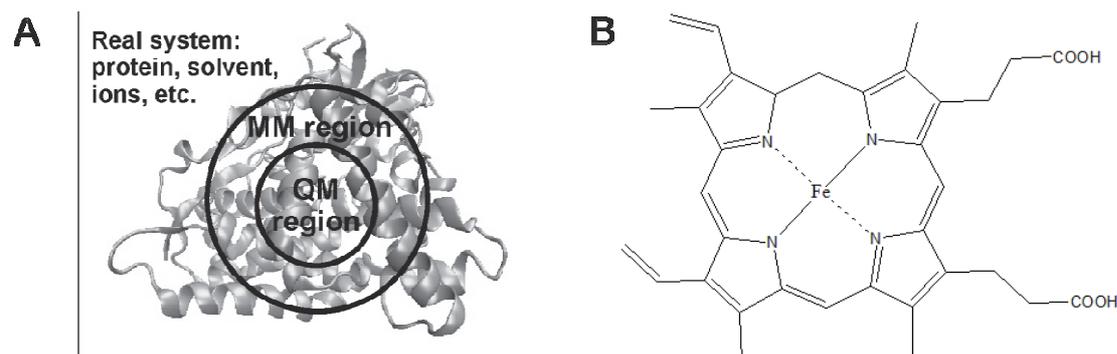


Figure 1: A: Splitting of the system in QM/MM calculations. B: Active site heme residue of cytochrome P450 enzymes

[1] B. Krámos, J. Oláh, *J. Phys. Chem. B*, **2014**, 118, 390-405

[2] B. Krámos, D.K. Menyhárd, *et al.*, *J. J. Phys. Chem. B* **2012**, 116, 872-885

[3] J. Oláh, A.J. Mulholland, *et al.*, *PNAS*, **2011**, 108, 6050-6055

[4] R. Lonsdale, J. Oláh, *et al.*, *J. Am. Chem. Soc.*, **2011**, 133, 15464-15474

The Wigner-Witmer Laws Call for a DFT Paradigm Shift and Boost Electronegativity Equalization by an Order of Magnitude

László v. Szentpály, Institut für Theoretische Chemie, Universität Stuttgart,
Pfaffenwaldring 55, D 70569 Stuttgart, Germany

The Wigner-Witmer “rules” state that the symmetry states of molecules and their dissociation products must be compatible ^[1]. In fact, these “rules” are strict laws establishing symmetry relations in bond formation and bond breaking processes ^[1]. Mulliken’s valence-state electronegativity scale (VSEN) ^[2] and its charge dependent generalizations ^[3, 4] correctly incorporate all these symmetry requirements. In contrast, the DFT type absolute electronegativity and the operational chemical potential ^[5] ignore the Wigner-Witmer laws in spite of the latter’s unrestricted validity. I here investigate the consequences for the electronegativity equalization (ENE) principle, and show that the consistent application of VSEN ^[4, 6] frequently improves the accuracy of ENE by orders of magnitude beyond that of the DFT type absolute electronegativity. Explicit considerations of changes in the external potential, $v(\mathbf{r})$, invoked by Nalewajski ^[7], are found unnecessary for VSEN equalization. The new results strongly challenge conceptual DFT’s “ground-states only” paradigm and many of its popular applications. In order to reach a comparable agreement by conceptual DFT, the “ground-states only” paradigm has to be significantly modified to incorporate valence-state concepts and properties.

References:

- [1] (a) E. Wigner, E. E. Witmer, *Z. Phys.* **1928**, *51*, 859-886;
(b) G. Herzberg, *Molecular Spectra and Molecular Structure. Vol. I. Spectra of Diatomic Molecules*, Van Nostrand, Princeton, N. J., USA; 1950. pp. 315-322.
- [2] (a) R. S. Mulliken *J. Chem. Phys.* **1934**, *2*, 782-793;
(b) R. S. Mulliken *J. Chem. Phys.* **1935**, *3*, 573-585.
- [3] (a) J. Hinze, H. H. Jaffé, *J. Am. Chem. Soc.* **1962**, *84*, 540-546;
(b) J. Hinze, M. A. Whitehead, H. H. Jaffé, *J. Am. Chem. Soc.* **1963**, *85*, 148-154.
- [4] (a) L. v. Szentpály, *J. Mol. Struct. (THEOCHEM)* **1991**, *233*, 71-81;
(b) L. Glasser, L. v. Szentpály, *J. Am. Chem. Soc.* **2006**, *128*, 12314-12321; with earlier references quoted therein.
- [5] (a) R. G. Parr, R. A. Donnelly, M. Levy W. E. Palke, *J. Chem. Phys.* **1978**, *68*, 3801-3807;
(b) R. G. Parr, W. Yang *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989.
- [6] (a) D. Datta, N. Shee, L. v. Szentpály *J. Phys. Chem. A* **2013**, *117*, 200-206;
(b) L. v. Szentpály, *Quantum Matter* **2014**, *in press*.
- [7] (a) R. F. Nalewajski *J. Am. Chem. Soc.* **1984**, *106*, 944-945;
(b) R. F. Nalewajski, M. Koninski *J. Phys. Chem.* **1984**, *88*, 6234-6240;
(c) R. F. Nalewajski *J. Phys. Chem.* **1985**, *89*, 2831-2837;
(d) R. F. Nalewajski *J. Phys. Chem.* **1989**, *93*, 2658-2666.

DFT for gold-ligand interactions: Separating true effects from artifacts

M. Hapka¹, J. V. Koppen², M. Modrzejewski¹, G. Chałasiński¹, M. M. Szczyński^{2*}

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

²*Department of Chemistry, Oakland University, Rochester, Michigan 48309-4477, United States;
bryant@oakland.edu*

Donor-acceptor interactions are notoriously difficult for conventional DFT methodologies. We present a reliable computational treatment of gold-ligand interactions of the donor-acceptor type within (DFT). A proper account of the ionization potential of the electron donor and electron affinity of the electron acceptor is accomplished via a two-parameter tuning of range-separated functionals.^[1] Our approach is validated using the water dimer and the (HAuPH₃)₂ aurophilic complex. Binding energies are computed for Au₄ interacting with the following ligands: SCN⁻, benzenethiol, benzenethiolate anion, pyridine and trimethylphosphine. The dispersion contribution is taken into account via DFT-D3 correction.^[2] The presented methodology leads to very good agreement with the reference coupled-cluster values.

[1] Stein, T.; Kronik, L.; Baer R. *J. Am. Chem. Soc.* **2009**, *131*, 2818.

[2] Grimme, S.; Antony, J.; Ehrlich S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.

Geometric and Electronic Properties of Fe^{IV}=O Active Sites and their Correlation to Reactivity: Interplay of Spectroscopy and Theory

Martin Srnec^a, E. I. Solomon^b

^a J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic;

^b Department of Chemistry, Stanford University, USA

The non-heme ferryl active sites are of significant interest for their application in biomedical and green catalysis. These sites have been shown to have an $S = 1$ or $S = 2$ ground spin state; the latter is functional in biology.¹ Low-temperature magnetic circular dichroism (LT MCD) spectroscopy probes the nature of the excited states in these species including ligand-field (LF) states that are otherwise difficult to study by other spectroscopies. In particular, some MCD bands exhibit vibronic structures that allow mapping of excited-state interactions and their effects on the potential energy surfaces (PESs).² These experimental data are correlated with quantum-chemical calculations that are further extended to analyze the low-lying electronic states and the evolution of their multiconfigurational characters along the Fe–O PESs.² These investigations show that the $S = 1$ species has only one channel reactive towards H-atom abstraction that requires the C–H bond of a substrate to approach perpendicular to the Fe–oxo bond (the π channel). In contrast, there are three reactive channels (one σ and two π) available for the $S = 2$ non-heme Fe^{IV}=O system allowing C–H substrate approach both along and perpendicular to the Fe–oxo bond that have important implications for enzymatic selectivity, as demonstrated for the non-heme iron halogenase that catalyzes chlorination vs. hydroxylation depending on the substrate.³

1/ Srnec, M.; Wong, S. D.; Solomon, E. I. *Dalton. Trans.* 2014, DOI: 10.1039/C4DT01366B

2/ Srnec, M.; Wong, S. D.; England, J.; Que Jr., L.; Solomon, E. I. *Proc. Natl. Acad. Sci. U.S.A.* 2012, 109, 14326-14331.

3/ Wong, S. D.; Srnec, M.; Matthews M. L.; Liu, L. V.; Kwak, Y.; Park, K.; Bell, C. B.; Alp, E. E.; Zhao, J.; Yoda, Y.; Kitao, S.; Seto, M.; Krebs, C.; Bollinger, J. M.; Solomon, E. I. *Nature* 2013, 499, 320-323.

Investigation of metal-insulator like transition through the ab initio density matrix renormalization group approach

G. Barcza^{1*}, E. Fertitta², B. Paulus², Ö. Legeza¹

¹*Strongly correlated systems „Lendület“ research group, Wigner Research Centre for Physics, P.O.Box 49, Budapest, Hungary*

²*Institut für Chemie und Biochemie, Freie Universität, Takustr. 3., 14195 Berlin, Germany*
**barcza.gergely@wigner.mta.hu*

The density matrix renormalization group (DMRG) is a numerical method developed originally to study low-dimensional physical models which can be also employed to investigate molecules with strongly correlated electrons. First, we present the DMRG algorithm from the perspective of recent developments in tensor product approximation. As an application, we study the metal-insulator like transition in lithium and beryllium ring-shaped clusters. Performing accurate DMRG calculations for different interatomic distances and using quantum information theory, we investigate the changes occurring in the wave function between a metallic-like state and an insulating state built from free atoms. We also discuss entanglement and relevant excitations among the molecular orbitals and show that the transition bond length can be detected using orbital entropy functions. Also, the effect of choosing different orbital bases on the effectiveness of the DMRG procedure is analyzed comparing the convergence behavior.

Geminals with strong orthogonality - varieties, capabilities

Ágnes Szabados, Tamás Zoboki, Péter Jeszenszki and Péter R. Surján

Eötvös Loránd University, Laboratory of Theoretical Chemistry, Pázmány Péter sétány 1/A, 1117 Budapest, Hungary

Geminal based wavefunctions represent a conceptually simple multireference framework, which retains the efficiency of the mean-field description regarding inter-geminal interactions. Intra-geminal correlation on the other hand is accounted for exactly, offering the advantage of breaking covalent bonds correctly. The presentation will focus on a class of models, exploiting the so-called strong orthogonality condition.

There are several varieties of strongly orthogonal geminals. It is little known, that the UHF wavefunction is a specimen, belonging to this category. An overview of existing models will be given, both in terms of formulae and application. The latter will focus on the description of multiple bond dissociation and monitor the spin-state of the fragment(s). We show, that imposing a singlet character of each geminal - the so-called singlet coupling - proves to be defective from the point of view of fragment spin. For a complete remedy one needs both singlet and triplet geminals, spin purification of the total wavefunction and subsequent orbital optimization. Some steps taken along this line will be evaluated in numerical terms.^[1]

Simplicity of the geminal model sets it an ideal starting function for multireference correlation schemes, provided that static correlation is accounted for. Applying a perturbative (PT) correction^[2] we show, that the latter condition may not be always met. In particular, singlet coupling undermines correlation corrections when dissociating multiple bonds. The reason behind the failure is triplet geminals coupling to an overall singlet, which constitutes an essential part of static correlation when multiple bonds are broken. The role of triplet geminals can be made evident both in an effective Hamiltonian PT framework as well as adopting a single-but-multi strategy.

[1] P. Jeszenszki, V. Rassolov, P. R. Surján and Á. Szabados, *Mol. Phys.*, **2014**, DOI: 10.1080/00268976.2014.936919

[2] T. Zoboki, Á. Szabados and P. R. Surján, *J. Chem. Theory Comput.*, **2013**, 6, 2602.

Relativistic calculations of fine atomic constants

Miroslav Iliáš, A. Borschevsky et al.

Department of Chemistry, Faculty of Natural Sciences, Matej Bel University, Tajovského 40, SK-97400 Banská Bystrica, Slovakia, email: Miroslav.Ilias@umb.sk

It is known that nuclear-spin-dependent (NSD) parity-violating (PV) effects can be strongly enhanced in diatomic molecules containing heavy atoms. Therefore heavy diatomic molecules are very good candidates for the successful measurement of the nuclear anapole moment, which is the dominant NSD parity violation term in heavy elements. In my talk I shall mention results of our collaborative calculations^[1] which were also motivated by rapid developments in trapping techniques for such systems at low temperatures. Strong enhancement of W_A constants is observed for the group 12 diatomic halides, which should be helpful in future determination of the nuclear anapole moment. The computational method of choice was relativistic Hartree-Fock and density-functional theory together with “semiempirical” accounting for core polarization effects.

I shall also mention initial relativistic Coupled Cluster calculations of the electron electric dipole moment enhancement factors of Na, K, Rb and Cs atoms using double finite-field perturbation theory^[2].

References

[1] A. Borschevsky, M. Iliáš *et al.*, *Phys. Rev. A* **2012**, Vol. 86, 050501; A. Borschevsky, M. Iliáš *et al.*, *Phys. Rev. A* **2012**, Vol. 85, 052509; A. Borschevsky, M. Iliáš *et al.* *Phys. Review A* **2013**, Vol. 88, 022125.

[2] E. Eliav, M. Iliáš, Calculations of electron electric dipole moment enhancement factors using double finite-field perturbation theory. 2014, manuscript in preparation.

Charge Sensitivity Analysis in the Resolution of Force-Field Atoms: Formalism and Applications

Jacek Korchowiec* and Anna Stachowicz

K. Gumiński Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, R. Ingardena 3, Kraków, Poland, korchow@chemia.uj.edu.pl

Charge sensitivity analysis^[1] (CSA) offers a variety of properties of great importance in determining the behavior of the molecular system. It can be formulated in different resolutions. Its variant in atomic resolution is a simple and fast semi-empirical method for deriving charge distribution in molecules. It is based on second order Taylor expansion of the system's energy in terms of population variables and electronegativity equalization (EE) principle. We have recently parameterized CSA in force field atoms resolution.^[2-4]

Generalized charge sensitivity measures a response of a given parameter characterizing one fragment of the system per unit displacement of another parameter describing the second fragment. The response is measured under specific constraints imposed on the molecular remainder. Molecular fragments resolution is typical for classical Molecular Dynamics (MD) simulations. In this resolution, the system is regarded as a collection of molecules, each maintaining its chemical identity. This presentation demonstrates application of CSA to different systems. The presentation includes time evolution of the system energy, charge distribution, Fukui function indices, polarization matrix elements and softness/hardness data (see Fig. 1). The results obtained clearly indicate that the combination of charge sensitivity analysis with MD simulations is a very promising tool in analyzing molecular systems.

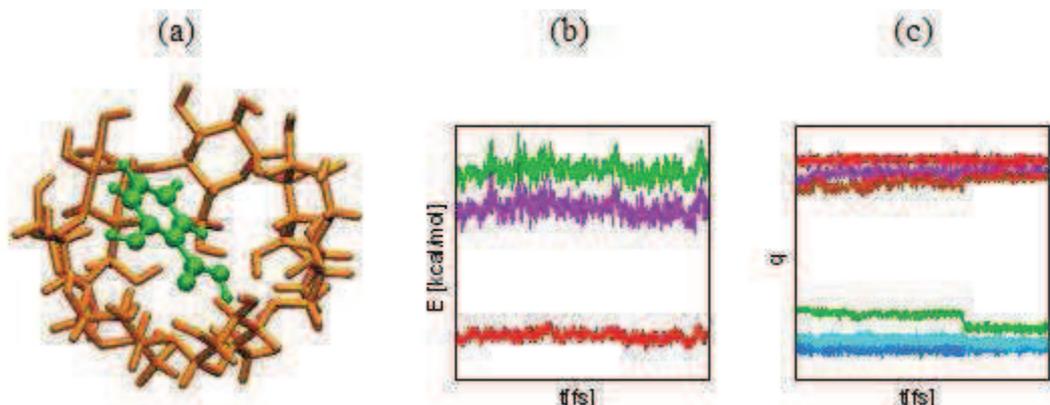


Figure 1: Illustrative example of CSA performance for Inclusion complex of β -cyclodextrin with salicylic acid (part a), together with time evolution of the system's energy (part b) calculated with Born-Oppenheimer MD (red), additive/non-additive CSA CHARMM force fields (green/purple) and time evolution of charges assigned to the selected atoms from salicylic acid (part c).

[1] R. F. Nalewajski and J. Korchowiec, *Charge Sensitivity Approach to Electronic Structure and Chemical Reactivity*, World Scientific Publishing, Singapore, 1998.

[2] A. Stachowicz, J. Korchowiec *J. Struct. Chem.* **2012**, 23, 1449-1458.

[3] A. Stachowicz, M. Rogalski, J. Korchowiec, *J. Mol. Model.* **2013**, 19, 4163-4172.

[4] A. Stachowicz, J. Korchowiec, *J. Comput. Chem.* **2013**, 34, 2261-2269

Development of highly-accurate approximate scheme for computing charge transfer integral

Anton Pershin and Péter G. Szalay*

Laboratory of Theoretical Chemistry, Institute of Chemistry, Eötvös University, P.O. Box 32, H-1518, Budapest 112, Hungary, szalay@chem.elte.hu

Charge transfer integral is a keystone parameter, which is required by various theoretical models to describe the charge transport properties, e.g. in organic semiconductors. Our goal is to calculate this important property with high level ab initio techniques, such as equation-of-motion Coupled Cluster theory. The cost of such calculation prevents us, however, from obtaining a full representation of this quantity along a large range of geometry parameters. Therefore, in this work, we develop a novel approximate scheme based on Taylor expansion to calculate the geometry dependence of the transfer integrals. Here the required derivatives can be calculated at the ab initio level of choice. By applying our computational strategy to a case of hole transport in ethylene dimer, we show that for a wide range of conformational changes of donor-acceptor complex the approximate values of transfer integrals are in perfect agreement with the directly calculated values obtained at equation-of-motion Coupled Cluster theory level. Moreover, we also demonstrate that our approach outperforms the "energy split in dimer" and "fragment charge difference" methods, which are extensively used in the literature to describe this quantity.

Energetics of N–H Bond Dissociation in Diphenylamine Derivatives – Effect of Substituent and Torsional Deformation

Peter Poliak¹, Adam Vagánek¹, Vladimír Lukeš¹, Erik Klein¹

¹*Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, SK-812 37, Bratislava, Slovakia, peter.poliak@stuba.sk*

Derivatives of diphenylamine, the paraphenylenediamines, are widely used as effective antioxidants in the industry of rubber and plastics. In amine type antioxidants, N–H bond dissociation enthalpy (BDE) is one of the most important parameters in the evaluation of their antioxidant action. In our work, BDE values of 88 substituted diphenylamines were approximated from the gas-phase total electronic energies using the density functional theory, B3LYP hybrid functional in 6-311++G** basis set. The changes of the BDE value invoked by the substituent are up to 50 kJ mol⁻¹, thus extensive alteration of antioxidant activity is available. The strength of influence of the substituent on the BDE value grows in the order of *meta* < *para* < *ortho*. Presented theoretical values are in satisfactory agreement with available electrochemical experimental data giving correlation coefficient of 0.972. Results have also been compared to similar data obtained for substituted anilines^[1]. Strong correlation of BDE values with Hammett constants has been found in the case of 4-mono and 4,4'-disubstituted diphenylamine. According to the recent works on diphenylamine-type antioxidants^[2, 3, 4] and published crystallographic data^[5], the mutual benzene ring orientation could be one of the main factors altering the antioxidant activity in various solid-phase matrices. The dependence of the BDE value on the dihedral angles between the rings has been evaluated. By twisting the dihedral angle, the BDE value can alter by up to 24 kJ mol⁻¹ depending on the type, position and number of the substituents. The maxima and minima of BDE dependence are slightly shifted with the substitution too. In the case of *ortho*-substitution, the shape of the dependency is changed significantly. Presented results serve as important essentials for research and development of novel and more efficient antioxidants for common or new materials.

Acknowledgment

This work was supported by courtesy of the Slovak Grant Agency (VEGA 1/0735/13).

[1] Vagánek, J. Rimarčík, *et al.*, *Comp. Theor. Chem.* **2013**, 1014, 60-67.

[2] Z. Cibulková, P. Šimon, *et al.*, *J. Therm. Anal. Cal.* **2005**, 80, 357-361.

[3] Z. Cibulková, P. Šimon, *et al.*, *J. Therm. Anal. Cal.* **2009**, 97, 535-540.

[4] Kortišová, M. Breza, *et. al.*, *J. Mol. Struct. (Theochem)* **2005**, 723, 23-28.

[5] M.A. Rodriguez, S.D. Bunge, *Acta Cryst. E: Structure Reports Online* **2003**, 59, 1123-1125.

Surface Hopping with Arbitrary Couplings and Computation of Photoelectron Spectra Therein

Matthias Ruckebauer^{1*}, Philipp Marquetand¹, Sebastian Mai¹, Leticia González¹

¹*University of Vienna, Institute for Theoretical Chemistry, Waehringerstr. 17, 1210 Vienna, Austria*

**matthias.ruckebauer@univie.ac.at*

Surface Hopping with Arbitrary Couplings (SHARC)^[1] has been used for the investigation of the photodynamics of Cytosine including spin-orbit couplings to the excited triplet states. The results show that triplet states play a significant role in the relaxation of the keto tautomer, whereas they are less important in the enol tautomer.

(Time-resolved) photoelectron spectroscopy ((TR-)PES) has become a versatile tool for scientists in the exploration of the molecular and electronic structure.^[2-4] The interpretation of the resulting spectra relies heavily on the theoretical description of the ionization process. Consequently various approaches for the simulation of photoionization have been developed and applied.^[5-10]

We concentrate on the description of the relative one-photon ionization probability from multiple excited states using *Dyson-Orbitals*^[9] and their norm. This ansatz is intended for the on-the-fly estimation of TRPES with trajectory-based surface hopping dynamics including nonadiabatic and spin-orbit couplings within the SHARC-simulation program.

- [1] M. Richter, P. Marquetand et al, *ChemTheoComp.*, **2011**, 7, 1253-1258.
- [2] Neumark D., *AnnuRevPhysChem*, **2001**, 52, 255-277.
- [3] Bisgaard C., Stolow A. et al, *Science*, **2009**, 323, 1464-1468.
- [4] Suzuki T., *IntRevPhysChem*, **2012**, 31, 265-318.
- [5] Rozgonyi T., Glaß A., and Feurer T, *JApplPhys*, **2000**, 88, 2936-2942
- [6] Oana C. M. and Krylov A. I., *JCP*, **2009**, 131, 124114.
- [7] Guorong W., Hockett P. and Stolow A., *PCCP*, **2011**, 13, 18447-18467.
- [8] Hudock H. R., Martínez T. J. et al, *JPCA*, **2011**, 111, 8500-8508.
- [9] Spanner M., Patchkovskii S. et al, *PhysRev*, **2012**, 86, 053406.
- [10] Humeniuk A., Mitrić R. et al, *JCP*, **2013**, 139, 134104.

Molecular dynamics with non-adiabatic and spin-orbit effects applied to thiophene molecule

Marek Pederzoli¹, Jiri Pittner^{1*}

¹*J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic, e-mail: jiri.pittner@jh-inst.cas.cz*

Thiophene (thiofuran, C₄H₄S) is an important heterocyclic compound on its own and it also serves as a building block of many thiophene-based polymers, semiconductors and various photochromic materials.

The mechanism of ultrafast decay upon excitation to the S₁ and S₂ states is not fully understood and poses a very interesting problem because it involves interactions of states with different spin multiplicity.

We have recently implemented into the Newton-X program package^[1] the surface hopping on potential energy surfaces resulting from spin-orbit splitting, which allows us to treat also intersystem crossings between states of different multiplicity.

Two different versions of this algorithm were used: first one is an implementation of the SHARK scheme^[2], while the second one employs the local diabatization procedure^[3]. We compared these algorithms on the example of IBr molecule and we are currently using them to study the dynamics of thiophene, where the intersystem crossing competes with spin-conserving non-radiative processes.

[1] M. Barbatti, *et al.*, *J. Photochem. Photobiol. A* **2007**, 190, 228

[2] M. Richter, L. J. González, *et al.*, *Chem. Theory Comput.* **2011**, 7, 1253

[3] G. Granucci, M. Persico, *et al.*, *J. Chem. Phys.* **2001**, 114, 10608

Helium in chirped laser fields as a time-asymmetric atomic switch

Petra Ruth Kaprálová-Žďánská^{1,2*} and Nimrod Moiseyev^{3*}

¹Department of Radiation and Chemical Physics, Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 182 21 Prague 8, Czech Republic

²J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic, kapralova@jh-inst.cas.cz

³Schulich Faculty of Chemistry and Faculty of Physics, Technion – Israel Institute of Technology, Haifa, 32000, Israel, nimrod@tx.technion.ac.il

A switch between two bound states accomplished by chirped laser fields has been long known as the adiabatic rapid passage. Here we study the case, where the excited state for the one-photon transition is not a bound but autoionizing state^[1]. The excitation process is controlled by a very specific non-adiabatic phenomenon that does not cease even in long pulses, supposed that the change of the photon energy $\hbar\omega$ within the chirped pulse is comparable to the resonance width Γ (inverse lifetime) and the laser strength ε_0 is comparable to $\Gamma/Re\mu$, where $Re\mu$ is the real part of the transition dipole moment between the bound and resonance states. The phenomenon, which is due to the occurrence of an exceptional point in the non-hermitian Floquet Hamiltonian, results in time-asymmetric electronic dynamics, which differs for negative and positive chirped pulses, respectively (Figure 1).

As a vehicle for studying the above outlined phenomenological problem, we use full-dimensional ab initio simulations of the driven atom in strong femtosecond XUV chirped pulses with the characteristic duration from few to few hundreds of femtoseconds, the peak intensities ranging from GW/cm² to PW/cm², and the wavelengths of about tens of nanometers. The highlights of our methodology include an efficient quantum dynamical method based on composing the exact solution from the more easily calculated Floquet states^[1,2]; a truncation scheme for the basis set of the field-free states based on the use of complex scaling for the classification of the field-free spectrum^[2]; and last but not least the use of unusually large series of Gaussian basis sets which have been optimized up to the spectroscopic precision for energies of the ground up to the lower Rydberg states ($n = 5 - 7$)^[2,3].

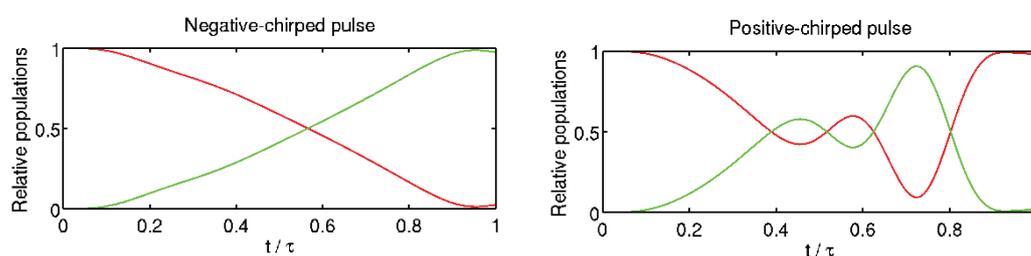


Figure 1: Development of populations of the helium ground state (red) and $2\ ^1P^{(0)}(a)$ ($2s2p$) autoionizing state (green), respectively, during 50 fs intense chirped pulses of $120\ \text{TW}/\text{cm}^2$ and $\lambda = 20.61 \pm 0.02\ \text{nm}$.

While the negative-chirped pulse leads to a complete population switch (left), the same but positive-chirped pulse displays no switch of populations at all (right).

[1] P. R. Kapralova-Zdanska and N. Moiseyev, *Helium in chirped laser fields as a time-asymmetric atomic switch*, the *Journal of Chemical Physics*, accepted.

[2] P. R. Kapralova-Zdanska, J. Smydke, and S. Civis, the *Journal of Chemical Physics* **2013**, 139(10), 104314.

[3] P. R. Kapralova-Zdanska and J. Smydke, the *Journal of Chemical Physics* **2013**, 138(2), 024105.

Study of structural phase transitions in crystals by ab initio metadynamics simulations

Roman Martoňák

Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina F2, 842 48 Bratislava, Slovakia,
martonak@fmph.uniba.sk

I will present in the talk a review of principles and applications of the metadynamics-based algorithm for simulation of structural phase transitions in crystals [1,2,3]. The technique is based on the generic discrete metadynamics algorithm [4] and uses the supercell matrix as collective variable driving the system from one crystal structure to another, following low Gibbs free-energy pathways. By iteratively constructing a biasing potential allowing crossing of barriers this approach eliminates the need for substantial overpressurization typically needed in constant-pressure MD simulations. This results in more realistic transformation mechanisms as well as substantially improved predictive power, in particular in combination with ab initio MD simulations. The algorithm has been successfully employed to study of pressure-induced structural transformations in a number of materials (for review, see Ref. [3]). I will illustrate the application of the algorithm to several inorganic crystals, in particular CO₂[5], Ca[6], BN[7] and MoS₂[8].

References:

- [1] R. Martoňák, A. Laio, and M. Parrinello: Phys. Rev. Lett. **90**, 075503 (2003)
- [2] R. Martoňák, D. Donadio, A. R. Oganov and M. Parrinello: Nature Materials **5**, 623 (2006)
- [3] R. Martoňák, Eur. Phys. J. B **79**, 241–252 (2011)
- [4] A. Laio and M. Parrinello, PNAS **99**, 12562 (2002)
- [5] J. Sun, D. D. Klug, R. Martoňák, J. A. Montoya, Mal-Soon Lee, S. Scandolo and E. Tosatti, PNAS **106**, 6077 (2009)
- [6] Yansun Yao, Dennis D. Klug, Jian Sun and Roman Martoňák, Phys. Rev. Lett. **103**, 055503 (2009)
- [7] Liliana Hromadová and Roman Martoňák, Phys. Rev. B **84**, 224108 (2011)
- [8] Liliana Hromadová, Roman Martoňák and Erio Tosatti, Phys. Rev. B **87**, 144105 (2013)

DFT studies of camptothecin in solutions

Martin Breza^{1*}

¹Department of Physical Chemistry, Slovak Technical University, Radlinského 9, SK-81237 Bratislava, Slovakia, martin.breza@stuba.sk

Camptothecin (CPT), (S)-4-ethyl-4-hydroxy-1H-pyrano[3',4':6,7]-indolizino-[1,2-b]-quinoline-3,14-(4H,12H)-dione, is a potent anticancer drug. The biologically active CPT lactone form (stable at pH < 5.5) hydrolyses under biological conditions and converts to its inactive carboxylate form (Fig. 1). Experimental UV/Vis spectrum of CPT lactone in water exhibits two strong ($\lambda_1 = 369$ nm and $\lambda_2 = 354$ nm of comparable heights) and one weak ($\lambda_3 = 334$ nm) spectral bands in the problematic 300-400 nm region.^[1] TD-DFT//PCM(B3LYP/6-31G*) calculations of CPT lactone in water reproduce quite well the experimental λ_1 and λ_3 bands, but never showed the λ_2 band. Sanna *et al.*^[1] explained this band by the formation of one or more hydrogen bonds between the D ring C=O site and one or more water molecules. As the height of the λ_2 absorption band in the solvents with the lower ability of hydrogen bonds formation must be lower than the λ_1 one, this theory is in contradiction with our previous UV/Vis spectral study^[2] of CPT lactone in dimethylsulfoxide solutions. Despite vanishing water content, the λ_2 absorption band was by ca 20% higher than the λ_1 one.

Based on TD-DFT//PCM(B3LYP/cc-pVDZ) calculations in toluene, acetone, ethanol, acetonitrile, dimethylsulfoxide and aqueous solutions, we have explained the λ_2 band by CPT lactone π -dimers formation.^[3] Even better agreement with experimental UV/Vis spectra can be obtained for CPT lactone π -trimers and π -tetramers.^[4] According to our calculations, H-bonded CPT lactone dimers are more stable than the π -dimers. On the other hand, the π -dimers enable the formation of higher aggregates and so the above equilibrium is reversed. The CPT carboxylate cannot form π -dimers.

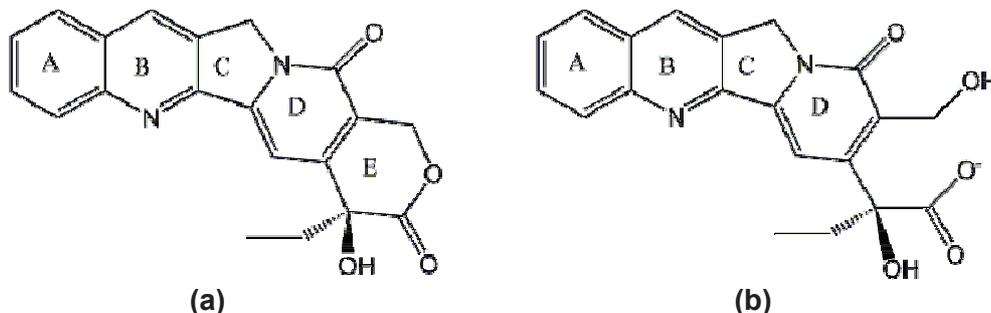


Figure 1: Molecular structure of CPT (a) in neutral lactone form and (b) in carboxylate anionic form.

This study was financially supported by Scientific Grant Agency VEGA (contract No. 1/0327/12) and Research and Development Agency of the Slovak Republic APVV (contract No. APVV-0202-10).

[1] N. Sanna, G. Chillemi, *et al.*, *J. Phys. Chem. B* **2009**, 113, 5369-5375.

[2] V. Brezová, M. Valko, *et al.*, *J. Phys. Chem. B* **2003**, 107, 2415-2325.

[3] D. Dvoranová, M. Bobeničová, *et al.*, *Chem. Phys. Lett.* **2013**, 580, 141-144.

[4] M. Breza, *Chem. Phys. Lett.* (submitted)

The role of repulsive interaction in the dimol emission of oxygen

Attila Tajti,[†] György Lendvay,[‡] and Péter G. Szalay[†]

[†] *Institute of Chemistry, Eötvös Loránd University, Budapest, Hungary, tat@chem.elte.hu*

[‡] *Institute of Materials and Environmental Chemistry,*

Research Centre for Natural Sciences of the Hungarian Academy of Sciences, Budapest, Hungary

The peculiar red light emitted by singlet molecular oxygen is a textbook example of chemiluminescence. The emitted energy is about twice that of the spin-forbidden transition. This so-called dimol emission is known to require the presence of two singlet oxygen molecules. Although the phenomenon is experimentally well characterized, theoretical studies suggest that the van der Waals interaction is weak and no long-lived complex is formed. Based on high-level *ab initio* calculations we show that even if formed, the complex could not emit light because in the bound domain of the dimer the oscillator strength is negligible. Instead, the calculated emission probability increases at smaller intermolecular separations where, however, the interaction is repulsive. We propose that the emission occurs “on-the-fly” during a collision when the system also accesses the repulsive part of the potential energy surface where the oscillator strength is relatively large.

CONNECTIONS 2000 KFT.

POSTER SESSION „A”

22 September, Monday

On the nature of N-oxo bond

Marlena Łukomska^{1*}, Agnieszka Rybarczyk-Pirek¹, Mirosław Jabłoński², Marcin Palusiak¹

¹Department of Structural and Theoretical Chemistry, Faculty of Chemistry, University of Lodz, Pomorska 163/165, 90-236 Łódź, Poland

²Department of Quantum Chemistry, Faculty of Chemistry, Nicolaus Copernicus University, Gagarina 7, 87-100 Toruń, Poland
mlukomska@uni.lodz.pl

The aim of the study was analysis of noncovalent interactions between pyridine *N*-oxides (Lewis bases) and Lewis acids. However, analysis of changes in electronic structure of oxygen atom in complex requires knowledge of the electronic structure of oxygen atom in isolated base molecule. Unfortunately there is not much information on this topic in the literature. Few papers on this subject do not provide complete information about the nature of *N*-oxo bond^[1].

The analysis of the structures of number of model compounds containing N-O bond was carried out. Compounds with single or double bond between nitrogen and oxygen atoms were studied for comparison. The nature of N-O bond in *N*-oxides was determined on the base of quantum chemical calculations using DFT method, NBO analysis and on the base of analysis of the topology of the electron density consistent with QTAIM theory^[2]. The results obtained from theoretical chemistry research were compared with experimental data obtained from search through CSD^[3].

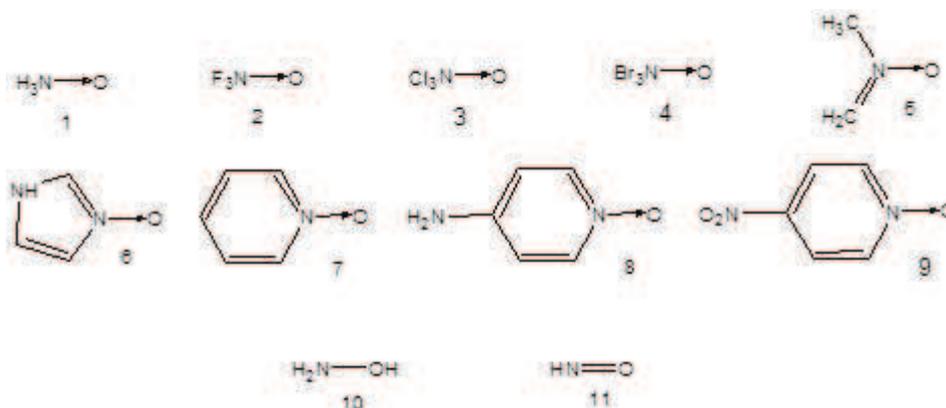


Figure 1: Structures of analyzed compounds

[1] J. A. Dobado, H. Martinez-Garcia, *et al.*, *Journal of Polintless Science* **1998**, 120, 8461-8471.

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

[3] F. H. Allen, *Acta Crystallographica Section B* **2002**, 58, 380-388.

DFT study of charged bis((μ_2 -diphenylamido)-diphenylamido-zinc(II))

Ingrid Puškárová^{1*}, Martin Breza¹

¹Department of Physical Chemistry, Slovak Technical University, SK-81237 Bratislava, Slovakia, ingrid.puskarova@stuba.sk

Binuclear transition metal complexes such as bis((μ_2 -diphenylamido)-diphenylamido-zinc(II)), $[\text{Zn}(\text{NPh}_2)_2]_2$ (Fig. 1)^[1] are possible products of the reaction of diphenylamine-type antioxidants with transition metals. We have investigated the optimal geometry and electronic structure of neutral as well as charged forms of this compound in the lowest spin state at DFT level of theory using hybrid B3LYP functional and cc-pVDZ basis sets for all atoms. Unlike the neutral and cationic forms, the anionic form of C_i symmetry is unstable and its stable structure is of C_1 symmetry. This symmetry descent may be explained by a pseudo-Jahn-Teller effect. QTAIM (Quantum Theory of Atoms-in-Molecule) analysis^[2] indicates no Zn-Zn bonding in all the systems under study. Zinc and nitrogen atomic volumes and charges imply that the stable C_1 anionic structure seems to be more reactive than the C_i symmetry one as well as than the neutral and cationic forms.

This work was supported by Science and Technology Assistance Agency of Slovak Republic under the contract No. APVV-0202-10 and by Slovak Grant Agency VEGA under the contract No. 1/0327/12.

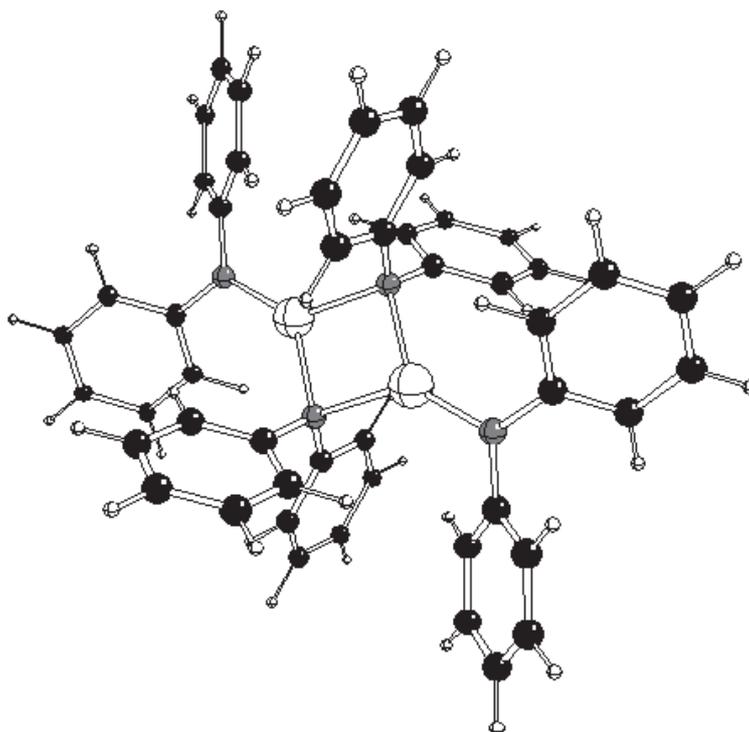


Figure 1: Optimized structure of $[\text{Zn}(\text{NPh}_2)_2]_2$ (Zn - white, C - black, N - grey, H - small white).

[1] M.A. Putzer, A. Dashti-Mommertz, *et al.*, *Z. Anorg. Allg. Chem.* **1998**, 624, 263- 266.

[2] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Clarendon Press, Oxford, 1990.

Towards ab initio dynamical simulations of atoms, molecules, and clusters in femtosecond XUV pulses

Petra Ruth Kaprálová-Žďánská^{1,2*} and Jan Šmydke^{2,1}

¹*Department of Radiation and Chemical Physics, Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 182 21 Prague 8, Czech Republic*

²*J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic, kapralova@jh-inst.cas.cz*

We are developing a methodology suitable for ab initio dynamical simulations of driven atoms, molecules, and perhaps even for small clusters in strong extreme UV fields. The method includes three key-points that we believe are crucial: (i) an efficient propagation method for many cycle chirped pulses^[1,2], (ii) the use of non-hermitian spectrum of many-electron states, and (iii) the use of one-electron Gaussian basis sets providing for a dense sampling from the core(s) up to the Rydberg phase-space^[2,3].

(i) The propagation method approximates the laser field by a number of stairs, where the laser intensity and frequency are constant and the dynamics can be expressed as evolution of a linear combination of the appropriate Floquet states^[1,2]. In many practical cases a converged dynamics is obtained for a number of stairs that is significantly smaller than the number of optical cycles within the pulse, which makes this approach far more efficient compared to a direct propagation.

(ii) The complex scaling transformation is used for two different reasons. First, it filters out outgoing electrons therefore spacially confined basis sets can be used. Second, it helps to classify the field-free states to bound, autoionizing, and ionized to different orders. Then, an algorithm for a truncation of the basis set for the Floquet states consisting of the field-free states, is derived based on such a classification^[1].

(iii) The one-electron basis sets for the driven electrons that visit regions of tens and more nanometers away from the nuclei must include the Rydberg space with a great accuracy. Another requirement to the basis set comes from the use of complex scaling – the transformed wavefunctions typically occupy a larger phase-space in the p -domain^[4]. Exponentially tempered series of Gaussian basis sets, which cover a giant phase-space compared to the standard basis sets and thus fit the outlined requirements, have been proposed^[3].

In this poster, we will discuss each of these points in detail and only briefly focus on applications.

[1] P. R. Kapralova-Zdanska, J. Smydke, and S. Civis, *the Journal of Chemical Physics* **2013**, 139(10), 104314.

[2] P. R. Kapralova-Zdanska and N. Moiseyev, *the Journal of Chemical Physics* **2014**, 141(1), 014307.

[3] P. R. Kapralova-Zdanska and J. Smydke, *the Journal of Chemical Physics* **2013**, 138(2), 024105.

[4] P. R. Kapralova-Zdanska, *the Journal of Chemical Physics* **2011**, 134(20), 204101.

Towards new nanomaterials based on $B_xC_yN_z$ molecules

Michal Novotný, Tomáš Bučko, Miroslav Urban, Ivan Černušák*

Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina CH1, Bratislava, Slovakia, cernusak@fns.uniba.sk

The aim of this work was to find an adequate DFT-vdW method and describe the properties of $B_xN_yC_z$ composite materials, which could serve as an alternative shielding material in fusion reactors. Using the program package VASP, three groups of methods have been tested: Grimme DFT-D, Tkatchenko-Scheffler methods and vdWDF methods. The quality of a given method was defined by the deviation of values in the cohesion energies and lattice parameters from the corresponding experimental values for graphite and h-BN. The best corrections of the dispersion energy were obtained from the Grimme DFT-D3BJ variant and self-consistent screening Tkatchenko-Scheffler method (DFT-TS+SCS). For the description of the suggested C(BN) composite we used the D3BJ correction because the values of cohesive energies were in better agreement with experimental values than the TS+SCS method. The calculations indicate that the suggested material should fulfill the requirements for use in fusion reactors and furthermore it should not suffer from some of the deficiencies that are present in the currently used materials.

Basis Set Optimization Method for Rydberg States: GTO Basis for Be

Jan Šmydke^{1,2}, Petra Ruth Kaprálová-Žďánská^{1,2}

¹J. Heyrovský Inst. of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i.,
Dolejškova 3, 182 23 Prague, Czech Republic

²Institute of Physics, Academy of Sciences of the Czech Republic, v.v.i.,
Na Slovance 2, 182 21 Prague, Czech Republic

jan.smydke@jh-inst.cas.cz

An approach for basis set optimization suitable for Rydberg states description that was developed in our group for helium^[1,2] has been applied to beryllium basis.

The method is based on a variational optimization of the *improved virtual* orbitals^[3], which lead to dominant configurations in the CI excited states expansion and thus more properly describe excited states than the standard Hartree-Fock orbitals.

We have also introduced the exponentially tempered Gaussian basis set scheme (ExTG)^[1,2]

$$\log_{10} \zeta_k = a 10^{-bk} + c; \quad k = 0 \dots (N-1)$$

which naturally emerged after a series of improved virtual orbitals had consecutively been optimized. Compared to the even tempered Gaussian scheme (ETG)

$$\log_{10} \zeta_k = ak + b; \quad k = 0 \dots (N-1)$$

the ExTG basis increases density of diffuse Gaussians and achieves the same quality with much smaller number of basis functions.

The resulting ExTG basis set has been used to calculate CI and EOM-CCSD excitation energies which were compared to other basis set calculations and to experiment.

[1] P.-R. Kaprálová-Žďánská, J. Šmydke, *J. Chem. Phys.* **138**, 024105 (2013)

[2] P.-R. Kaprálová-Žďánská, J. Šmydke, S. Civiš, *J. Chem. Phys.* **139**, 104314 (2013)

[3] W. J. Hunt, W. A. Goddard III, *Chem. Phys. Lett.* **3**, 414 (1969)

How do dispersion interactions influence electric properties of weakly bounded complexes?

Miroslav Medved^{1*}, Šimon Budzák¹, Adèle D. Laurent², Denis Jacquemin^{2,3}

¹ Department of Chemistry, Faculty of Natural Sciences, Matej Bel University, Tajovského 40, SK-97400 Banská Bystrica, Slovak Republic, miroslav.medved@umb.sk

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

³ Institut Universitaire de France, 103, bd Saint-Michel, F-75005 Paris Cedex 05, France

Properties of molecules in the presence of a solvent or in the solid state (e.g. in molecular crystals) can be significantly modified by intermolecular interactions between the molecules and the surrounding environment compared to their gas phase properties.^[1-3] Therefore, accurate description of the environmental effects remains of serious interest in various fields of material science (non-linear optics, nano-optoelectronics, photonics, adsorption processes, etc.) and molecular biotechnology (structure and properties of biomolecules) where the properties such as dipole moment and (hyper)polarizability appear to be essential.

In our study we first analyze the nature of intermolecular interactions for weakly interacting complex of p-aminobenzoic acid (pABA) as a push-pull type molecule with benzene (Be) by the Symmetry-Adapted Perturbation Theory (SAPT) method. Then the dependence of the interaction energy on the intersystem distance is addressed by using various DFT methods including standard hybrid (B3LYP), long-range exchange corrected (CAM-B3LYP) and selected dispersion-corrected DFT methods as well as by MP2 and its spin-component-scaled version (SCS-MP2). Most of the methods are afterwards applied to obtain longitudinal interaction-induced properties (dipole moment, dipole polarizability, and first hyperpolarizability) of the complex.

[1] R.W. Gora, R. Zalesny, *et al.*, *J. Phys. Chem. A* **2011**, 115, 4691–4700.

[2] A. Zawada, A. Kaczmarek-Kędziera, *et al.*, *Chem. Phys. Lett.* **2011**, 503, 39–44.

[3] Z. Czyznikowska, R. W. Góra, *et al.*, *Chem. Phys. Lett.* **2013**, 555, 230–234.

Solvents effect on excited-state polarizabilities with the corrected linear-response model

Šimon Budzák^{1*}, Miroslav Medved' ¹, Benedetta Mennucci², Denis Jacquemin^{3,4}

¹ Department of Chemistry, Faculty of Natural Sciences, Matej Bel University, Tajovského 40, SK-97400 Banská Bystrica, Slovak Republic, simon.budzak@umb.sk

² Department of Chemistry, University of Pisa, Via Risorgimento 35, 56126 Pisa, Italy

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

⁴ Institut Universitaire de France, 103, bd Saint-Michel, F-75005 Paris Cedex 05, France

In order to assess the environmental effects on the dipole moments and polarizabilities of electronically excited-states, we have applied a combined Polarizable Continuum Model/Time-Dependent Density Functional Theory (PCM/TD-DFT) approach on six representative chromophores.^[1] We compare polarizabilities obtained with gas phase, linear-response^[2,3] and corrected linear response^[4,5] continuum models and we also investigate the relative importance of direct (electronic) and indirect (geometric) environmental contributions for these properties. It is shown that the solvent effects on excited-state polarizabilities tend to be large and can often, but not always, be captured with the computationally efficient linear-response formalism.

[1] Š. Budzák, M. Medved', *et al.*, *J. Phys. Chem. A* **2014**, 118, 5652–5656.

[2] R. Cammi, B. Mennucci, B., *J. Chem. Phys.* **1999**, 110, 9877–9886.

[3] M. Cossi, V. Barone, *J. Chem. Phys.* **2001**, 115, 4708–4717.

[4] M. Caricato, B. Mennucci, *et al.*, *J. Chem. Phys.* **2006**, 124, 124520.

[5] S. Chibani, A. D. Laurent, *et al.*, *J. Chem. Theory Comput.* **2014**, 10, 1848–1851.

Accurate noncovalent interaction CCSD(T) calculations of large systems with off-center gaussian basis set functions

Miroslav Melicherčík^{1*}, Michal Pitoňák^{2,3*}, Vladimír Kellö², Pavel Hobza⁴, Pavel Neogrady²

¹*Department of Computer Science, Faculty of Natural Sciences, Matej Bel University, Tajovského 40, 974 05 Banská Bystrica, Slovakia, miroslav.melichercik@umb.sk*

²*Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská Dolina, 842 15 Bratislava, Slovakia, pitonak@fns.uniba.sk*

³*Computing Center of the SAS, Dúbravská cesta č. 9, 845 35 Bratislava, Slovakia*

⁴*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, v. v. i., Flemingovo nám. 2, 166 10 Praha 6, Czech Republic and Department of Physical Chemistry, Palacký University, 771 46 Olomouc, Czech Republic*

Accurate and reliable prediction of interaction energies is crucial for understanding the noncovalent binding between molecules and clusters, important in many fields of science focused on biomolecules, drug design, catalysis, etc.^[1] We have proposed a computational methodology, which would suffer from no linear dependence of atomic orbital basis set.^[2] The idea is to replace diffuse basis function by a grid of off-center gaussian s-type functions surrounding molecules in interaction. Accuracy of this approach was tested on popular data sets, such as S22 and S66.^[3]

In order to obtain results of comparable accuracy with the Dunnig-type augmented basis sets, it is necessary to optimize parameters of the grid of s-functions. This is done on selected subset of S22 test set. We have optimized the grid parameters to be used with cc-pVDZ and cc-pVTZ basis sets on MP2 level. We present the accuracy assessment of the grid approach also for higher-level correlation treatment such as MP3 (MP2.5) and CCSD(T).

This work was supported by the Slovak Research and Development Agency, contract No. APVV-0059-10 and Research project No. Z40550506 of the Institute of Organic Chemistry and Biochemistry, AS CR. Part of the calculations were performed in the Computing Centre of the SAS and HPC Center of the UMB in Banská Bystrica using the supercomputing infrastructure acquired in project ITMS 26230120002 and 26210120002 supported by the Research & Development Operational Programme funded by the ERDF.

[1] E. C. Lee and D. Kim, P. Jurečka, P. Tarakeshwar, P. Hobza and K. S. Kim, *J. Phys. Chem. A* **2007**, 111, 3446.

[2] M. Melicherčík, M. Pitoňák, V. Kellö, P. Hobza and P. Neogrady, *J. Chem. Theory Comput.* **2013**, 9, 5296.

[3] P. Jurečka, J. Šponer, J. Černý and P. Hobza, *Phys. Chem. Chem. Phys.* **2006**, 8, 1985.

A theoretical study of the kinetics of gas-phase elementary reactions containing caesium species of nuclear safety interest

Katarína Šulková^{1,2}, Laurent Cantrel^{2,4}, Florent Louis^{3,4}

¹ *Research Centre of Progressive Technologies, Faculty of Materials Science and Technology, Slovak University of Technology in Bratislava, Hajdóczyho 1, 917 24 Trnava, Slovakia, katarina.sulkova@stuba.sk*

² *Institut de Radioprotection et de Sûreté Nucléaire, PSN-RES/SAG/LETR, Centre de Cadarache Bât 702, BP3, 13115 Saint Paul Lez Durance Cedex, France*

³ *PhysicoChimie des Processus de Combustion et de l'Atmosphère (PC2A), UMR CNRS 8522, Université Lille 1 Sciences et Technologies, 59655 Villeneuve d'Ascq Cedex, France*

⁴ *Laboratoire de Recherche Commun IRSN-CNRS-Lille1 "Cinétique Chimique, Combustion, Réactivité" (C³R), Centre de Cadarache, BP3, 13115 Saint Paul Lez Durance, Cedex, France*

In case of severe accident occurring to a Pressurized Nuclear Reactor (PWR), elementary gaseous reactions involving fission products (FPs) and structural materials govern the chemical speciation at the break and thus the potential source-term in case of outside releases. Among all FPs a special attention is paid to iodine due to its ability to form volatile species as well as its high contribution to radiological consequences in case of outside releases. To predict the quantity of gaseous iodine reaching the nuclear containment building, depending on accident scenarios, the thermokinetic parameters have to be known. Resulting from literature lack in this field, we report the results of a theoretical study of the reactivity of four reactions containing caesium species (CsI, CsOH) using quantum chemistry calculations because caesium is supposed to be very reactive with respect to iodine. On the basis of these calculations including all necessary corrections to the potential energies (relativistic effects, spin-orbit effects, spin-adaptation, and vibration contributions), rate constants will be predicted using the transition state theory for the different temperatures.

Reactants, weak molecular complexes, transition states and products in the reactions as well as the energy profile at 0K have been determined by second-order perturbation theory (MP2) and DFT hybrid functionals M06-HF, M06-2X, B3LYP and MPW1K. All calculations were performed with the Gaussian09 program package. Special care was taken to determine minimum energy pathways (MEPs), performing Intrinsic Reaction Coordinate analysis (IRC) in order to check that specific TS connects the different local minima. Single-point energy calculations at all the stationary points of the reaction profile were performed using the CCSD(T) level of theory as implemented in the Gaussian program. The calculated potential energies were extrapolated to the complete basis set limit (CBS) using two extrapolation techniques proposed by Halkier and Peterson.

The obtained thermodynamic and kinetic properties (activation and reaction enthalpies, rate constants) for the reactions will be used to develop and validate a physical chemistry model implemented in the ASTEC (Accident Source Term Evaluation Code) severe accident simulation program ^[1].

[1] J. P. Van Dorselaere, C. Seropian, P. Chatelard, F. Jacq, J. Fleurot, P. Giordano, N. Reinke, B. Schwinges, H. J. Allelein, W. Luther, *Nucl. Technology* **2009**, 165, 293.

Theoretical study of Plutonium(IV) complexes formed within the PUREX process: A proposal of Plutonium surrogates.

Martin Šulka^{1,2*}, Laurent Cantrel², Valérie Vallet³

¹Research Centre of Progressive Technologies, Faculty of Materials Science and Technology, Slovak University of Technology in Bratislava, Hajdóczyho 1, 917 24 Trnava, Slovakia, martin.sulka@stuba.sk

²IRSN - PSN-RES/SAG/LETR Cadarache Bat 702, 13115 St Paul Lez Durance, France

³Université de Lille 1, Laboratoire PhLAM, CNRS UMR 8523, CNRS FR 2416, Bat P5, F-59655 Villeneuve d'Ascq Cedex, France

We present a relativistic quantum chemical study to determine the best surrogate for plutonium(IV) to be used in experimental investigations of the behavior of plutonium-nitrate-TBP in fire conditions that might occur in the nuclear fuel refining process known as PUREX. In this study geometries and stabilities of $\text{Pu}(\text{NO}_3)_6^{2-}$ and $\text{Pu}(\text{NO}_3)_4(\text{TBP})_2$ complexes were compared to that of equivalent complexes of selected elements from lanthanide and actinide series (Ce, Pr, Nd, Sm, Th, U) chosen on the basis of similar ionic radii or electronic configuration. PBE and PBE0 DFT functionals have proven to be sufficient and affordable for qualitative studies, in problematic cases even outperforming the wave-function based correlated method MP2. Based on our results, cerium(IV) appears to be the best surrogate for plutonium(IV).

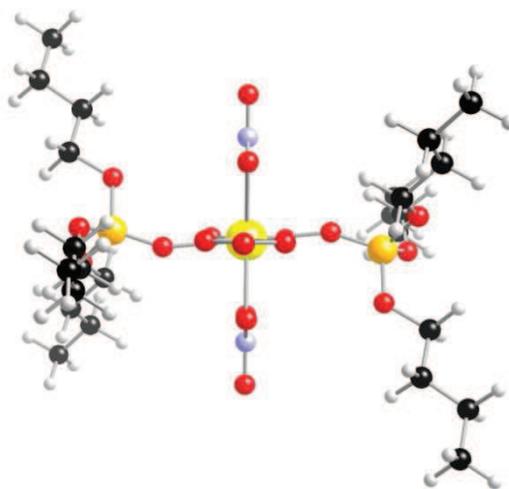


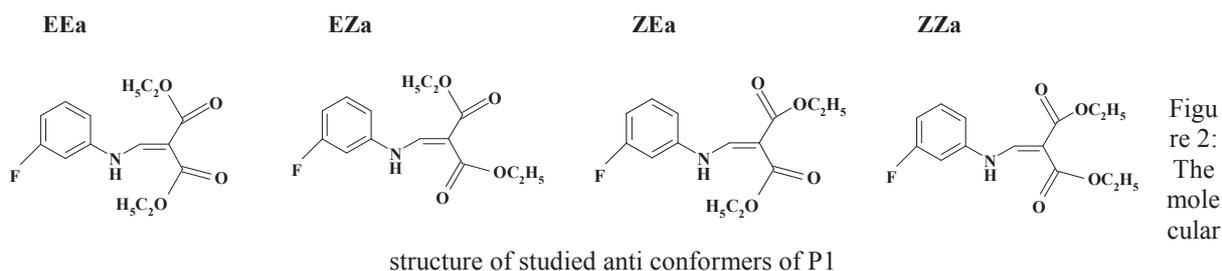
Figure 1: The structure of $\text{Pu}(\text{NO}_3)_4(\text{TBP})_2$ complex

[1] M. Šulka, L. Cantrel, V. Vallet, in preparation.

Conformational and molecular dynamics DFT study of 3-fluorophenylamino derivatives

Dorotíková Sandra*, Malček Michal, Dana Dvoranová, Bučinský Lukáš
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, sandra.dorotikova@stuba.sk

Biological activity, functionality and synthesis of (fluoro)quinolones is closely related to their precursors, *i.e.* their functional groups, conformational behavior and/or electronic structure. Herein, the theoretical study of 3-fluorophenylamino derivatives is presented. Impact of substituent; ethyl ester (P1), methyl ester (P2) and acetyl (P3) on the conformational analysis is investigated. The B3LYP/6-311++G**^[1-4] computational protocol is utilized. It is found that the intramolecular hydrogen bond N–H···O is responsible for the energetic preference of *anti* (a) conformer (*anti* position of 3-fluorophenylamino group with respect to the C=C double bond). The Boltzmann ratios of the conformers are related to the differences of the particular dipole moments and/or their dependence on the solvent polarity. The studied acetyl, ethyl ester (see Figure 1) and methyl ester substituted fluoroquinolone precursors prefer in the solvent either EZA, ZZa or both conformers equally, respectively. In order to understand the degree of freedom of rotation of the *trans* ethyl ester group, B3LYP/6-311G** molecular dynamic simulations were carried out.



Acknowledgement

This work was financially supported by APVV under the contracts No. APVV-0202-10 and APVV-0339-10 and VEGA (Project 1/0289/12). The calculations were performed at HPC center, SUT Bratislava (SIVVP project, ITMS code 26230120002, funded by the European region development funds) and Computing Centre SAS, code 26210120002 (Slovak infrastructure for high-performance computing) supported by the Research & Development Operational Programme funded by the ERDF.

- [1] A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648–5652.
- [2] P. J. Stephens, F.J. Devlin *et al.*, *J. Phys. Chem.* **1994**, 98, 11623–11627.
- [3] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, 58, 1200–1211.
- [4] R. Krishnan, J. S. Binkley, Seeger *et al.*, *J. Chem. Phys.* **1980**, 100, 12960–12973.

QM/MM assessment of the proton and electron affinities of ligated heme iron centers in various enzyme families

Anikó Lábás¹, Balázs Krámos², Tibor Szilvási¹, Julianna Oláh^{1*}

¹Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Szent Gellért tér 4., 1111 Budapest, Hungary, labasaniko@gmail.com

²Theoretical Chemistry Research Group, Research Centre for Natural Sciences of the Hungarian Academy of Sciences, Magyar tudósok körútja 2., 1117 Budapest, Hungary

Heme, an iron porphyrin, is one of the most important prosthetic groups in metalloproteins. It is the active agent of various enzyme families, e.g. if cytochrome P450s, peroxidases and globins. These proteins show striking diversity in their mode of action, and are involved in many biological processes, like drug metabolism or hormone synthesis. A remarkable feature of cytochrome P450 enzymes is their ability to oxidize inert carbon-hydrogen bonds, which keeps on inspiring the design of novel catalysts. According to the “rebound mechanism”, the generally accepted mechanism of cytochrome P450s is shown in **Figure 1**: compound I abstracts a hydrogen from the substrate to form the hydroxo complex and a substrate radical, which are rapidly recombined to generate the hydroxylated product.[1]

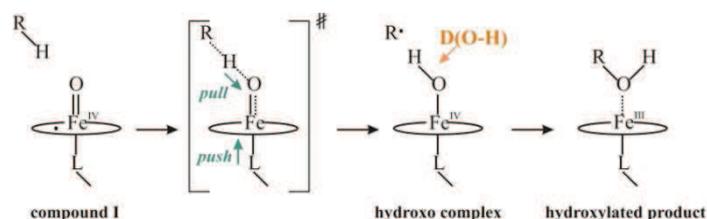


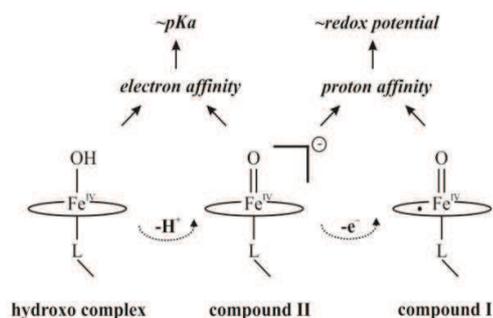
Figure 3: Rebound reaction mechanism of heme-driven oxidation reaction. The porphyrin macrocycle is represented by an ellipse, the proximal ligand is shown as “L”.

The ability of the Fe^{IV}-oxo complex to abstract a hydrogen is facilitated by the electron push effect of the proximal ligand (see **Figure 1**) and is related to the bond energy of the forming O-H bond (D(O-H)) of the hydroxo complex. This bond energy can be approximated by an empirical form,[2] containing the pKa of hydroxo complex and the one-electron reduction potential of compound I:

$$D(\text{O-H}) = 23.06 \cdot E^0_{\text{compound I}} + 1.37 \cdot \text{pK}_{\text{a,hydroxo complex}} + \text{constant}$$

The goal of this computational study is to compare the relationship between the proton and electron affinities of the heme centres of various enzyme families (CYPs, APOs, HRP, LiP) and to examine the electron donating effect of the different proximal ligands. For this, molecular dynamics simulations were carried out in the hydroxo complex state, and QM/MM geometry optimizations of a large number of protein conformations were carried out in order to collect statistically significant data that can be used to estimate the pKa and redox potential values of the various enzymes (**Figure 2**).

Acknowledgement: This work was supported by Gedeon Richter Plc. and OTKA Grant No 108721.



[1] John T. Groves, *Nat. Chem.* **2014**, 6, 89–91

[2] James M. Mayer, *Acc. Chem. Res.* **1998**, 31, 441-450

The theoretical study of charge transfer through damaged DNA duplexes

Jakub Šebera^{1,3*}, Jana Humpolíčková², Martin Hof², Irena Kratochvilová³, Ondřej Páv¹, Ivan Rosenberg¹, Radim Nencka¹, Yoshiyuki Tanaka⁴, Vladimír Sychrovský¹

¹*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo 2, CZ-166 10 Prague 6, Czech Republic, sebera@uochb.cas.cz*

²*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-182 23 Prague, Czech Republic*

³*Institute of Physics, Academy of Sciences of the Czech Republic, V.v.i, Na Slovance 2, CZ-182 21 Prague 8, Czech Republic*

⁴*Graduate School of Pharmaceutical Sciences, Tohoku University, 6-3 Aza-Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8578, Japan*

We calculated the charge transfer efficiency for donor-acceptor pairs in DNA duplexes containing damaged nucleosides. The donor was 2-aminopurine (Ap) while the acceptor was guanine (G), 8-oxoguanine (OxoG) or 2,6-diamino-4-oxo-5-formamidopyrimidine (FapyG). The OxoG and FapyG are mutations of normal guanine that occur owing to interaction of DNA with free radicals. The human 8-oxoguanine DNA glycosylase 1 (hOGG1) repair enzyme that performs excision of damaged bases, however, the excision mechanism is currently unknown. Recently, we proposed new catalytic scheme for hOGG1 enzyme.^[1] In the current study we wanted to find out whether the base excision by hOGG1 could be in principle monitored in real time employing fluorescence spectroscopy. In our previous studies on charge transfer the calculated donor – acceptor coupling integrals described successfully modulation of charge transfer efficiency that was measured in DNA.^[2,3] In particular, the coupling integrals described quenching of fluorescence radiation from 2-aminopurine by guanine in relation with the hole transfer from Ap to G.^[2,3] The coupling integrals in the current study were calculated for DNA segment including Ap-T-T-X (X = G, OxoG, and FapyG, T = thymine) by employing the B97D3 DFT functional, def2-SVP basis set, and COSMO implicit solvent of water. The calculated coupling integrals showed that guanine is better quencher than OxoG or FapyG. The results indicated that experimental detection of damaged nucleosides within DNA duplex employing fluorescence spectroscopy is possible.

Acknowledgements: This work was supported by the Grant Agency of the Czech Republic 13-27676S. Y.T. and V.S. acknowledge the Young Investigator's Grant of the Human Frontier Science Program (HFSP). V.S. and Y.T. were supported by Daiichi-Sankyo Foundation of Life Science and the Invitation Fellowship for Research in Japan (Short-Term) from JSPS. The access to the MetaCentrum computing facilities is appreciated.

[1] J. Šebera, *et al.*, *Journal of Physical Chemistry B* **2012**, 116, 12535–12544.

[2] I. Kratochvilova, M. Vala, *et al.*, *Biophysical Chemistry* **2013**, 180, 127-134.

[3] I. Kratochvilova, M. Golan, *et al.*, *Journal of Physical Chemistry B* **2014**, 118, 5374–5381.

Theoretical study of ion mobility in nitrogen gas

Ján Matúška¹ and Stanislav Biskupič¹

¹*Institute of Physical Chemistry and Chemical Physics, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic, matúška@stuba.sk*

Different ions have different drift velocities as they drift in a drift gas in a weak homogeneous electric field. This fact is used to separate ions in the method called Ion Mobility Spectrometry (IMS). Drift of ions is described by their mobility.

The ion mobility in drift gas in weak homogeneous electric field is calculated by equation^[1,2]:

$$\mu = \frac{3}{8} \sqrt{\frac{\pi k T}{2 m_r}} \frac{q}{p \Omega(T)} \quad (1)$$

where m_r is the reduced mass of the studied ion and molecule of the drift gas, T is the temperature of the drift gas, p is the pressure of the drift gas, q is the ion charge, $\Omega(T)$ is the collision cross section between ion and molecule of the drift gas and k is the Boltzmann constant. The collision cross section is obtained by Monte Carlo numerical integration of the classical mechanical collision integral. The dependence of the scattering angle on the initial condition is determined by the numerical integration of the classical equations of motion. Both calculations are carried out in ANT 13 package^[3].

Description of the interaction between the ion and the molecule is based on the Universal forcefield^[4], accounting only for dipole-dipole interaction between elements. The theory of Stone^[5] is used to describe interaction between charge on the ion and induced dipole generated on the nitrogen molecule.

The mobility of three ions in nitrogen is investigated. First studied ion is NO_3^- . The calculated mobility is compared to measured value^[6] and to the value predicted by the polarization limit theory^[1]. The mobility of the other two ions (CO_3^- , N_2O_2^-) is compared to measurements and polarization limit theory too. Moreover, they are compared to each other. Polarization limit theory predicts the same mobility for ions CO_3^- , N_2O_2^- , because they have almost the same mass. However, the measurements have shown that the mobilities are different.^[7,8]

This work is supported by the Slovak Grant Agency VEGA, project Nr. V-1/0327/12. 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] E.A. Mason, E.W. McDaniel, *Transport Properties of Ions in Gases*, Wiley, New York, **1988**.

[2] G. A. Eiceman, and Z. Karpas, *Ion Mobility Spectrometry*, CRC Press, **2004**.

[3] Z.-H. Li, A. W. Jasper, *et al.*, ANT 2013, University of Minnesota, Minneapolis, **2013**

[4] A.K. Rappe, C.J. Casewit, *et al.*, *J. Am. Chem. Soc.* **1992**, 114, 10024-10035.

[5] A. J. Stone, *The Theory of Intermolecular Forces*, Oxford University Press, **1997**.

[6] L. A. Viehland, D. W. Fahey, *J. Chem. Phys.*, **1983**, 78, 435-441.

[7] F. L. Eisele, M. D. Perkins and E. W. McDaniel, *J. Chem. Phys.*, **1980**, 73, 2517-2518

[8] J. de Urquijo, J. V. Jovanović, *et al.*, *Plasma Sources Science and Technology*, **2013**, 22, 025004.

Properties of small and medium sized beryllium clusters containing hydrogen

Daniel Labanc¹, Michal Pitoňák^{2,3}, Ivan Černušák², Pavel Neogrady²,

1Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences,
Comenius University,

Mlynská Dolina, 842 15 Bratislava 4, Slovak Republic

2EURATOM/CU, Department of Physical and Theoretical Chemistry,
Faculty of Natural Sciences,

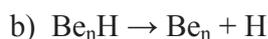
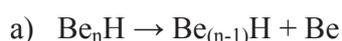
Comenius University, Mlynská Dolina, 842 15 Bratislava 4, Slovak Republic

3Computing Center of the Slovak Academy of Sciences, Dúbravská cesta č. 9,
845 35 Bratislava, Slovak Republic

Abstract

We present results of theoretical investigation of the stability and ionization potentials of small and medium sized beryllium clusters, Be_{2-12} and beryllium clusters containing hydrogen atom, Be_nH where n varies from 7 to 12. Be_{2-12} clusters are homonuclear so their stability is sufficiently represented by the binding energy D_e calculated per atom. The knowledge of this quantity offers a possibility of calculating more complex energetic effects, such as destruction or fusion of the beryllium clusters and adding or detaching a beryllium atom. Reactions of our interest are mostly those where single atom of beryllium or hydrogen atom detaches from original structure to form smaller cluster.

The following schemes represent the reactions mentioned above.



References

- [1] Adamowicz L, Bartlett R J and Sadlej A J **1988** J. Chem. Phys.
- [2] Sulka M. Pitonak M., Neogrady P. and Urban M **2008** Int. J. Quant. Chem
- [3] Srinivas S and Jellinek J **2004** J. Chem. Phys.
- [4] R. A. Kendall, T. H. Dunning Jr. and R. J. Harrison, J. Chem. Phys, **1992** 96, 6796.
- [5] A. J. Sadlej, M. Urban, J. Mol. Struct. (THEOCHEM), **1991**.
- [6] J. Wang, G. Wang and J. Zhao, J. Phys. Condens. Matter **2001**,13, 753

Bonding character of small Au clusters with lone-pair ligands

Tomáš Rajský¹, Miroslav Urban^{1,2}*

¹*Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina, SK-842 15 Bratislava, Slovakia, rajsky.tomas@gmail.com;*

²*Institute of Materials, Faculty of Materials Science and Technology, Slovak University of Technology, SK-917 24 Trnava, Slovakia, urban@fns.uniba.sk*

Recently [1], we analyzed interaction energies ΔE of complexes of Cu, Ag, and Au and a series of lone-pair ligands (ML complexes). Exceptional stability of AuL complexes is due to large relativistic enhancement of the electron affinity (EA) of Au. Along with the electron affinity of a metal we link the pattern of interaction energies in ML complexes with ionization potentials (IPs) of ligands. Strong interaction with P containing ligands is attributed to their lower IP and the lone pair \rightarrow metal electron donation accompanied with the back-donation characteristic for P containing ligands. Energy data are supplemented with the Natural Bond Orbital (NBO) analysis. Density Functional Theory (DFT) computations with the PBE0 functional provide correct pattern of interaction energies when compared with benchmark CCSD(T) results. Au clusters exhibit oscillatory pattern of EA's [2]. Our recent calculations of interactions of small Au₁₋₇ clusters with selected ligands show that for odd (open-shell) clusters the order of ΔE 's is similar as for AuL complexes. Higher ΔE 's are calculated for odd Au_n clusters having high EA's and P-containing ligands (Fig. 1). The mechanism of interactions of even closed shell Au_n clusters with ligands is different. The question remains how these findings can be extrapolated to metal – ligand nanostructures.

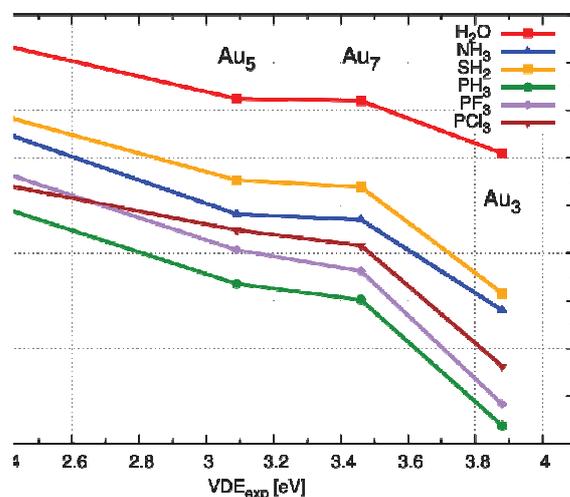


Fig. 1. Correlation of ΔE of odd Au_n-L clusters with vertical detachment energies of a ligand.

Acknowledgments: This work was supported by the Slovak Research and Development Agency, contract No. APVV-0059-10, and the Grant Agency VEGA, contract 1/0770/13. Support from EURATOM, contract No.FU07-CT-2006-00441 is also gratefully acknowledged.

References:

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

[2] B. Assadollahzadeh, P. Schwerdfeger, *J. Chem. Phys.* **2009**, 131, 064306.

The nature of binding of Zn, Cd and Hg metal atoms to benzene and coronene

Jaroslav Granatier¹, Stanislav Biskupič¹, Pavel Hobza²

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

²Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, 166
10 Prague, Czech Republic

The adsorption of aromatic molecules on metal surfaces is an important process in surface science, catalysis, molecular electronics, and spintronics. Theoretical calculations can provide essential understanding of the nature of binding between various aromatic adsorbates and metals. Consequently, studies on the interactions between graphene and metals have relied heavily on various plane-wave density functional theory (DFT) methods. However, the use of DFT approach can lead to overestimating of interaction energy.

The interaction of Zn, Cd and Hg metal atoms between benzene and coronene have been studied at the single-reference WFT and DFT levels. The dispersion nature of interaction between metal atoms and benzene/coronene lead to necessity used approaches describing correlation energy.

The WFT approaches used to include the DKH relativistic MP2, MP2.5 and CCSD(T) methods. On the other hand, the DFT calculations were provided with Grimme D3 dispersion correction. The metal atoms were modeled as being adsorbed at one of three different positions: (t) a top site directly above a C atom, (b) a bridge site above the midpoint of a C-C bond, and (h) the hollow site above the center of the aromatic ring.

This work is supported by the Slovak Grant Agency VEGA, project Nr. V-1/0327/12. 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.

Coupled Cluster Benchmark Study on Valence Singlet Excited States

Dániel Kánnár¹, Péter G. Szalay^{1*}

¹Laboratory of Theoretical Chemistry, Institute of Chemistry, Eötvös University, P.O. Box 32, H-1518, Budapest, Hungary, szalay@chem.elte.hu

Proper description of excited states by theoretical methods has been always paid great attention. Recently, even the characterization of the excited states of the building blocks of DNA became possible.^[1] In our study, benchmark results are presented on singlet excited states and the corresponding oscillator strength of 28 organic molecules calculated by Coupled Cluster methods.^[2] The accuracy of the members of hierarchy CC2–CCSD–CC3–CCSDT has been analyzed. For the nucleobases, also the non-iterative triples methods, CCSDR(3) and EOM-CCSD(T) tested against the CC3 method. The results show that CCSD more systematic than CC2, however the former gives larger mean error (0.2 eV) with respect to the CC3 values, while the latter's error is close to zero (Figure 1).

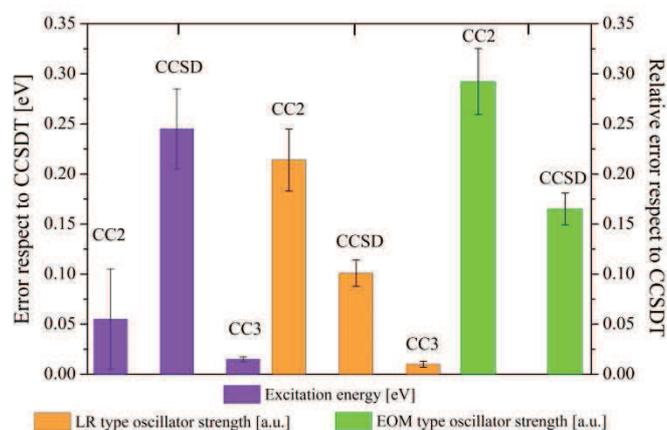


Figure 1: Mean and standard deviation of the excitation energies (eV) and both types of oscillator strength obtained at CC2, CCSD and CC3 levels with respect to the CCSDT values

The standard deviation for CCSD is smaller, however, in the case of uracil, surprisingly large error of the excitation energies have been found for two of the four lowest $n - \pi^*$ transition. Even the non-iterative triples corrections (CCSDR(3) and EOM-CCSD(T)) can not balance this failure of the underlying CCSD.

The LR (Linear Response) and EOM (Equation of Motion) type oscillator strengths have also been compared at both CC2 and CCSD levels. In contrary to the tendency of the excitation energies, CC2 gives larger error with respect to the CC3 method, but qualitatively still correct. The LR style oscillator strength is more accurate, however, the difference between the two types of oscillator strength is only 1–2% in case of CCSD.

[1] P. G. Szalay, *Int. J. Quantum Chem.* **2013**, 113, 1821 - 1827

[2] D. Kánnár, P. G. Szalay, *J. Chem. Theory Comput.* **2014**, doi: 10.1021/ct500495n (in press)

CONNECTIONS 2000 KFT.

POSTER SESSION „B”

24 September, Wednesday

Intermolecular interactions in organometallic crystal

Wojciech Jankiewicz¹, Rafał Podeszwa¹

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

CuJN₂₄- (5-chloro-7-carboxy-2-methyl-N,O-quinoline)bis(triphenylphosphine)copper(1) is a recently obtained complex consisting of two phenylphosphines and quinoline derivative. We performed a theoretical study of intermolecular interactions between molecules in this system and of the effects of changes in the intramonomer geometries. Empirically obtained coordinates by X-ray crystallography were used as a starting point to perform computations based on density functional theory (DFT) and second-order Møller-Plesset perturbation theory (MP2). Due to size of the molecule (92 atoms), the use of the wavefunction-based computation methods was very challenging. The DFT results for the interaction energies were corrected by empirical dispersion contribution (DFT-D). The results obtained allowed us to establish the most important configurations of interacting monomers in the examined system and an estimate of the cohesion energy of the crystal. We found that the dominant stabilising role in the crystal is played by the dispersion forces. The non-dispersion part of the interaction energies is either small or repulsive. By comparing the monomer energy from the crystal geometry with the energy of a theoretically-optimized one, we also found a very large difference of a few hundred kcal/mol showing that the locations of hydrogen atoms from the X-ray data positions were inaccurate. Therefore, it is necessary to compare the results with the energy values calculated with theoretically-optimized hydrogen positions.

π-ELECTRON CONJUGATION IN POLYENES

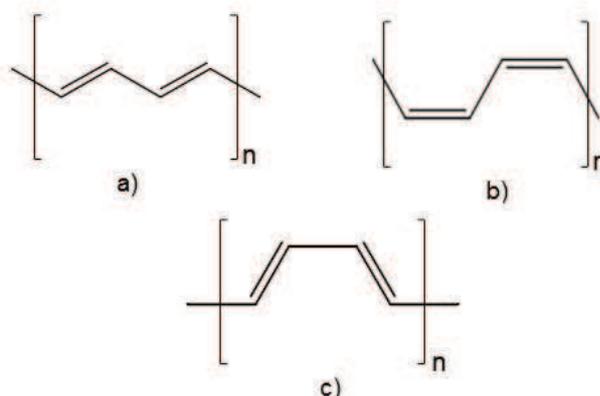
A. Sieradzka, M. Palusiak

*Faculty of Chemistry, University of Lodz
Pomorska 163/165, 90-236 Lodz
anetas@uni.lodz.pl*

One of the most important linear polymer is polyacetylene, which is the subject of many studies, both experimental and theoretical. Polyacetylene is composed of long chains, in which the carbon atoms are bonded with alternate double and a single bonds. It exists in two forms, *cis* and *trans*, of which there are two variations of the *cis* form, that is, *cis-transoid* and *trans-cisoid*.

The purpose of our study was to estimate the degree of delocalization of π-electrons in polyacetylene (in the form of an infinite chain) and its analogs with a finite number of bonds. In the first stage of the study the geometry optimization was performed in Gaussian09 program (DFT-B3LYP/6-31+G(d) level of theory), and then the degree of delocalization was estimated as a function of the length (number of C atoms) of the hydrocarbon chain (up to 42 carbon atoms). The measure used to calculate the degree of delocalization was the structural aromaticity index HOMA (Harmonic Oscillator Model of Aromaticity)^[1]. The obtained energy parameters indicate the *trans* form as the one being the most stable (thermodynamically). When considering the two *cis* forms, it turned out that the more stable is the *cis-transoid* one.

The next step was to carry out the periodic calculations, which were performed using a B3LYP functional and a series of various basis sets. The use of different basis sets allowed to estimate the effect of level of calculations on the final result achieved. Obtained results are consistent with experimental data available in the CSD^[2].



Isomeric forms of polyacetylene a) trans b) cis-transoid c) trans-cisoid.

[1] T.M. Krygowski, Journal of Chemical Information and Computer Sciences (1993) 33-70.

[2] F. H. Allen, Acta Crystallographica., Section B (2002) B58, 380-388.

Dynamic Polarizability of Carbazole and Fluorene

Tadeusz Pluta^{1*}, Joanna Kauczor²

¹*Institute of Chemistry, University of Silesia, Szkolna 9, 40-006 Katowice, Poland,
tadeusz.pluta@gmail.com

²*Department of Physics, Chemistry and Biology, University of Linköping, 581 83 Linköping,
Sweden*

Carbazole and fluorene are aromatic molecules with tricyclic structure (Fig. 1a, 1b). Dipole moment and components of the frequency dependent polarizability tensor $\alpha(\omega)$ have been determined for these molecules by means of the DFT calculations. In order to treat frequency dependence of polarizability properly in the vicinity of the electronic resonances the Complex Polarization Propagator method^[1] has been employed. The essential point is to introduce empirical parameter γ describing the limited lifetime of the electronic excited states and to replace frequency by its generalized complex form:

$\omega \rightarrow \omega + i\gamma$. The presence of divergent terms in the denominators of the standard Sum-Over-States (SOS) formalism is thus avoided. The Pol basis set specifically developed for the electric properties calculations and its more compact Z3Pol version^[2] were used in all calculations. Dalton 2013 suite of programs^[3] has been used in this work.

It has been found that the polarizability components for both studied molecules are very close. Static polarizability has been also determined by the Coupled Cluster (CCSD) calculations. The performance of DFT calculations of the dipole moments and polarizability tensor compared to the CCSD results is found to be very good. Good performance of the compact Z3Pol basis for the polarizability calculations should also be noted.

Dynamic polarizability of carbazole evaluated at frequencies close to the resonance obtained at the DFT level were calculated as the first step toward modeling the Raman spectrum.

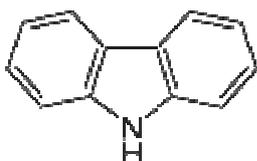


Figure 1a: Carbazole

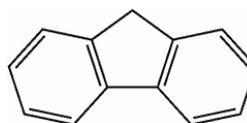


Figure 1b: Fluorene

Acknowledgements: Calculations were performed at the Wrocław Supercomputer Centre.

[1] P. Norman, D.M. Bishop, H.J.A. Jensen, J. Oddershede, *J.Chem.Phys.*, **2001**, 115, 10323, J. Kauczor, P. Norman, *J.Chem.Theory Comput.*, **2014**, 10, 2449.

[2] Z. Benkova, A.J. Sadlej, R.E. Oakes, S.E.J. Bell, *J.Comput. Chem.*, **2000**, 11, 123.

[3] DALTON2013, see: <http://daltonprogram.org>.

Calculation of the molecular integrals with the asymptotically correct correlation factor in the Gaussian basis set

Michał Siłkowski

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

Recently, a “range-separated” model of the correlation factor for explicitly correlated methods has been proposed^[1]. The virtue of this correlation factor consists in its asymptotically correct, short- and long-range r_{12} behavior smoothly connected by a switching function. Before its application to the F12 methods^[2] can be tested, all necessary matrix elements must be calculated, possibly analytically. It is a well-known fact that the application of the resolution of identity approximations in the F12 methods leads to the factorization of the many-electron integrals into two-electron ones^[2]. Precisely, six generic types of the integrals need to be evaluated analytically^{[2][3]} in a Gaussian basis. We present a general scheme for the calculation of these integrals, employing the popular McMurchie-Davidson recursive technique^[4]. Once the necessary integrals are calculated, they can be incorporated in the already available programs for the F12 methods, such as Molpro^[5], with a little or no modifications. We believe that the incorporation of the “range-separated” correlation factor will result in a significant boost in the accuracy of the F12 calculations.

[1] M. Lesiuk, B. Jeziorski, R. Moszyński, *J. Chem. Phys.* **139**, 134102 (2013)

[2] A. J. May, F. R. Manby, *J. Chem. Phys.* **121**, 4479, (2004);
S. Ten-no, *Chem. Phys. Lett.* **398**, 56 (2004)

[3] C. C. M. Samson, W. Klopper, T. Helgaker, *Comp. Phys. Commun.* **149**, 1 (2002)

[4] L. E. McMurchie, E. R. Davidson, *J. Comp. Phys.* **26**, 218 (1978)

[5] H. J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, *WIREs Comput Mol Sci* **2**, 242-253 (2012); MOLPRO, version 2012.1, a package of ab initio programs, H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, and others, see <http://www.molpro.net>.

Closer inspection of the reaction of excited oxygen ion with methane

Jan Hrušák*, Ivana Paidarová

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
jan.hrusak@jh-inst.cas.cz

Theoretical investigation of collisions of methane molecules with excited ionic oxygen are indispensable for understanding of chemistry of Saturn's moon Titan atmosphere. They are complementary to the experiments and to the findings of space craft Cassini^[1]. We are looking for an efficient computational strategy that allows chemically reasonable and computationally feasible treatment of the CH_4/O^+ system. We intend to develop multilevel approaches to non-adiabatic molecular dynamics simulations that will be implemented in a software package combining semi-classical methods for dynamics modeling and quantum chemistry methods for underlying electronic structure calculations.

In the first stage of our research we focus on the construction of potential energy surfaces using a smart concept of “chemically reasonable intuitive reaction coordinate”^[2] (see Fig.1) and on the analysis of surfaces of electric dipole and transition moments of the CH_4/O^+ system in several excited electronic states. The relaxed guided scan was performed using MCSCF method for the particular reaction $[\text{CH}_4 + \text{O} \rightarrow \text{CH}_3 + \text{OH}]^+$. The lowest 19 electronic states of A' symmetry have been considered. In this contribution we present the calculation of the surfaces of electric dipole and transition moments. The analysis of the numerous data will help us to design the strategy for dynamical calculation.

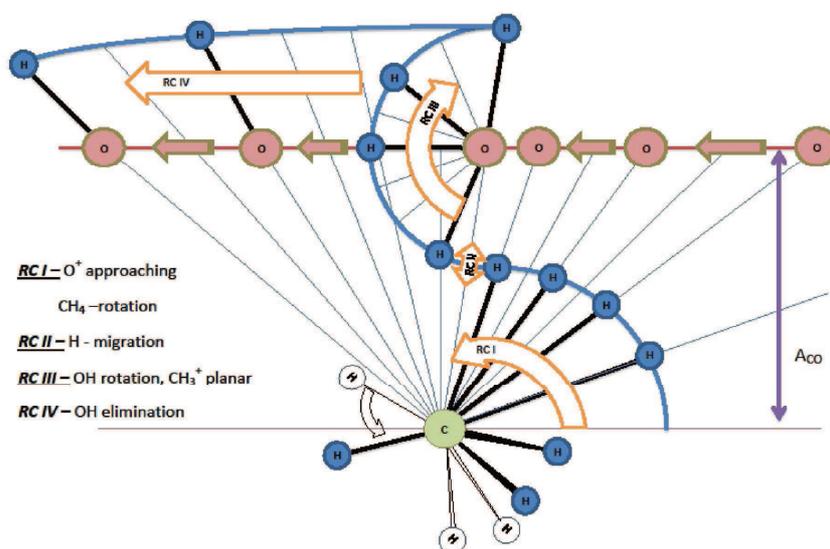


Figure 1: Schematic diagram of the “chemically reasonable intuitive reaction coordinate”. The principal movement of the oxygen is accompanied by CH₄ rotation (RC I), by hydride migration (RC II), by OH rotation (RC III), and OH departure (RC IV).

[1] B. Cunha de Miranda, C. Romanzin, S. Chefdeville, V. Vuitton, J. Žabka, M. Polášek, and Ch. Alcaraz, “Reactions of state-selected $\text{O}^+(^4\text{S}, ^2\text{D}, ^2\text{P})$ oxygen ions relevant to the chemistry of Titan's ionosphere”, lecture, Oxygen in planetary systems : chemistry of the molecule of powerful life, A COST CM-0805 WG-3 workshop, Perugia, 17-18. 9. 2012.

Noncovalent Interactions by Quantum Monte Carlo

Matúš Dubecký^{1*}, Petr Jurečka¹, René Derian², Lubos Mitas³, Pavel Hobza^{4,1},
Michal Otyepka¹

¹*Regional Centre of Advanced Technologies and Materials, Department of Physical Chemistry, Faculty of Science, Palacký University Olomouc, tř. 17 listopadu 12, 771 46 Olomouc, Czech Republic, matus.dubecky@upol.cz*

²*Institute of Physics, Slovak Academy of Sciences, 845 11 Bratislava, Slovakia*

³*Department of Physics and CHiPS, North Carolina State University, NC 27695 Raleigh, USA*

⁴*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, 166 10 Prague 6, Czech Republic*

An accurate description of noncovalent molecular interaction energies is one of the most challenging tasks in computational quantum chemistry. Typically, high-level theories like CCSD(T)/CBS have been used as a benchmark reference in order to reach a benchmark accuracy of ~ 0.1 kcal/mol. The practical use of the CCSD(T) is however fairly limited due to the rapid growth of its computational cost with the number of considered basis functions. Here we present an alternative benchmark approaches based on the the fixed-node diffusion Monte Carlo (FN-DMC) method, capable of reaching CCSD(T)/CBS reference within ~ 0.1 ^[1] and ~ 0.2 ^[2] kcal/mol, respectively, while keeping a low-order polynomial scaling feature. The tests include the A24 set of noncovalent complexes and larger complexes including: benzene dimer, benzene water, benzene methane, stacked DNA base pair, etc. The demonstrated predictive power in conjunction with the favorable scaling of the FN-DMC thus provides new opportunities for studies of the vast and important class of medium/large noncovalent complexes.

[1] M. Dubecký, P. Jurečka, R. Derian, *et al.*, *J. Chem. Theory Comput.* **2013**, 9, 4287-4292.

[2] M. Dubecký, R. Derian, P. Jurečka, *et al.*, *Phys. Chem. Chem. Phys.* **2014**, accepted (preprint at <http://arXiv.org/abs/1403.0604>).

Implementation of the LTDF-ADC(2) method

Michał Chojecki^{1*}, Tatiana Korona¹

¹*University of Warsaw, Faculty of chemistry, Quantum Chemistry Laboratory,
Pasteura 1, 02-093 Warsaw, Poland,
mhs@tiger.chem.uw.edu.pl*

We present the new implementation of the algebraic-diagrammatic construction method [1] corrected to the second order, ADC(2).

We also discuss mathematical tools allowing for enhancement of the efficiency and applicability of this implementation, such as: density-fitting approach for the evaluation of two-electron repulsion integrals and Laplace transform of the energy denominators [2, 3].

Numerical results for the molecular properties of the second order, such as excitation energies, transition moments and polarisation propagators have also been presented.

The new implementation will allow us to perform efficient studies of the electronic excited states in the vicinity of the conical intersections.

[1] A. Trofimov, J. Schirmer, *J. Phys. B.* **1995**, *28*, 2299-2324.

[2] D. Kats, D. Usvyat, M. Schütz, *PCCP.* **2008**, *10*, 3430-3439.

[3] G. Walz, D. Kats, D. Usvyat, T. Korona, M. Schütz, *Phys. Rev. A.* **2012**, *86*, 3430, 052519

Long-range corrected hybrid functionals in the symmetry-adapted perturbation theory

M. Hapka*¹, Ł. Rajchel², M. Modrzejewski¹, G. Chałasiński¹, M. M. Szczyński³

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

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

³*Department of Chemistry, Oakland University, Rochester, Michigan 48309-4477, United States*

The aim of this study is to present a performance test of optimally-tuned long-range corrected (LRC) functionals applied to the symmetry-adapted perturbation theory (SAPT). In the present variant the second-order energy components are evaluated at the coupled level of theory. We demonstrate that the Generalized Kohn-Sham (GKS) description of monomers with optimally-tuned LRC functionals is essential for the quality of SAPT interaction energy components. This is connected to the minimization of many-electron self-interaction error and exemplified by two model systems: polyacetylenes of increasing length and stretching of He_3^+ . Next we provide a comparison of SAPT approaches based on Kohn-Sham and Generalized Kohn-Sham description of the monomers. We show that LRC leads to results better or comparable with the hitherto prevailing asymptotically-corrected functionals.^[1, 2] Finally, the advantages and possible limitations of SAPT based on LRC are discussed.

[1] W. Cencek, K. Szalewicz, *J. Chem. Phys.* **2013**, 139, 024104.

[2] K. U. Lao, J. M. Herbert, *J. Chem. Phys.* **2014**, 140, 044108.

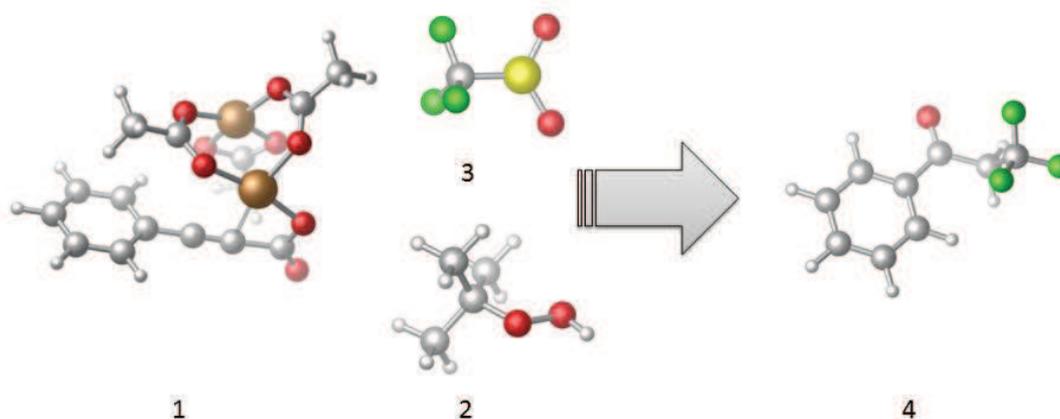
Computational study of a copper-catalyzed radical reaction

Tamás Bihari¹, Balázs Tóth², Zoltán Novák², András Stirling¹

¹*Institute of Organic Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar tudósok körútja 2., H-1117, Budapest, Hungary*

²*Department of Organic Chemistry, Institute of Chemistry, Eötvös University, Pázmány Péter stny. 1/A, H-1117, Budapest, Hungary*

A copper-catalyzed decarboxylative trifluoromethylation of an unsaturated carbonic acid (3-phenylpropionic acid (1) to 3,3,3-trifluoro-1-phenylpropane-1-one (4)) has been performed by our experimental partners. The incorporation of a CF₃ group in a pharmacological candidate molecule usually results in significant enhancement of its lipophilicity, binding selectivity and metabolic stability^[1].



In the experiments a stable and inexpensive solid compound, the Langlois reagent (3) has been used as incorporating agent and TBHP (2) has been also employed to form the radical CF₃ species. The aim of the present study is to elucidate the mechanism of the reaction. To this end we have explored several possible pathways and compared the free energy profiles of the reaction routes. In the poster we will show the details of the computations and interpret the experimental observations on the basis of the calculated free energy profiles.

Recent progress in the quasiparticle-based multi-reference coupled-cluster method

Zoltán Rolik, Mihály Kállay

MTA-BME “Lendület” Quantum Chemistry Research Group, Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, H-1521 Budapest, Hungary, rolik@mail.bme.hu

The purpose of this poster is to present our recent progress in the development of a quasiparticle-based multi-reference coupled-cluster (MRCC) approach. The quasiparticles are introduced via a unitary transformation which allows us to represent a complete active space reference function and other elements of an orthonormal multi-reference (MR) basis in a determinant-like form. The quasiparticle creation and annihilation operators satisfy the fermion anti-commutation relations. On the basis of these quasiparticles a generalization of the normal-ordered operator products for the MR case can be introduced as an alternative to Mukherjee and Kutzelnigg's approach^[1-2]. Based on the new normal ordering any quasiparticle-based theory can be formulated using the well-known diagram techniques. Beyond the general quasiparticle framework we focus on a possible realization of the unitary transformation. The suggested transformation has an exponential form where the parameters, holding exclusively active indices, are defined in a form similar to the wave operator of the unitary coupled-cluster approach. For the definition of quasiparticle-based MRCC approach a properly chosen principal determinant (PD) is also needed. Some options for the definition of the PD are also discussed and the various approaches are numerically compared for small systems using a pilot implementation of the new method.

[1] D. Mukherjee, *Recent Progress in Many-Body Theories* **1995**, 4, 127-133.

[2] W. Kutzelnigg, D. Mukherjee, *J. Chem. Phys.* **1997**, 107, 432-449.

Cheap and accurate DFT: Spin-Component Scaled Optimized Effective Potential method

Adam Buksztel¹, Szymon Śmiga¹, Ireneusz Grabowski¹

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

The proper description of physical and chemical properties of ordinary matter (atoms, molecules and solids) is a subject of great interest in a broad range of fields. Nowadays the most popular approach to this problem is density functional theory (DFT) within the Kohn-Sham (KS) scheme. Despite its success, the KS-DFT approach shows some severe limitations, thus it is not entirely satisfactory.

In the last decade, a large effort has been dedicated to the development of explicitly orbital-dependent functionals based on optimized effective potential (OEP) method,^[1,2,3] which can be considered as a natural extension to the standard KS-DFT procedure. The OEP approach is likewise referred to as *ab initio* DFT, since it provides a systematic way for construction a hierarchy of functionals of increasing accuracy.^[4]

The spin-component-scaled (SCS) scheme proposed by S. Grimme^[5] was recently adapted to the simplest second-order (Görling-Levy energy expression) OEP (OEP-GL2) method.^[6,7] Accuracy of the resulting OEP2-SCS family of methods is comparable to accuracy of the CCSD(T). The scaled-opposite-spin (SOS) variant seems to be the most interesting one because of the $O(N^4)$ scaling. Moreover, the OEP2-SCS are more numerically stable and free of some problems known for the OEP-GL2.

We have applied the newly developed OEP2-SOS methods to some simple atomic and molecular systems. The case of weakly interacting systems and non-equilibrium geometries is also considered. The results analysis is made in terms of the total and correlation energies, ionization potentials, HOMO-LUMO gaps and correlation potentials.

[1] I. Grabowski, S. Hirata, *et al.*, *J. Chem. Phys.* **2002**, 116, 4415-4425

[2] R. J. Bartlett, I. Grabowski, *et al.*, *J. Chem. Phys.* **2005**, 122, 034104

[3] I. Grabowski, V. Lotrich, *et al.*, *J. Chem. Phys.* **2007**, 127, 154111

[4] I. Grabowski, A. Teale, *et al.*, *J. Chem. Phys.* **2011**, 135, 11411

[5] S. Grimme, *J. Chem. Phys.* **2003**, 118, 90951

[6] I. Grabowski, E. Fabiano, *et al.*, *Phys. Rev. B* **2013**, 87, 075103

[7] I. Grabowski, E. Fabiano, *et al.*, *J. Chem. Phys.* **2014**, 141, 024113

Ultracold gas of fermions in a harmonic trap: a quantum chemical point of view

Tomasz Grining^{1*}, Monika Musiał², and Robert Moszynski¹

¹*Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland
grining@tiger.chem.uw.edu.pl*

²*Institute of Chemistry, University of Silesia, Szkolna 9, 40-006 Katowice, Poland*

The state-of-the-art *ab initio* methods of quantum chemistry have not been used yet to study the behaviour of the ultracold quantum gases. We have tackled the problem of a gas of ultracold spin-1/2 fermions with the interaction described by the contact potential (Dirac delta function) in a harmonic trap. The description of such systems and the treatment of the correlation energy constitutes a significant challenge for the community of ultracold gases. To our knowledge, only systems up to five atoms in a one-dimensional harmonic trap have been thoroughly studied¹ by the methods of direct diagonalization.

The use of the state-of-the-art *ab initio* methods of quantum chemistry allows us to treat the essential problem of fermionic gases – that is, the antisymmetry of the wavefunction – by the tools usually used in the electronic structure theory. We have employed a variety of coupled cluster methods up to CCSDTQ for precise calculations of the correlation energy in the harmonic oscillator eigenfunctions basis set. We have investigated the behaviour of the system for the different values of the interaction strength, which is a function of the scattering length and can be finely tuned by modifying the external magnetic field. Our preliminary results for a small number of particles coincide well with the analytical results for the two particles as well as the results for a higher number of particles obtained by the means of direct diagonalization.

[1] T. Sowiński, T. Grass, O. Dutta, M. Lewenstein, *Phys. Rev. A* **2013**, 88, 033607.

Adiabatic state preparation study of methylene

Libor Veis^{*}, Jiří Pittner

*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic,
Dolejšková 3, 18223 Prague 8, Czech Republic*

**libor.veis@jh-inst.cas.cz*

Quantum computers attract much attention as they promise to outperform their classical counterparts in solving certain type of problems. One of them with practical applications in quantum chemistry is simulation of complex quantum systems. An essential ingredient of efficient quantum simulation algorithms are initial guesses of the exact wave functions with high enough fidelity. As was proposed in ^[1], the exact ground states can in principle be prepared by the adiabatic state preparation method. Here, we apply this approach to preparation of the lowest lying multireference singlet electronic state of methylene and numerically investigate preparation of this state at different molecular geometries. We then propose modifications that lead to speeding up the preparation process. Finally, we decompose the minimal adiabatic state preparation employing the direct mapping in terms of two-qubit interactions.

[1] A. Aspuru-Guzik, A. D. Dutoi, *et al.*, *Science* **2005**, 309, 1704-1707.

Imidazolium-acetate ionic liquids – new possibilities?

Zsolt Kelemen,¹ Oldamur Hollóczki,¹ Barbara Péter-Szabó,² Edit Székely,²
József Nagy,³ Gábor Turczel,¹ Dénes Szieberth,¹ László Nyulászi^{1*}

1 Department of Inorganic and Analytical Chemistry

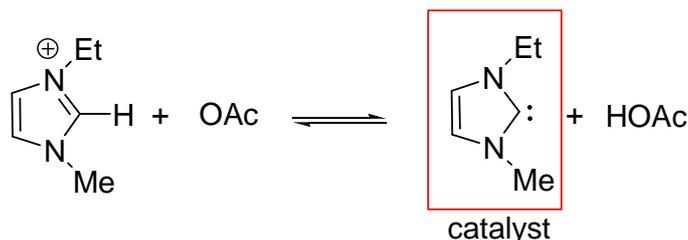
2 Department of Chemical and Environmental Process Engineering

3 Department of Organic Chemistry and Technology

Budapest University of Technology and Economics, Szt Gellért tér 4. H-1111 Budapest, Hungary

nyulaszi@mail.bme.hu, kelemen.zsolt@mail.bme.hu

Imidazolium acetate ionic liquids (eg. 1-ethyl-3-methylimidazolium acetate, EMIM-Ac) are of current interest due to their applicability in cellulose processing^[1], and carbon-dioxide absorption.^[2] A key characteristic of this type of ionic liquids is that the basicity of the N-heterocyclic carbene (NHC) (derived from the imidazolium salt by the removal of the proton at the 2-position) has comparable basicity to that of the acetate anion. However the presence of NHC was demonstrated earlier,^[3] the amount of NHC in the liquid phase still may not be enough to provide the organocatalytic activity.



Scheme 1: Formation of NHC in EMIM-Ac

The aim of this presented study to investigate the organocatalytic activity of EMIM-Ac in several reactions^[4] furthermore the behaviour of CO₂ in the IL under different conditions.

Acknowledgments: Financial support from OTKA K 105417 is gratefully acknowledged.

References:

- [1] a) Sun, N.; Jiang, X.; L., M. M.; Metlen, A.; Rogers, R. D. *ChemSusChem* **2011**, *4*, 65–73. b) Wang, H.; Gurau, G.; Rogers, R. D. *Chem. Soc. Rev.*, **2012**, *41*, 1519–1537
- [2] a) X. Zhang, X. Zhang, H. Dong, Z. Zhao, S. Zhang, Y. Huang, *Energy Environ. Sci.* **2012**, *5*, 6668 – 6681; b) F. Jutz, J.-M. Andanson, A. Baiker *Chem. Rev.* **2011**, *111*, 322–353 c) J. F. Brennecke, B. E. Gurkan, *J. Phys. Chem. Lett.* **2010**, *1*, 3459 – 3464
- [3] a) O. Hollóczki, D. Gerhard, K. Massone, L. Szarvas, B. Németh, T. Veszprémi and L. Nyulászi, *New J. Chem.*, **2010**, *34*, 3004. b) G. Gurau, H. Rodriguez, S. P. Kelley, P. Janiczek, R. S. Kalb, R. D. Rogers *Angew. Chem. Int. Ed.* **2011**, *50*, 12024 –12026 c) H. Rodríguez, G. Gurau, J. D. Holbrey, R. D. Rogers, *Chem. Commun.*, **2011**, *47*, 3222.
- [4] Z. Kelemen, O. Hollóczki, J. Nagy, L. Nyulászi *Org. Biomol. Chem.*, **2011**, *9*, 5362–5364.

Lower bounds via Löwdin's bracketing function

Zsuzsanna Tóth, Ágnes Szabados

Laboratory of Theoretical Chemistry, Eötvös University, Hungary

E-mail: tzsuzsi@coulson.chem.elte.hu

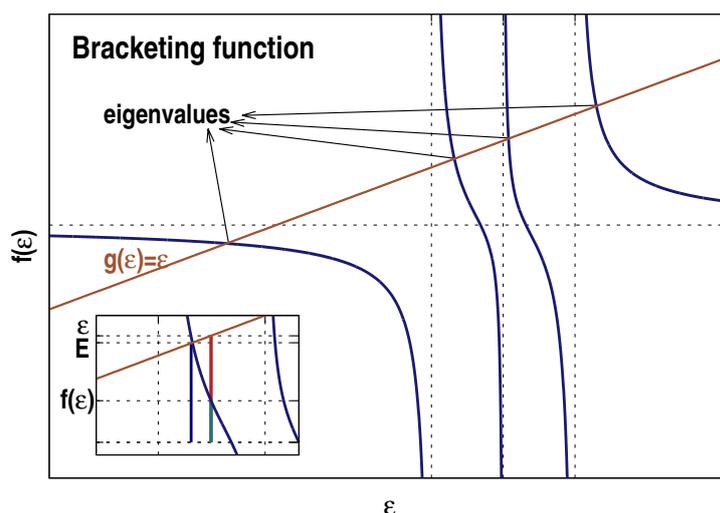
In quantum chemistry the usage of upper bounds to the energy is well spread. In contrast to upper bounds, lower bounds are barely used, because they are much more complicated and can only be applied if appropriate conditions are fulfilled.

Löwdin's bracketing function[1], $f(\varepsilon)$ gives a lower bound if the argument ε is an appropriate upper bound. In general the argument and the value of the function „brackets” at least one eigenvalue. Taking a normalised reference function φ , the bracketing function is expressed as:

$$f(\varepsilon) = \langle \varphi | H + H \frac{P}{\varepsilon - H} H | \varphi \rangle, \quad P = 1 - |\varphi\rangle\langle \varphi|.$$

A variational principle for the bracketing functions is proven. This enables to search for the wavefunction maximising the lower bound. An Eckart-type inequality holds for the wavefunction optimised this way. The Temple lower bound is derived as the special case of Löwdin's lower bound.

Calculation of the bracketing function is computationally demanding due to the operator inverse. The effect of approximate inversion is also examined.[2]



[1] P.-O. Löwdin *Phys. Rev.*, 139:A357-A372, 1965.

[2] Á. Szabados, Zs. Tóth *J. Math. Chem.*, 52:2210-2221, 2014.

Computational insights into fixation of CO₂ into RZnOH species

Adam Tulewicz^{1,2*}, Anne Milet³, Robert Moszyński¹, Janusz Lewiński²

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

²*Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland*

³*Universite Joseph Fourier, Laboratoire de Chimie Théorique 301 rue de la Chimie, 38400 Saint Martin d'Hères, France*

Carbon dioxide fixation process has attracted the attention of chemists from different fields as the structures of the active sites of the connected enzymes (eg. carbonic anhydrase) have become known. In our work the bio-inspired route of the CO₂ conversion based on the reaction with the tert-butyl zinc hydroxide will be presented. The zinc atom of the studied molecule is bonded with the hydroxide group and the organic tert-butyl group, serving as a template for the fixation process. The reaction rate should not be limited due to the values of the activation energies. Moreover, the overall energetical gain of the reaction is predicted to be negative. Our results are in a semi-quantitative agreement with recent experimental findings.

In the second part, the mechanism of the proton-transfer from the tert-butyl zinc bicarbonate to the alkyl group of the tert-butylzinc will be presented.

All calculations have been carried out with the DFT method and the 6-31++G(2d,2p) basis set. The nature of the minimas and the corresponding transition states have been checked via the frequency analysis. The IRC calculations for the reaction paths will be provided as well.

Perturbative triples correction for explicitly correlated Mukherjee's state-specific coupled cluster method

Ondřej Demel¹, Stanislav Kedžuch^{2,3}, Jozef Noga^{2,3} and Jiří Pittner¹

¹J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, CZ-18223 Prague 8, Czech Republic

²Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-84536 Bratislava, Slovakia

³Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University, SK-84215 Bratislava, Slovakia

This paper reports incorporation of the perturbative triples correction within the explicitly correlated Mukherjee's multireference coupled cluster method using the SP ansatz. In accord with the standard approximation, these corrections are not directly entered by the correlation factor amplitudes, but the explicitly correlated part of the effective Hamiltonian is included in full. The performance of the new method is tested on singlet methylene, potential curve of fluorine molecule and automerisation barrier of cyclobutadiene. It has been found that the convergence pattern of the MkCCSD(T)-F12 results with increasing basis set is improved by approximately one cardinal number, as compared to conventional MkCCSD(T). This improvement appears at the level of single and double excitations, whereas no significant impact of the explicit treatment of the electron correlation on the (T) correction has been observed, in analogy to a single-reference approach.

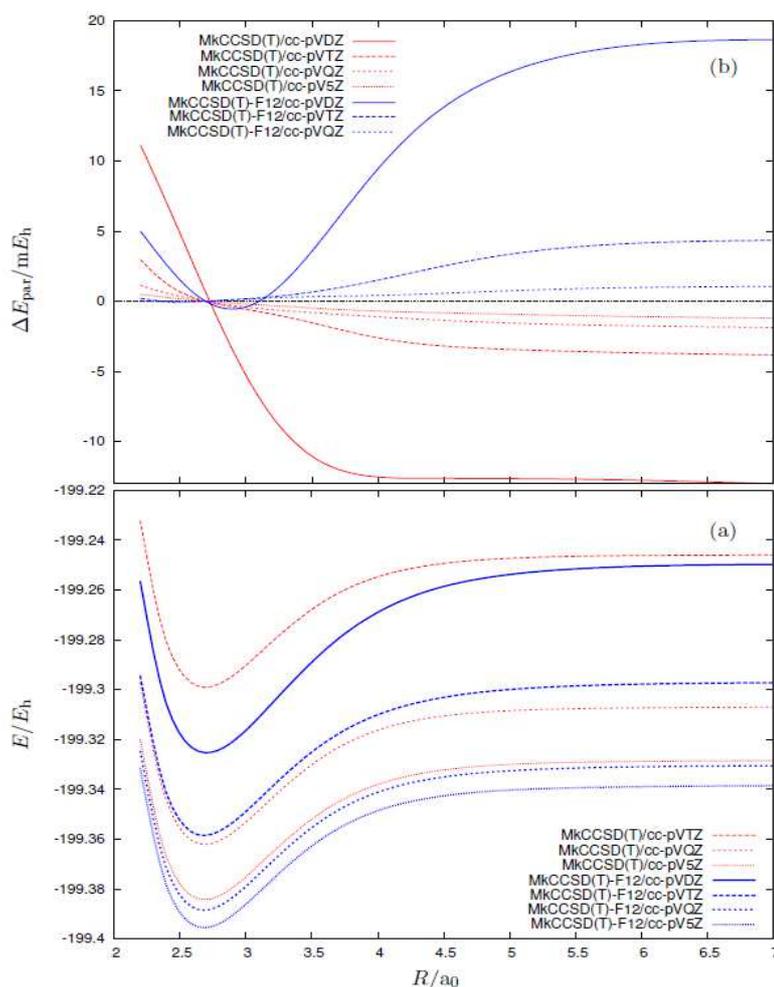


Figure 1: Potential energy curves (a) of the fluorine molecule calculated at MkCCSD(T) and MkCCSD(T)-F12 levels with cc-pVXZ basis sets using CAS orbitals. Deviations from the parallelity with respect to MkCCSD(T)-F12/cc-pV5Z curve are given in (b). $\Delta E_{\text{par}} = \Delta E_x - \Delta E_{\text{ref}}$; $\Delta E_x = E_x(R) - E_{\text{method}}(R_e)$, where "x" stands for any methods and "ref" for the reference curve.

Acknowledgement: This work has been supported by Slovak Research and Development Agency (project APVV-0510-12), as well as by Slovak Grant Agency VEGA (project 0148/13) and by Grant Agency of the Czech Republic (GACR 208/11/2222).

Theoretical Investigation of Condensed P-Containing Systems

Rózsa Szűcs¹, Pierre-Antoine Bouit², Muriel Hissler², László Nyulászi^{1*}

¹ Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Szt. Gellért tér 4, H-1111 Budapest, Hungary

² Institut des Sciences Chimiques de Rennes, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

nyulaszi@mail.bme.hu

The chemistry of polycyclic aromatic hydrocarbons⁷ (PAHs) is an area of current interest because of their unique optical and electronic properties. These important features might be influenced by the presence of heteroatoms such as phosphorus.

Recently, we have observed that the FMOs of a symmetric phosphole based PAH are determined by the phosphole moiety, while the conjugation with the π -system of the PAH is also pronounced. Further modifications at the reactive phosphorus atom can be used for fine-tuning the HOMO-LUMO gap, and accordingly the photophysical properties.^[1]

Our further investigations show, that the situation is similar for even larger PAHs, thus the conjugation can be significantly influenced by the presence of the phosphorus heteroatom.

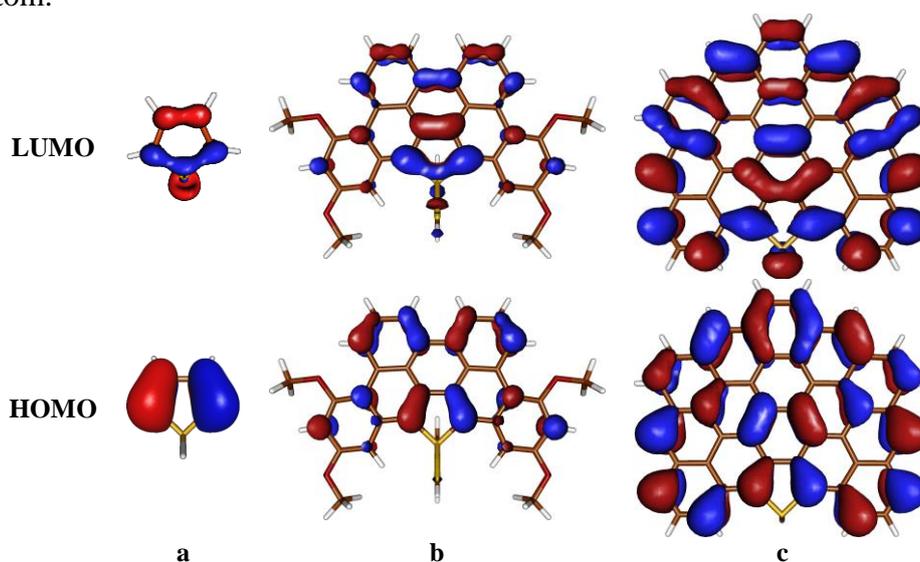


Figure 1: Similarity in the shape of the FMOs' in the case of phosphole (a), the synthesised systems (b) and even larger systems (c)

Aromaticity measures of the different rings will be discussed.

Acknowledgements: Campus France, Campus Hungary, TÉT_12_FR-1-2013-0017

[1] P.-A. Bouit, A. Escande, R. Szűcs, D. Szieberth, C. Lescop, L. Nyulászi, M. Hissler, R. Réau, *Journal of the American Chemical Society* **2012**, 134 (15), 6524-6527