POSTER SESSION 3

Theoretical study of a lipase-catalyzed reaction in organic solvent

Zuzana Sochorová Vokáčová[1], **Damien Laage**[2], **Eva Pluhařová**[1]

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

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

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

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

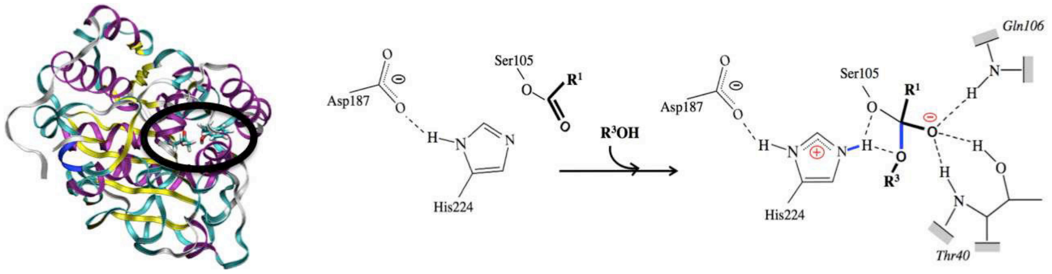


Figure 1 Candida antarctica lipase B with highlighted active site (left) with the scheme of the rate-limiting step of the transesterification reaction (right).

References

[1] A. M. Klibanov, *Nature* **409**, 241 (2001).
[2] S. Tawaki, A. M. Klibanov, *J. Am. Chem. Soc.* **114**, 1882 (1992).
[3] Y. Kitamoto, Y. Kuruma, K. Suzuki, T Hattori, *J. Org. Chem.* **80**, 521 (2015).

Temperature-dependent Triplet State Decay of Ir(ppz)$_2$(F$_2$ppy): Role of Metal Centered State

Xu Zhang[1], **Qian Peng**[2], **Zhigang Shuai**[1,2]

[1]*Key Laboratory of Organic Optoelectronics and Molecular Engineering,*

Department of Chemistry, Tsinghua University, Beijing 10084 P. R. China.

[2]*Key Laboratory of Organic Solids, Beijing National Laboratory for Molecular Sciences,*

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China.

Abstract: Cyclometalated iridium(III) complexes are widely used in the emissive layer of organic light-emitting diodes (OLEDs) due to their remarkable optical properties. Previous experiment investigations have shown that for the Ir(III) complexes, the temperature-dependent decay behavior demonstrated a competing mechanism between metal-ligand charge transfer (MLCT) state and metal centered (MC) state. However, there have been only a few theoretical studies on quantitatively description on the rate constant for various decay pathways. In this work, we have constructed a computation model to systematically investigate the decay mechanism of Ir(ppz)$_2$(F$_2$ppy). Both MLCT→S_0 transition and MLCT→MC transformation are considered in this model with decay rate constants calculated at the first-principles level. Two distinct optimized geometries are found on T_1 PES and then identified as MLCT or MC state based on spin density analysis. We found that the energy barrier of MLCT→MC transformation is low enough to overcome, and the rate constant of MLCT→MC transformation grows drastically as temperature increases, which indicates this pathway could be significant at high temperature. Strikingly, the calculated decay time vs. temperature shows a double-exponential form, which agrees with the experimental data. It is expected that the computation model in this work could be generalized to other Ir(III) complexes, as they have similar temperature-dependent decay behaviors.

[1] T. Sajoto, P. I. Djurovich, A. B. Tamayo, J. Oxgaard, W. A. Goddard III, M. E. Thompson, *J. Am. Chem. Soc.* **131**, 9813 (2009).

[2] Q. Peng, Y. Niu, Q. Shi, X. Gao, Z. Shuai, *J. Chem. Theory Comput.* **9**, 1132 (2013).

[3] D. Escudero, *Chem. Sci.* **7**, 1262 (2016).

Mechanism of Drug Resistance of Chloroethylnitrosoureas Mediated by O^6-Alkylguanine-DNA Alkyltransferase: An ONIOM Investigation

Lijiao Zhao, Ting Ren, Rugang Zhong

Beijing Key Laboratory of Environmental & Viral Oncology, College of Life Science and Bioengineering, Beijing University of Technology, Beijing 100124, China

Abstract: Chloroethylnitrosoureas (CENUs) are an important family of anticancer alkylating agents widely used in the clinical treatments of cancer. Experimental evidences indicated that CENUs induced formation of DNA alkylations, in which DNA interstrand crosslinks (ICLs) between G-C base pair was the most important lesion related to the anticancer effect of CENUs. However, O^6-alkylguanine-DNA alkyltransferase (AGT) in tumor cells can repair DNA alkylation by removing the alkyl group on the O^6 position of guanine and consequently lead to drug resistance. In this study, the mechanisms of AGT-mediated repair of DNA ICLs were investigated using molecular docking, molecular dynamics (MD) simulation and ONIOM method. Moreover, the mechanism of DNA repair was compared with the mechanism of DNA ICLs formation to reveal the preference between drug resistance and anticancer effect of CENUs. Molecular docking and MD simulation were performed to obtain the stable conformations of the two complexes, AGT-O^6-ClEtG and AGT-O^6,N1-EtG. Then the active sites of these two stabe conformations were picked out, and were employed as the computitional models for the ONIOM computations at the B3LYP/6-31+G(d,p):AM1 theoretical level. This work will contribute to the further understanding of the mechanism of drug resistance of CENUs and will assist in the development of novel AGT inhibitors as adjuvant alkylating chemotherapies.

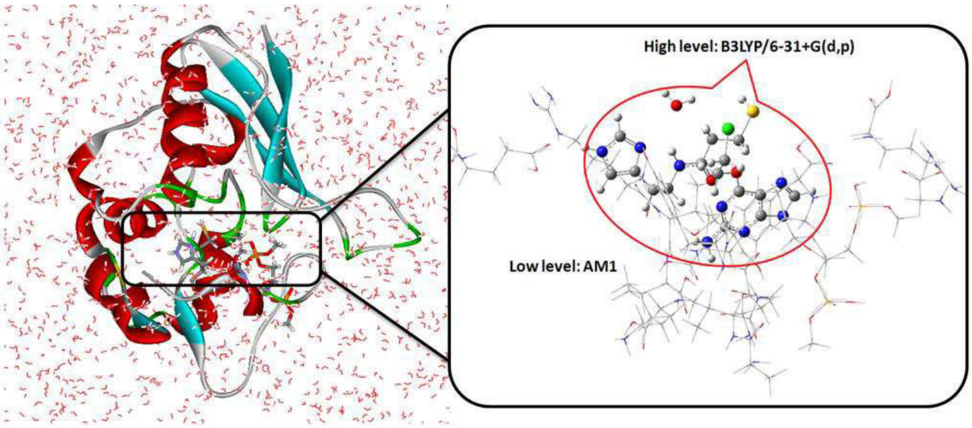


Figure 1 AGT-O^6-ClEtG complex obtained from MD simulation and the active site employed as the ONIOM computational model

A wave function model for magnetic clusters

Tilmann Bodenstein, Jeppe Olsen

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

A compact wave function model for describing magnetic clusters comprising several open-shell metal ions (sites) is introduced. The approach is based on multireference ab initio wave function methods. A reduction of the parameter space dimensions is obtained by combining physically reasonable approximations with efficient numerical methods.
In particular, the interactions in magnetic clusters may be grouped such that, to zero order, the magnetic sites can be 'disentangled' by neglecting explicit inter-site couplings, i. e. charge-transfer configurations, leading to a direct product wave function

$$|\tilde{0}(\boldsymbol{\kappa}, \mathbf{c})\rangle = \exp(-\hat{\boldsymbol{\kappa}}) \prod_{K=1}^{\text{sites}} \sum_{I} c_{I_K} \mathcal{A}_{I_K} \mathcal{I} |\text{vac}\rangle \tag{1}$$

where the CI-basis is spanned by Slaterdeterminants, factorized into creation strings for inactive ($\mathcal{I}$) and active ($\mathcal{A}_{I_K}$) orbitals. The generator for infinitesimal orbital rotations is denoted $\hat{\boldsymbol{\kappa}}$. Ansatz (1) yet contains inter-site interactions implicitly because of the spatial extent of the orbitals used to expand the electronic states.
Using non-orthogonal orbital expansions, the parameter space of such a MCSCF calculation can be further reduced [1, 2] while simultaneously improving the description of inter-site interactions compared to orthogonal (ground-manifold) MCSCF methods. [3, 4] Remaining contributions can be considered using techniques of internal contraction, e. g.

$$|\text{IC}\rangle = \sum_{[L,L']} C_{LL'} O_L^{L'} |0\rangle \tag{2}$$

where $|0\rangle$ represents the wave function (1) at the optimal expansion point. The brackets denote that the excitation strings $O_L^{L'}$ may be grouped and restricted to certain domains, e. g. adjacent sites L, L', owing to the inherent strongly-correlated character of magnetic clusters. The present ansatz is compared to well-established multireference methods.

[1] J. Olsen, *J. Chem. Phys.* **143**, 114102 (2015).

[2] R. Broer, W. C. Nieuwpoort, *Theor. Chim. Acta* **73**, 405 (1988).

[3] O. Kahn, *Molecular Magnetism*, Wiley-VCH,Weinheim (1993).

[4] K. Fink, V. Staemmler, *Mol. Phys.* **111**, 2594 (2013).

The impact of cholesterol flip-flop and concentration on the plasma membrane

Sebastian Thallmair[1], **Antara Mazumdar**[1], **Elisabeth A. Ploetz**[2], **Helgi I. Ingólfsson**[3], **Siewert-Jan Marrink**[1]

[1]*Faculty of Science and Engineering, University of Groningen, Nijenborgh 7, 9747 AG Groningen, The Netherlands*
[2]*John Hopkins University, Baltimore, Maryland, USA*
[3]*Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550, USA*

Cell membranes are highly complex systems consisting of various lipids and membrane proteins. They serve as the border of living cells, separating the cell interior from its environment. Typically, hundreds of different lipid types are present in a plasma membrane (PM). The detailed organization of cell membranes is therefore rather elusive. Cholesterol is known to stabilize liquid-ordered domains and flip-flops rapidly between both membrane leaflets. Recently, large-scale coarse-grained molecular dynamics (MD) simulations provided a near atomic view on the lipid organization of PMs [1]. The investigated PM model consists of 63 different lipid types (Fig. 1). The formation of transient domains with liquid-ordered character was observed. Here, we investigate the influence of cholesterol flip-flop as well as concentration on the PM properties. In doing so, we performed 50 µs coarse grained MD simulations of membrane patches with a size of ~$40 \times 40\,\mathrm{nm}^2$. We compare simulations where the cholesterol flip-flop was suppressed with ones allowing cholesterol flip-flop. Besides the influence on global membrane properties like area per lipid, lipid tail order, and lateral density, our particular focus is on the inter-leaflet coupling. We find that correlations of the transient domains enriched with cholesterol occur on a hundreds of nanoseconds time scale and show a spatial extent of ~10 nm.

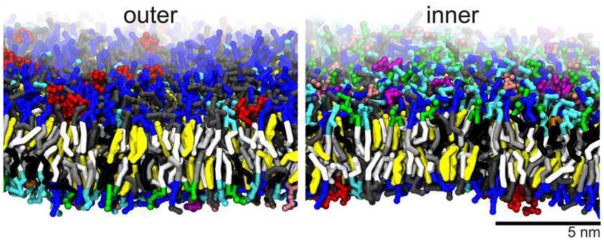


Figure 1: View on the outer and inner leaflet of the plasma membrane [1].

In addition, we varied the cholesterol concentration in our PM model from 0 – 50 mol-%. The cholesterol distribution between the leaflets shows an asymmetry which decreases as the cholesterol concentration increases. The global membrane properties reveal the effect of increasing lipid tail order with higher cholesterol concentration. Furthermore, we will discuss its effect on the inter-leaflet coupling in comparison with the other results.

[1] H. I. Ingólfsson, et al., *J. Am. Chem. Soc.* **136**, 14554 (2014).

Thermodynamic aspects of the electrocatalysis of proton reduction by diiron benzenedithiolate carbonyl complex

Mihajlo Etinski[1], **Rakesh C. Puthenkalathil**[2], **Bernd Ensing**[2]

[1] *Faculty of Physical Chemistry, University of Belgrade Studentski trg 12-16 11000 Belgrade, Serbia*
[2] *Van 't Hoff Institute for Molecular Sciences (HIMS), University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands*

The transformation of electric into chemical energy by electrochemical reduction of protons to molecular hydrogen has gained considerable attention as a promising process for the global aim to switch to a clean fuel economy. The design of reduction catalyst is a critical step for the development of suitable technology. Although noble metals are efficient catalysts for this reaction, cheaper catalysts based on abundant materials are desirable for broad application. Diiron benzenedithiolate (bdt) carbonyl complex is a biomimetic catalyst based on diiron-hydrogenases a class of enzymes responsible for H_2 production in microbes. It is a robust catalyst whose proton reduction mechanisms depend on proton donor strength [1,2]. Although many experimental and theoretical studies examined its properties, the catalytic mechanisms are still not completely understood. We have examined the catalytic pathways of proton reduction by Fe-bdt employing density functional theory and implicit solvent model. The computed free energies of singly, doubly and triply reduced and/or protonated Fe-bdt isomers were used to compute a thermodynamic map and Pourbaix diagram for the catalyst. Based on the relative energies of the isomers and their proton dissociation constants we propose electrochemical mechanisms for the proton reduction.

[1] J. F. Capon, F. Gloaguen, P. Schollhammer, J. Talarmin, *J. Electroanal. Chem.*, **595**, 47 (2006).
[2] G. A. N. Felton, A. K. Vannucci, J. Chen, L. T. Lockett, N. Okumura, B. J. Petro, U. I. Zakai, D. H. Evans, R. S. Glass, D. L. Lichtenberger, *J. Am. Chem. Soc*, **129**, 12521 (2007).

Accelerated Dynamics Simulations of Supramolecular Ruthenium-Based Water Oxidation Catalysis

Joachim O. Lindner[1]**, Merle I. S. Röhr**[1]**, Roland Mitrić**[1]

[1]*Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, 97074 Würzburg, Germany*

Water oxidation is a key step in the development of new sustainable methods towards artificial photosynthesis and solar fuels. A promising approach for efficient water splitting is the design of supramolecular Ru-based catalysts. [1] Only recently, a macrocyclic system containing three Ru(bda) units (bda = 2,2'-bipyridine-6,6'-dicarboxylate) has been synthesized that is able to compete with the best catalysts up to date in TOF and TON while mechanistically following a pathway characterized by the nucleophilic attack of a water molecule. [2]

QM/MM molecular dynamics simulations allowed us to observe the whole catalytic cycle of this supramolecular catalyst in solution. Furthermore, by comparison of systems with increasing ring sizes we could show that the high catalytic activity and characteristic absorption bands in the UV/Vis spectra are due to pronounced hydrogen bonding networks that are formed preferably in the macrocycle with intermediate size. [3] Cooperative effects lead to the stabilization of dissociated protons and thus facilitate proton-coupled electron transfer processes.

In order to gain a deeper understanding of the mechanistic details in these supramolecular systems, we apply the metadynamics approach to quantitatively identify the rate-determining steps of the catalytic cycle as well as possible changes in the reaction pathway affecting the enhanced water oxidation activity of the macrocycle.

[1] V. Kunz, D. Schmidt, M. I. S. Röhr, R. Mitrić, F. Würthner, *Adv. Energy Mater.*, doi: 10.1002/aenm.201602939 (2017).

[2] M. Schulze, V. Kunz, P. D. Frischmann, F. Würthner, *Nat. Chem.* **8**, 576–583 (2016).

[3] V. Kunz, J. O. Lindner, M. Schulze, M. I. S. Röhr, D. Schmidt, R. Mitrić, F. Würthner, *Energy Environ. Sci.*, submitted.

Spontaneous insertion and interaction of non-structure 3 protease protein domain with PIP2-containing membrane

Huynh Minh Hung, Tran Dieu Hang and Minh Tho Nguyen

Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium

Abstract: Hepatitis C virus (HCV), the leading cause of liver cirrhosis, viral hepatitis and hepatocellular carcinoma, affected more than 150 million people globally. The HCV non-structure 3 (NS3) protease protein domain plays a key role in HCV replication and pathogenesis; and is currently a primary target for HCV antiviral therapy. Through unbiased molecular dynamics simulations taking advantage of the novel highly mobile membrane mimetic model, we constructed the membrane-bound state of the protein domain at the atomic level. Our results indicated that protease domain of NS3 protein can spontaneously bind and penetrate to an endoplasmic reticulum complex membrane containing phosphatidylinositol 4,5-bisphosphate (PIP2). An amphipathic helix α_0 (amino acids 13-22) which deeply inserted into the membrane shows as the primary anchoring role to keep the protein on the membrane surface, which agrees well with previous experimental studies. Along with the role of helix α0, a loop S1 around residue T40 was found to deeply penetrate to the membrane while the small helix S2 and loop S3 bind but incompletely insert into the membrane. Proper orientation of the protein domain at membrane surface was also identified through measuring tilt angles of two specific vectors, in which residue R161 play a crucial role in its final orientation. Importantly, PIP2 molecules were found to bind to three main sites of the protease via electrostatic contacts and hydrogen bonds. Hydrophobic interactions between inserted parts of NS3pro with the membrane along with these PIP2-interactions have tendency to stabilize the NS3 - membrane complex.

[1] J. L. Baylon, I. L. Lenov, S. G. Sligar and E. Tajkhorshid, J. Am. Chem. Soc.135, 8542–8551 (2013).

[2] H.M. Hung, T.D. Hang, M.T. Nguyen, Biochem. Biophys. Res. Commun. 478, 193–198 (2016).

[3] D.I. Soumana, N. Kurt Yilmaz, A. Ali, K.L. Prachanronarong, C.A. Schiffer, , J. Am. Chem. Soc. 138 (2016) 11850–11859.

Theoretical insights of supramolecular assembly on 2D atomic crystals

Hongde Yu[1], and Dong Wang*[1]

[1]MOE Key Laboratory of Organic OptoElectronics and Molecular Engineering,
Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China

A large variety of organic molecules are known to assemble on various 2D atomic crystals and form specific patterns, which have been investigated by STM since 1990s. Herein, using both DFT-D3 method and Grimme's D3 dispersion parameters, we explored the interplay of substrate-adsorbate and adsorbate-adsorbate interactions in the assembly of oleamide on hexagonal BN lattice. By calculating the translational and rotational potential energy surfaces of a single oleamide molecule adsorbed on monolayer BN, we corroborated that alkyl chains of oleamide molecules tend to align along a specific direction on BN, which is the zigzag lattice direction with the densest atomic density. More importantly, when oleamide molecules are adsorbed on the periodic lattice of BN substrate at the energetically most favorable positions, they will assemble into a one-dimensional nanoribbon along the zigzag crystal direction of BN. Our potential energy scans of a 2nd layer of oleamide adsorbed on the 1st molecular layer of nanoribbon showed that oleamide molecules in the 2nd layer prefer to align parallel to the underneath 1st layer ones and stack right on top of them. We concluded that substrate-adsorbate interactions serve as primary interactions, and adsorbate-adsorbate interactions as secondary ones in the assembly of oleamide on 2D atomic crystals. Our investigation highlights the feasibility of probing the crystallographic orientation of 2D atomic crystals with supramolecular assembly

References

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

Structural properties and THz spectroscopic fingerprints of microsolvated ion-water clusters

Prashant Kumar Gupta, János Daru, Dominik Marx

Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum

Small ion-water clusters are excellent model systems to study microsolvation and its impact on spectroscopic properties. It is, however, unclear to what extent such small clusters are meaningful minimal models of the first solvation shell of ions in bulk solution, keeping in mind that it is well established from experiments that the effect of ions on the water structure is largely limited to their first solvation shells. In this study we have undertaken an extensive density functional-based *ab initio* molecular dynamics study of various equilibrium structures and the corresponding THz spectra of cationic and anionic solvation in small water clusters, namely $X\bullet(H_2O)_n$ where $X = Na^+$ and Cl^-, $n = 3$–7. In this context, the issue of including or rather omitting empirical dispersion interaction corrections turns out to be intricate with reference to wavefunction-based benchmarks on structure and relative energetics. *Ab initio* molecular dynamics simulations are performed at several temperatures in order to probe the structural dynamics of distinct microsolvated clusters in direct comparison to the same ions at bulk solvation conditions. Finally, their THz spectra are computed and also decomposed in terms of well-defined intra- and inter-molecular contributions including solute-solvent couplings in order to compare those to what has been found in the bulk solvation limit.

Density functional theory predictions of self-assembly on metal surfaces: Is it successful?

James Hooper[1], **E. Zurek**[2], **A. Enders**[3]

[1]*Department of Theoretical Chemistry, Jagiellonian University, R. Ingardena 3, Krakow, Poland*
[2]*Department of Chemistry, State University of New York at Buffalo, 14260, Buffalo, USA*
[3]*Physikalisches Institut, Universität Bayreuth, 95440 Bayreuth, Germany*

The ability to predict from computations alone whether or not small molecules will form interesting networks on a given substrate is a particularly challenging and enticing problem. One example, among many, is croconic acid (CA), a polar organic molecule which crystallizes with ferroelectric behavior in its bulk form.[1] Such a molecule may also be of interest when deposited on a surface to, for example, create a two-dimensional network with ferroelectric behavior.

In this work, we first explore experimentally-characterized hydrogen-bonded networks which assemble from CA when it is deposited on coinage metal substrates, ie. Cu, Ag, and Au.[2] The networks are influenced by the substrate onto which they are deposited and, as could be expected from the literature, can be predicted from first-principles with Density Functional Theory (DFT) energies with varying degrees of success. Building on this, DFT calculations are used here to explore how the dependence of the CA-inspired network architectures compare with, in particular, inter-molecular binding (ie. hydrogen-bonding), preferential binding sites, and electrostatic interactions between the adsorbate and substrate. From this, we show what is needed from computations, beyond energies, to simply predict the networks. Further, we comment on modelling the adsorption of a bis-BN cyclohexane precursor molecule ($B_2N_2C_2H_{12}$) on reactive Rh(111) and Ir(111) substrates, and discuss its role in helping to fashion an elusive metastable graphene-like boron-carbon-nitrogen monolayer.[3]

[1] S. Horiuchi, R. Kumai, Y. Tokura, *Adv. Mater.* **11**, 123–456 (2011).

[2] J. Hooper, D. Kunkel, E. Zurek, A. Enders, *J. Phys. Chem. C*, **119**, 26429 (2015).

[3] S. Beniwal, J. Hooper, D. Miller, P. Costa, G. Chan, S. Y. Liu, P. A. Dowben, E. C. H. Sykes, E. Zurek, A. Enders, *ACS Nano*, **11**, 2486 (2017).

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

Patricia Saura[1], **Ville R. I. Kaila**[1]

[1]*Department Chemie, Technische Universität München, Lichtenbergstr. 4, Garching, Germany.*

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

Rational design of single molecule magnets

Asha Roberts, Peter Comba

Institute of Inorganic Chemistry, Heidelberg University, INF 270,
Interdisciplinary Center for Scientific Computing (IWR), INF 205,
HGS MathComp Graduate School, INF 205,
69120 Heidelberg, Germany

Single molecule magnets (SMMs) are a class of compounds containing one or more magnetic centres (d- or f-block metals). In many cases the discovery of new SMMs is left to chance, with serendipitous assembly of metal clusters being a common synthetic approach. As a better understanding of the structural requirements of these complexes is obtained, a rational approach to their design is highly desirable and advantageous. While early SMMs were comprised primarily of transition metal ions, significant spin-orbit coupling and strong magnetic anisotropy of lanthanides makes them particularly suitable in this field. To date the best SMMs have been simple mononuclear lanthanide complexes.[1-2] Although ligand field effects for lanthanides are comparatively weak, they are a significant perturbation upon spin-orbit coupling, and are crucial in controlling SMM behaviour. This study presents investigations into geometrical influences on the electronic and magnetic properties of a series of mononuclear complexes with the aim of rationally designing complexes for application as SMMs. Structures are designed and optimised in Gaussian 09. Single point calculations to determine the magnetic properties are carried out using MOLCAS 8.0,[3] whereby spin-free CASSCF wave functions are first generated, spin-orbit coupling is introduced through RAS state interaction, and the relevant magnetic properties are calculated from the spin-orbit multiplets with the SINGLE_ANISO module.

[1] J. Liu, Y. C. Chen, J. L. Liu, V. Vieru, L. Ungur, J. H. Jia, L. F Chibotaru, Y. Lan, W. Wernsdorfer, S. Gao, X. M. Chen, M. L. Tong, *J. Am. Chem. Soc.***138**, 16 (2016).

[2] C. R. Ganivet, B. Ballesteros, G. de la Torre, J. M. Clemente-Juan, E. Coronado, T. Torres, *Chemistry* **19**, 4, (2013).

[3] F. Aquilante, L. De Vico, N. Ferré, G. Ghigo, P. A. Malmqvist, P. Neogrády, T. B. Pedersen, M. Pitonak, M. Reiher, B. O. Roos, L. Serrano-Andrés, M. Urban, V. Veryazov, R. Lindh, *J. Comput. Chem.* **31**, (2010).

Computational DFT-D3 and Amber FF Study of Z-DNA and its Sugar-Guanine Stacking Motif

Holger Kruse[1], **Klaudia Mráziková**[1], **Jiri Šponer**[1]

[1]*Institute of Biophysics of the CAS, Královopolská 135, 61265 Brno, Czech Republic*

The peculiar left-handed, zig-zag structure of Z-DNA features a highly rigid backbone skeleton and typically comprises alternating d(CG) dinucleotide sequences. Among the special structural features is the T-shaped stacking of a ribose sugar with a guanine nucleobase (cf. Fig. 1). Analysis of X-ray databases shows that this geometrical motif exhibits a suprisingly short oxygen-to-nucleobase distance ('oxygen-π interaction') of about ca. 2.9 Å ; much shorter than the typical nucleobase stacking distances of about 3.4 Å in helical structures.

To study the motif we mapped the PES of the sugar-nucleobase interaction with a model system at the B3LYP-D3(BJ)/def2-QZVP level of theory (cf. Fig. 1, 399 energy evaluations), and could support the correctness of bioinformatics studies, showing that the unexpected short distance in the X-ray structures is physically correct. As modern DNA force fields (FFs) are still deemed problematic for Z-DNA we repeated the scan using the non-bonded parameters of the Amber FF. While the Amber FF sufficiently reproduces the main features of the DFT-D3 surface, it has clear limitations with details. Geometry-adapted point charges are explored, but only offer a small improvement.

A COSMO-TPSS-D3(BJ)/def2-TZVP optimization of a high-resolution, 12-nt large X-ray structure validates the findings from the model and also shows the applicability of DFT-D3 for Z-DNA beyond toy systems.

Furthermore we discuss why the so-called oxygen-π interaction is best understood as a mere geometrical descriptor instead of a 'new' interaction type using the accurate SAP2+3/jun-cc-pVTZ energy decomposition scheme.

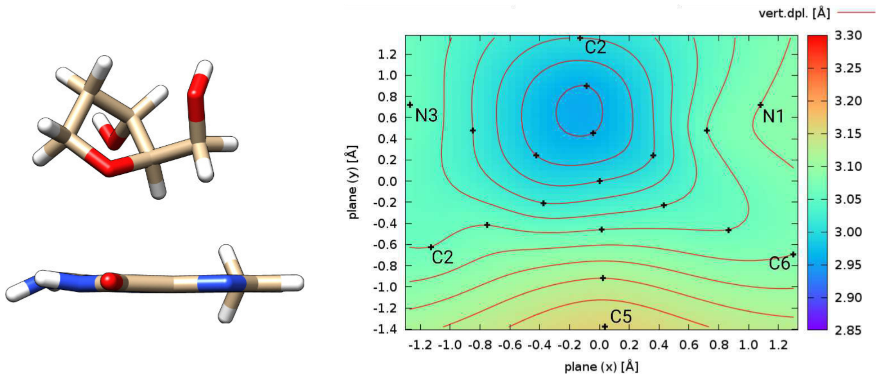


Figure 1: left: guanine-sugar model; right: lowest-energy distance surface of the guanine-sugar motif over the pyrimidine ring of guanine with atom labels.

H. Kruse, K. Mráziková, L. D'Ascenzo, P. Auffinger, J. Šponer *in preparation*

Linking Protein Motion and Function: Combining Markov State Modelling and Hybrid Quantum Mechanics/Molecular Mechanics

Eliot Boulanger[1], **Jeremy Harvey**[1]

[1]*Department of Chemistry, Quantum Chemistry and Physical Chemistry, KU Leuven,*
Celestijnenlaan 200F, 3001 Leuven, Belgium

Understanding the link between the molecular structure and the function of biomolecules is one of the key scientific challenges, and addressing this question requires drawing in techniques from biology, chemistry and physics. Furthermore, it has also been known for some time that protein structure is not fixed – proteins are intrinsically dynamical in the sense that they are constantly in motion, and it is also known that the structural changes can be linked to functional changes.

We aim at bridging those two aspects by the mean of computational methods. First, we run extensive molecular dynamics simulations on the protein and its surrounding to sample its conformational space. Out of the generated data we construct a Markov State Model (MSM)[1] which allows us to identify the different key conformers of the protein, get their relative free energies and the transition rates in between them. We then generate structures belonging to the different sampled conformations and use hybrid Quantum Mechanics/Molecular Mechanics (QM/MM)[2] to compute electronic properties proper to the function of the studied protein such as chemical reaction or electronic excitation. Combining both, we obtain a complete picture of the mode of action of the protein.

To exemplify our approach, we first focus on Myoglobin which has been extensively studied both computationally and experimentally. This protein has two well defined states (R and T) which are differently accessed depending on the binding of oxygen or carbon monoxide to the heme group.[3] We then apply our method to the P2Y12 G-Protein-Coupled Receptor (GPCR) which is found in blood platelets and is a common target for antithrombic agent.[4] Drugs like Clopidogrel or Prasugrel bind covalently to the protein, inducing significant conformational changes to trigger a biological response. The covalent binding necessitates QM/MM to be studied and MSM is used to characterize the conformational changes.

[1] J. Chodera, F. Noé, *Curr. Opin. in Stuct. Bio.* **25**, 135 (2014).
[2] H. M. Senn, W. Thiel, *Angew. Chem. Int. Ed.* **48**, 1198 (2009).
[3] N. Strickland, A. J. Mulholland, J. N. Harvey, *Biophys. J.* **90**, L27 (2006).
[4] K. Zhang et al., *Nature* **509**, 115 (2014).

FROM SURFACES TO NANOPARTICLES: AB-INITIO STUDY OF RUTHENIUM OXIDE AND ITS INTERACTION WITH WATER

J.Heras-Domingo, X.Solans-Monfort, M. Sodupe

Dept. Química, Facultat de Ciències, Universitat Autònoma de Barcelona,

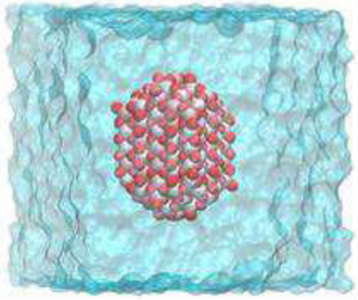
08193 Bellatera (Cerdanyola del Vallès), Spain

e-mail: Javier.heras.domingo@uab.cat

The formation of molecular oxygen from the oxidation of water is the most challenging step in water splitting process. To overcome this critical semi-reaction, heterogeneous catalyst or nanoparticles based on metal oxides have been used. In particular, ruthenium oxide based materials can be a good candidate, due to its unique redox surface chemistry and versatile behaviors in oxidative reactions.[1] RuO2 is widely applied in chemistry due to its with many industrial applications such as electrochemical capacitors, sensor or catalyst due to its conductive behaviors and high thermal stability.

In this contribution, DFT calculations with periodic boundary conditions [2] have been carried out to analyze the electronic and adsorption properties of RuO2 materials. In particular, the surface energy of the most relevant low-index crystallographic orientations has been determined. After that, water adsorptions onto these surfaces have been studied paying special attention in to the effect of water coverage. Moreover, computed surface energies have allowed us to determine the shape of nanoparticle different size through the Wulff construction [3] approach and analyze size-dependent properties and enhanced surface capabilities as compared with those of the bulk material.

Results show that water coverage and the surface morphology play an important role in the degree of water dissociation and that the formation of [H3O2]- units appears to be a driving force to allow the proton transfer process [4].



[1] H.Over *Chem. Rev.*, **2012**, 112 (6), 3356–3426
[2] G. Kresse, J. Fuhrmuller, *Phys. Rev. B,* **1993**
[3] G. Wulff, *Z. Kyrstal. Min.* **1901,** 34, 449
[4] R.Mu, D.C.Cantu, V-A.Glezakou, I.Lyubinetsky, *et al. J.Phys.Chem.C*, **2015**, 119, 23552-23558

Unexpected contrast and “dark contours” in chiral STM markers

Sanz-Matias, Ana[1]**, Harvey, Jeremy N.**[1]

[1] *Chemistry Department, KU Leuven, Celestijnenlaan 200F, Heverlee, Belgium*

The design of chiral organic building blocks for two-dimensional self-assembled systems often involves using substituents to create stereogenic centers. Being able to visualize the stereogenic centers with Scanning Tunneling Microscopy (STM) is highly convenient for assessing their impact on self-assembly. Chiral substituents that serve as STM markers make it possible to identify the chiral components of the system and facilitate investigating kinetic and thermodynamic interfacial phenomena[1]. Despite the frequent use of methyl substituents as building block modifiers, there is little research on their STM marker characteristics: they are difficult to unambiguously detect in STM images, and when they have been detected[2, 3], image topography displays unexpected and stark contrast variations (i.e. “dark contours” and “bright features").

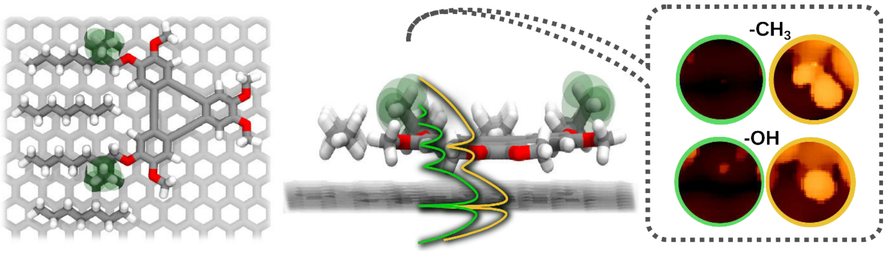


Figure 1: Chiral DBA on graphene with log(LDOS) curves as a function of z and STM simulated images.

We investigate computationally the STM marker characteristics of methylated, as well as hydroxylated, chiral derivatives of alkanes and dehydrobenzo[12]annulenes (DBAs) on graphitic surfaces (Fig. 1a). Self-interaction corrected density functional theory (DFT) calculations reveal a sharp change of the local density of states in the substituent regions in the energy range close to the Fermi level (Fig. 1b). As a result, the marker appearance depends heavily on the bias voltage used for image simulation (Fig. 1c), gradually ’illuminating’ from a topographical depression to a protrusion. This appears to explain not only the unexpected “dark contours” observed in cDBAs experimental images, but also the general contrast variations. Furthermore, subtle differences in the voltage at which the contrast variation occurs for methyl and hydroxyl substituents may allow to distinguish between them, in a sort of traffic light effect.

[1] C. L. Claypool et al, *Langmuir* **15**, 2817 (1999).

[2] Y. Fang et al, *Nat. Chem.* **8**, 711 (2016).

[3] S. de Feyter et al, *J. Phys. Chem. B* **101**, 5978 (1997).

A quantum-chemical study of the DNA base-excision repair of 8-oxoguanine

Andrea Kreppel[1], **Christian Ochsenfeld**[1]

[1]*Chair of Theoretical Chemistry, Department of Chemistry, Ludwig-Maximilians-University,*
Butenandtstr. 7, D-81377 Munich, Germany

For the binding of the DNA lesion 8-oxoguanine (8OG) in the active site of the enzyme formamidopyrimidine DNA glycosylase (Fpg), two different binding modes have been proposed, one where the purine base adopts the *anti*-conformation and another with the base in *syn*-conformation (see Figure 1 a)). While it was found that both orientations of 8OG are stable within the active site [1, 2], it remained unclear whether the base can also be excised by Fpg in both orientations. Therefore we performed systematic QM/MM calculations. For *syn*-bound 8OG we recently found an excision mechanism with base specific protonation [3]. For another *anti*-bound DNA lesion we revealed an excision mechanism that is base independent [4]. In our present work, we calculated the energy profile of the excision of 8OG in both orientations (Figure 1 b)) following the path of the base independent excision mechanism. Our calculations allow for comparing both energy profiles and indicate that 8OG can possibly be excised by Fpg in both conformations. Additionally, we show that *syn*-bound 8OG is not only excised by the base specific mechanism but also by the base independent mechanism. The findings of this work provide further evidence that the base excision mechanism is base independent and that no discrimination between DNA lesions occurs within the active site.

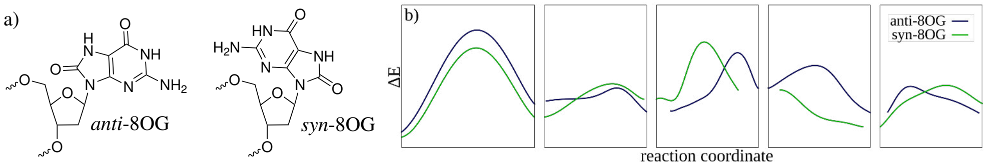


Figure 1: a) 8OG nucleotide in *anti*- and *syn*-conformation b) energy profile of the excision of 8OG by Fpg in both conformations.

[1] K. Song, V. Hornak, C. de Los Santos, A. P. Grollman, C. Simmerling, *Biochemistry* **45**, 10886 (2006).

[2] R. A. Perlow-Poehnelt, D. O. Zharkov, A. P. Grollman, S. Broyde, *Biochemistry* **43**, 16092 (2004).

[3] K. Sadeghian, D. Flaig, I. D. Blank, S. Schneider, R. Strasser, D. Stathis, M. Winnacker, T. Carell, C. Ochsenfeld, *Angew. Chem., Int. Ed.* **53**, 10044 (2014)

[4] I. D. Blank, K. Sadeghian, C. Ochsenfeld, *Sci. Rep.* **5**, 10369 (2015)

Quantum entanglement within the polarization propagator approach

Leonardo A. Millán[1], Claudia G. Giribet[2] and Gustavo A. Aucar[1]

[1]*Physics Department, Natural and Exact Science Faculty, Northeastern University of Argentina and Institute of Modeling and Innovation on Technology (IMIT) CONICET-UNNE, Corrientes, Argentina*
[2]*Physics Department, Physics Institute of Buenos Aires, Natural and Exact Science Faculty, University of Buenos Aires and CONICET, Buenos Aires, Argentina*

For vicinal and indirect NMR J-couplings there is a well-known empirical rule, the Karplus rule, which states a functional dependence of such J-couplings with the dihedral angle between the coupled nuclei.

Recently we have found that the two-electron integrals that both, introduce the electron correlation at the RPA level of approach within the polarization propagator formalism and follow the Karplus rule, have a non-local behavior.[1] After this finding we started to think about whether the excitations that contain those orbitals are entangled. If indeed they are, we might suggest that quantum entanglement would be the phenomenon that can explain the Karplus rule.

Until now it was not possible to study the quantum entanglement applying polarization propagators. The reason is the fact that it is not an easy task to define a proper density function and then to calculate the entropy of the system using those propagators.

In this presentation we propose a partition function that is valid within the polarization propagator scheme.[2] From such a function we take an additional step forward and define a density function, which allow us to quantify the entanglement between molecular orbital excitations.[3]

We present preliminary results calculated with our novel scheme, where it is shown that the above mentioned excitations are actually entangled.

[1] G. A. Aucar, R. H. Romero, A. F. Maldonado, *Int. Rev. in Phys. Chem.* **29**, 1-64 (2010).
[2] G. A. Aucar, *Phys. Chem. Chem. Phys.* **16**, 4420-4438 (2014).
[3] K. Boguslawski, P. Tecmer, G. Barcza, O. Legeza, M. Reiher, *J. Chem. Theory Comput.* **9**, 2959-3973 (2013)

RmatReact: Developing Novel Theoretical Methodology to Investigate Ultra-cold Atom-Molecule Collisions over Deep Potential Wells

Laura K McKemmish[1,2], Tom Rivlin[1], Jonathan Tennyson[1]

[1] *Department of Physics and Astronomy, University College London, London, UK*
[2] *School of Chemistry, University of New South Wales, Kensington, Sydney, Australia*

Cutting-edge experimental studies in the field of molecular science are pushing the limits of current theoretical frameworks, requiring the development of new quantum chemistry methodologies that are capable of describing systems in increased detail, particularly at high levels of internal energy up to and above dissociation.

One key area that would benefit from improved theoretical description is experimental ultracold chemistry studies, which aim to understand and ultimately control chemical processes at the quantum level, with reactants and products being fully specified in terms of quantum numbers. Adequately conceptualising such reactions presents the greatest challenge to chemical theory whilst accurate computation presents the greatest challenges to both electronic-structure theory and the quantum theory of nuclear motion, especially when the collisions occur over deep potential wells. We are working on developing a new methodology [**?**], RmatReact, to address these significant challenges by dividing a modelled molecular collision into two spatial regions: an inner-region solved once using an expensive, high accuracy calculation and a fast outer-region calculation performed for a fine grid of collision energies that provides process and reaction cross-sections. This technique has the potential to provide the theoretical framework to describe and motivate a whole generation of new experiments, addressing important and fundamental scientific problems associated with quasi-bound resonance states formed when two atomic or molecular systems collide at specific ultra-cold energies over deep wells.

[1] J. Tennyson, LK McKemmish, T Rivlin, Faraday Discussions, 195 (2016)

From Sequence to Function, QM/MM and Virtual Screening identify enzyme function and substrate scope

Marco Bocola[1,2], Gaurao V. Dhoke[1], Mehdi D. Davari[1]

[1]Department/ Lehrstuhl für Biotechnologie, RWTH Aachen University,
Worringer Weg 3, D-52074 Aachen, Germany
[2]ProteDes , Protein Engineering and Design
Siemensstr. 6g, D-53757 Sankt Augustin, Germany

Bioinformatic databases contain sequence data for millions of proteins and enzymes of unknown function. Enzymes identified from natural sources often have interesting biocatalytic properties. NADH-dependent ADH from Candida parapsilosis (cpADH5), is a candidate for the selective reduction of diketones to industrially important chiral hydroxy ketones. [1] The natural function and substrate scope of cpADH5 is not known.

Computation methods can help to solve the quest from sequence to enzyme function by virtual screening and QM/MM calculations to identify function and substrate scope.

To this end we have investigated the catalytic mechanism by QM/MM calculations [3], based on the X-ray crystal structure [2] of cpADH5 in the substrate free resting state. We have validated a mechanism based predictive molecular docking method for the ranking of Zn^{2+}-dependent medium chain dehydrogenase substrates. [4,5]

The presented computational substrate screening strategy [6] combining virtual screening, pathway database search and QM/MM calculations for “in silico” substrate scope identification presents a promising technique for mechanism based enzyme annotation of (metallo)-enzymes of unknow function and set the stage for biocatalyst design.

[1] A. Jakoblinnert et al. *ChemBioChem*, **13**, 803−809 (2012).
[2] H. Man et al. *ChemCatChem*, **6**, 1103−1111 (2014).
[3] G. V. Dhoke et al,. *ACS Catalysis* **5**, 3207-3215 (2015).
[4] G. V. Dhoke et al., *J. Comput. Aided Mol. Des.* **29(11)**, 1057-1069 (2015).
[5] C. Loderer et al., *ChemBioChem* **16**, 1512–1519 (2015).
[6] G. V. Dhoke et al., *J. Chem. Inf. Model.* **56 (7)**, pp 1313–1323 (2016).

Probability current analysis and the charge transfer integral in organic semiconducting materials

<u>Sang-Yeon Hwang</u>[1] and Woo Youn Kim[1]

[1]Department of Chemistry, KAIST, 291, Daehak-ro, Yuseong-gu, Daejeon, Republic of Korea

Being one of the essential parameters characterizing molecular charge transfer reactions, the electronic coupling element, called the charge transfer integral, has served as a central subject of investigation in the field. Accordingly, a profuse number of theories have been developed for computing the quantity, where a standard method uses the frontier orbitals of a transfer pair and evaluates the matrix element of the (Kohn-Sham-)Fock Hamiltonian. Alexei Stuchebrukhov's tunneling current theory also estimates the charge transfer integral, based on its distinctive feature of incorporating the charge carrier's probability current [1-2]. As the theory was mostly applied to protein systems to analyze charge transfer pathways, in this research we focused on the charge transfer integral itself and probed the method's applicability on small and medium sized organic systems. To make quantitative analysis possible, we used the molecule dimers in the works of Adam Kubas and co-workers [3-4]. We evaluated the transfer integrals by the tunneling current theory as well as the standard Fock matrix method, and the former showed smaller errors from those by high-level calculations. As we used the same frozen-core diabatic determinants for the both methods, we attribute the performance to the exact derivation (after the frozen transition-state assumption) of the transfer integral in the former theory. In addition, we computed the probability currents in the dimer conformers of an organic semiconductor molecule and visualized how structural changes affect the charge transfer tendency. Besides reliable estimation of transfer integrals, the probability current makes structure-based design of improved charge transfer materials more viable.

[1] A. A. Stuchebrukhov, *J. Chem. Phys.* **104**, 8424 (1996).

[2] A. A. Stuchebrukhov, *J. Chem. Phys.* **108**, 8499 (1998).

[3] A. Kubas, F. Hoffmann, A. Heck, H. Oberhofer, M. Elstner, and J. Blumberger, *J. Chem. Phys.* **140**, 104105 (2014).

[4] A. Kubas, F. Gajdos, A. Heck, H. Oberhofer, M. Elstner, and J. Blumberger, *Phys. Chem. Chem. Phys.* **17**, 14342 (2015).

Pairwise specific reaction parameterization: a straightforward approach to improve semiempirical QM methods

Antoine Marion[1] **and Iris Antes**[1]

[1]*Center for Integrated Protein Science Munich at the Department of Biosciences, Technische Universität München, Emil-Erlenmeyer-Forum 8, D-85354 Freising, Germany*

Over the past decades, the interest in semiempirical quantum mechanical (SQM) methods has consistently increased together with the popularization of hybrid QM/MM approaches to model complex reactions within their corresponding environment. These approximate and parameterized QM Hamiltonians allow a quantum description of electronic structures for a computational cost that is compatible with extensive sampling techniques. Although very appealing and despite a constant improvement of the models, SQM approaches still suffer from several shortcomings that can result in quantitative or qualitative errors during the calculation of reaction energy profiles. This fact has led to the development of dedicated corrections focused either on the entire set of SQM parameters [1,2] or on specifically identified, faulty parts of the Hamiltonian [3,4]. Such approaches allow reaching qualitative and quantitative agreement between SQM methods and more accurate *ab initio* Hamiltonians. However, the development of such corrections is often tedious and requires a strong expertise in order to result in the optimization of an objective, consistent, and effective set of parameters.

We present a new and straightforward approach to improve SQM methods for a given reaction: Pairwise Specific Reaction Parameterization (PSRP). Unlike other strategies that optimize new parameters for all atoms in the molecular system [1-4], we introduce here the novel idea of a parameterization of only a few specific, targeted pairs, identified to be responsible for the inaccurate behavior of the original Hamiltonian, while all other atomic interactions remain unchanged. This crucial difference confers great advantages to the PSRP approach: i) the parameterization is straightforward and can be done on small isolated molecular models, and ii) the procedure is robust and does not introduce spurious artifacts for chemical groups that were not in the parameterization range since it is focused only on targeted parts of the system. Through our first applications we show that the PSRP strategy allows to successfully model reactions as complex and challenging as the catalytic activity of HCV-protease towards its natural substrate.

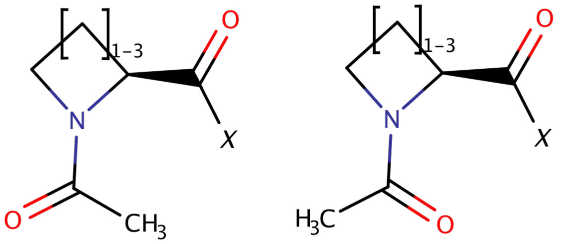
[1] X. Wu, W. Thiel, S. Pezeshki, H. Lin, *J. Chem. Theory. Comput.* **9**, 2672 (2013).
[2] S. Liang, A. E. Roitberg, *J. Chem. Theory. Comput.* **9**, 4470 (2013).
[3] M. I. Bernal-Uruchurtu, M. F. Ruiz-lópez, *Chem. Phys. Lett.* **330**, 118 (2000).
[4] A. Marion, G. Monard, M. F. Ruiz-lópez, F. Ingrosso *J. Chem. Phys.* **141**, 034106 (2014).

Quantum-Chemical Calculations on the Influence of Molecular Dipole Moments on Conformational Equilibria.

Johannes C. B. Dietschreit[1], **Tobias Schnitzer**[2], **Helma Wennemers**[2] ,
Christian Ochsenfeld[1]

[1]*Department of Chemistry, University of Munich (LMU), Butenandtstr. 7, 81377 Munich, Germany*
[2]*Laboratory of Organic Chemistry, D-CHAB, ETH Zürich, Vladimir Prelog Weg 3,CH-8093 Zürich, Switzerland.*

The correlation between dipole moments and solvent polarity on the conformational equilibrium of proline-analogues is investigated using quantum-chemical calculations. The proline-analogues are capped amino acids with four, five, and six membered rings. The N-terminus is acetylated and the C-terminus carries one of five possible modifications (X=NH_2, NHMe, NMe_2, OH, OMe). The different C-terminal cappings lead to different dipole moments and thus different cis-trans equilibria for the N-terminal cap.



X = NH_2, NHMe, NMe_2, OH, OMe

Our work is in line with an earlier study performed for prolines carrying different electron withdrawing groups on the ring [1]. In our present study, molecular geometries were obtained using the polarisable continuum model COSMO [2] at the PBEO-D3/def2-tzvp level [3-5]. The combined computational and experimental study indicates a connection between the solvent polarity and the molecular dipole. Their influence governs the conformational equilibrium measured in solution.

[1] C. Siebler et al. *Chem. Sci.* **6**, 6725 (2015).

[2] TURBOMOLE V7.02, 2015, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989?2007, TURBOMOLE GmbH, since 2007, available from http://www.turbomole.com.

[3] J.P. Perdew, M. Ernzerhof, K. Burke *J. Chem. Phys.* **105**, 9982 (1996).

[4] S. Grimme, J. Antony, S. Ehrlich, and S. Krieg *J. Chem. Phys.* **132**, 154104 (2010).

[5] F. Weigend, R. Ahlrichs *Phys. Chem. Chem. Phys.* **7**, 3297 (2005)

Reduced scaling explicitly correlated coupled cluster methods for large molecular systems

Fabijan Pavošević[1]**, Chong Peng**[1]**, Frank Neese**[2]**, Edward F. Valeev**[1]

[1]*Department of Chemistry, Virginia Tech, Blacksburg, Virginia, USA*
[2]*Max Planck Institute for Chemical Energy Conversion, Stiftstr. 34-36, 45470 Mülheim an der Ruhr, Germany*

In the first part of our talk, we will present a linear-scaling formulation and implementation of the coupled cluster singles doubles and perturbative triples method with perturbative treatment of explicit correlation. Our approach is based on the local domain pair natural orbital methodology using the SparseMap infrastructure developed by F. Neese and E. F. Valeev [1]. All post-mean-field steps in the DLPNO-CCSD(T)-F12 have computational cost that grows linearly with the system which is shown for *n*-alkane with up to 200 carbon atoms in the def2-TZVP basis set. The robustness of the DLPNO-CCSD(T)-F12 method was validated against the massively-parallel canonical CCSD(T)-F12 method in the MPQC4 package [2] for a 20-water cluster and applied to the L7 benchmark dataset for non-covalent interactions [3]. In the second part of our talk, we will present a massively-parallel implementation of the Laplace-transform perturbative triple correction (T) to the CCSD energy within density fitting framework [4]. We will validate precision of the method with respect to number of quadrature points on large molecular systems. Furthermore, we will compare the performance to a state of the art implementation in the NWChem quantum chemistry software [5] on a DNA base-pair, a system with more than one thousand basis functions.

[1] P. Pinski, C. Riplinger, E. F. Valeev, F. Neese, *J. Chem. Phys.* **143**, 034108 (2015).
[2] C. Peng, J. A. Calvin, F. Pavošević, J. Zhang, E. F. Valeev, *J. Phys. Chem. A.* **120**, 10231 (2016).
[3] F. Pavošević, C. Peng, P. Pinski, C. Riplinger, F. Neese, E. F. Valeev, *J. Chem. Phys.* **146**, 174108 (2017).
[4] F. Pavošević, C. Peng, E. F. Valeev, *Manuscript in preparation.*
[5] V. M. Anisimov, G. H. Bauer, K. Chadalavada, R. M. Olson, J. W. Glenski, W. T. C. Kramer, E. Aprà, K. J. Kowalski, *J. Chem. Theory Comput.* **10**, 4307 (2014).

Efficient and Accurate Born-Oppenheimer Molecular Dynamics for Large Molecular Systems

Laurens D. M. Peters[1, 2], **Jörg Kussmann**[1, 2], **Christian Ochsenfeld**[1, 2]

[1]*Chair of Theoretical Chemistry, Department of Chemistry, University of Munich (LMU), Butenandtstr. 7, D-81377 München, Germany*

[2]*Center for Integrated Protein Science (CIPSM) at the Department of Chemistry, University of Munich (LMU), Butenandtstr. 5–13, D-81377 München, Germany*

Born-Oppenheimer molecular dynamics (BOMD) simulations have become a powerful tool for sampling potential energy surfaces, predicting experimental spectra, and calculating thermodynamic properties. These observables are usually obtained as means or integrals of properties, so that many time steps are necessary to yield accurate results. Consequently, a huge number of minimizations of the electronic wavefunction and determinations of the gradient of the electronic ground state are required. BOMD simulations are, therefore, computationally demanding especially when the system contains more than 100 atoms.

Here, we introduce a scheme that enables efficient and accurate BOMD simulations of large molecular systems [1]. It combines three recent developments from the fields of BOMD, electronic structure theory, and computer technology: (1) The corrected small basis set Hartree-Fock (HF-3c) method by Sure and Grimme [2], which yields accurate interaction energies and geometries (comparable to large basis set density functional theory calculations) at the cost of one Hartree-Fock calculation with a minimal basis set, (2) the extended Lagrangian BOMD (XL-BOMD) method by Niklasson *et al.* [3], which reduces the number of necessary self-consistent field cycles, and (3) efficient methods for calculating Coulomb and exchange terms on graphics processing units (GPUs) within our FermiONs++ program package [4, 5].

To explore the performance of our strong scaling implementation of the method we present timings and first illustrative applications by extracting high-quality vibrational spectra from simulated trajectories of several molecular systems containing up to 500 atoms. We conclude that the presented BOMD scheme may be used as a cost-efficient and reliable tool for computing vibrational spectra and thermodynamics of large molecular systems with more than 100 atoms and explicit solvent molecules.

[1] L. D. M. Peters, J. Kussmann, C. Ochsenfeld, *to be published.*

[2] R. Sure, S. Grimme, *J. Comput. Chem.* **34**, 1672 (2013).

[3] A. M. N. Niklasson, P. Stenetag, A. Odell, N. Bock, M. Challacombe, C. J. Tymczak, E. Holmström, G. Zheng, V. Weber, *J. Chem. Phys.* **130**, 214109 (2009).

[4] J. Kussmann, C. Ochsenfeld, *J. Chem. Phys.* **138**, 134114 (2013).

[5] J. Kussmann, C. Ochsenfeld, *J. Chem. Theory Comput.* **11**, 918 (2015).

Resonant inelastic X-ray scattering amplitudes and cross-sections in the ADC/ISR framework

Dirk R. Rehn[1], **Andreas Dreuw**[2], **Patrick Norman**[1]

[1]*Department of Theoretical Chemistry and Biology, School of Biotechnology, Royal Institute of Technology, 100 44 Stockholm, Sweden*
[2]*Interdisciplinary Center for Scientific Computing, University of Heidelberg, Im Neuenheimer Feld 205, 69120 Heidelberg, Germany*

With the development of 4th generation synchrotron radiation sources one has not only reached an unprecedented control of energy, momentum, and polarization of the source photons but also provided access to light of ultra-high brilliance. This combination has in turn led to a rapid recent development in experiments based on the resonant inelastic X-ray scattering (RIXS) phenomenon. The refinement of RIXS remains in the spotlight even though it has been an established method for decades.

Ab initio simulations of RIXS cross-sections based on the Kramers-Heisenberg-Dirac (KHD) formula offer valuable support for the interpretation and in-depths understanding of the complex experimental spectra. However, common approaches based on the KHD expression are usually limited to a qualitative description including only selected channels.

The algebraic diagrammatic construction [1] (ADC) scheme of the polarization propagator together with the so-called intermediate state representation (ISR), offers a convenient and straightforward way to evaluate the full electronic part of the RIXS scattering amplitudes. This is achieved by transforming the KHD formula into a closed-form matrix expression which can be solved using standard numerical techniques.

We present an implementation [2] which provides to our knowledge for the first time access to a quantitative theoretical description of RIXS amplitudes and transition strengths for medium-sized molecular systems. Based on the ADC/ISR approach our implementation facilitates the simulation of RIXS maps up to third order in perturbation theory.

[1] A. Dreuw and M. Wormit, *WIREs Comput. Mol. Sci.* **5**, 82, 2015

[2] D. R. Rehn, A. Dreuw and P. Norman, *J. Chem. Theory Comput.*, submitted

Simulation of absorption and emission spectra of Laurdan in bilipid layer systems

Mirza Wasif Baig,[1] Marek Pederzoli,[1] Lukasz Cwiklik[1] and Jiri Pittner[1]

[1]Department of Theoretical Chemistry, J Heyrovsky Institute of Physical Chemistry
Dolejškova 2155/3, 182 23 Prague 8, Czech Republic

Abstract: Fluorescence is a process following light absorption in which a molecule emits photons of longer wavelength than the photon absorbed during absorption. This shift toward lower energy results from vibrational relaxation of the molecule in the excited state. In condensed phases, in particular in water, polarity of solvent often has a very pronounced effect on emission wavelength because in the excited state the relaxation processes include both fluorophore and solvent relaxation. This solvatochromic effect is often utilized in fluorescence spectroscopy methods, for instance, in time resolved emission spectroscopy (TRES) where both the total energy shift and relaxation kinetics can be measured. In biological environments, such as lipid bilayers, the solvatochromic effects are typically used for probing system hydration and dynamics at the nanometer and nanosecond levels. To this end, environmental sensitive fluorescent probes are which significant solvatochromic shifts are used.

Laurdan (6-Dodecanoyl-2-Dimethylaminonaphthalene), is often employed to investigate lipid membrane hydration and mobility. Still, exact mechanism of Laurdan fluorescence in lipid bilayers is not fully understood. We investigate absorption and fluorescence spectra of Laurdan in two phospholipid bilayers, DOPC and DPPC, characterized by different hydration and rigidity. Classical molecular dynamics simulations are employed to sample conformations of Laurdan in both membranes. Empirical force field is used to describe both ground and excited state dye in MD simulations. For selected snapshots, excited state molecular dynamics simulations employing a quantum mechanical and molecular mechanical approach with time-dependent density functional theory (TD-DFT QM/MM MD) are performed. The resulting spectra are compared with experimental ones in different membrane environments.

Reaching graphene-water systems: A new electronic-structure-based force field

Sergi Ruiz-Barragan[1]**, Daniel Muñoz-Santiburcio**[1]**, Dominik Marx**[1]

[1]*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum*

Since its discovery, graphene is receiving an ever-increasing attention due its fascinating properties and applications [1, 2]. Although there are many experimental and theoretical studies about graphene in contact with water [2], the interaction between these two components is difficult to determine experimentally [3]. On the other hand, the computational determination of the water/graphene interaction energy is rather cumbersome because of its really weak character, taking into account that the most exact methods are not feasible for large systems. For this reason, the values in the literature are discordant [4], which makes it difficult to properly define a force field for the water/graphene interaction.

In this work, a new force field based on RPBE-D3 calculations is presented. RPBE-D3 is computationally affordable and its description of the water/graphene interaction is in agreement with previous CCSD(T) results [5]. We show how this force field can reproduce properly the features of water/graphene interface obtained at the *ab initio* level. This new force field can be used to estimate slowly-converging properties only reachable with simulation times in the order of nanoseconds, not accessible with *ab initio* MD.

[1] A. Geim, K. Novoselov, *Nature Materials* **6**, 183 (2007).

[2] A. Striolo, M. Angelos, J.Laurent, *Annu. Rev. Chem. Biomol. Eng.* **7**, 533 (2016).

[3] F. Taherian, V. Marcon, N. van der Vegt, *Langmuir* **29**, 1457 (2013)

[4] Y. Wu , N. Aluru, *J. Phys. Chem. B* **117**, 8802 (2013)

[5] E. Voloshima , D. Usvyat, M. Schütz , Y. Dedkov, B. Paulus, *Phys. Chem. Chem. Phys.* **13**, 12041 (2011)

Site-Occupation Embedding Theory using Bethe Ansatz Local Density Approximation

B. Senjean[1], **N. Nakatani**[2], **M. Tsuchiizu**[3], **E. Fromager**[1]

[1]*Laboratoire de Chimie Quantique, Institut de Chimie, CNRS/Université de Strasbourg, Strasbourg, France*
[2]*Institute for Catalysis, Hokkaido University, N21 W10 Kita-ku, Sapporo, Hokkaido 001-0021, Japan*

[3]*Department of Physics, Nagoya University, Nagoya, Japan*

Modelling strongly correlated electronic systems is still challenging in both quantum chemistry and condensed matter physics. A system is said to be strongly correlated if its physical properties are governed by non-trivial electron-electron interactions. For instance, this is the case for transition metal oxides when the electrons are close to a metal-insulator transition. In this case, mean-field approaches such as the Hartree Fock give a wrong description of the properties of the system. To deal with such systems, we have to go beyond the mean-field approximation:

- On the one hand, the interaction can be computed thanks to an explicit treatment of the electronic wavefunction (Density Matrix Renormalization Group[1], post Hartree-Fock methods), which is computationally expensive.

- On the other hand, Kohn-Sham Density Functional Theory (KS-DFT)[2] is a computationally low cost method with a relatively good accuracy. However, standard approximations made for the density functionals often fail to describe strong correlation energies.

One strategy is to build a theory which makes the best compromise between computation time and accuracy. In this context, an embedding scheme in principle exact called Site-Occupation Embedding Theory (SOET)[3,4] treats the correlation explicitly on some sites (called impurities), while the rest of the system is noninteracting (called bath) and treated with a density functional. SOET is therefore a rigorous combination of wavefunction method (DMRG) and DFT. The Hubbard model (see Figure) will be our laboratory because of its simplicity as well as its physical richness. In this embedded context, approximate density functionals based on KS-DFT applied to model Hamiltonians[5] and on the standard Anderson impurity model[6] are studied.

[1] S.R. White, *Phys. Rev. Lett.* **69**, 2863 (1992)
[2] W. Kohn and L. Sham, *Phys. Rev.* **140**, A1133 (1965)
[3] E. Fromager, *Mol. Phys.* **113**, 419 (2015)
[4] B. Senjean, M. Tsuchiizu, V. Robert and E. Fromager, *Mol. Phys.* **115**, 48 (2017)
[5] N. Lima, M. Silva, L. Oliveira and K. Capelle, *Phys. Rev. Lett.* **90**, 146402 (2003)
[6] P.W. Anderson, *Phys. Rev.* **124**, 41 (1961) ; K. Yamada, *Progr. Theoret. Phys.* **53**, 970 (1975) ; J.P. Bergfield, Z.F. Liu, K. Burke and C.A. Stafford, *Phys. Rev. Lett.* **108**, 066801 (2012)

Chemical dynamics simulations to study tandem mass spectrometry peptide fragmentation: polyproline series $[\mathrm{pro}_n\text{-H}]^-$ as example.

Ana Martin-Somer[1,2], **William. L. Hase**[3], **and Riccardo Spezia**[2]

[1]*Departamento de Química, Universidad Autónoma de Madrid, Madrid (Spain)*
[2]*CNRS, Université d'Evry, Evry (France)*
[3]*Texas Tech University, Lubbock, Texas (USA)*

Positive mode mass spectrometry (MS) is routinely used in fields like proteomics [1]. Negative mode, is however less popular, while being a rather good complement to the aforementioned positive mode. A number of questions can be put forward about the fragmentation chemistry involved in negative mode MS. Where does the peptide deprotonate in absence of acidic residues? After activation of peptide anions, are protons mobile in a similar fashion as in their protonated analogues? Does the size of the peptide-chain influence the fragmentation?

Polyprolines are good models to address these questions since they possess no amide or acidic protons. In this work we studied pro_2^-, pro_3^- and pro_4^- fragmentation using direct dynamics simulations[2] (the potential energy surface is computed on-the-fly using PM3 semiempiric Hamiltonian). We performed two kinds of simulations: i) the molecule is internally excited, considering a uniform distribution of the energy within the molecule. ii) the anion is made to collide with Ar in such a way that the translational energy is transferred to the vibrational and rotational modes of the peptide.

Using this technique we could explain, at an atomic level, the unimolecular reactivity of $[\mathrm{pro}_n\text{-H}]^-$, *i.e.*, the mechanisms leading to the different fragments (as for example the typical b_2^- and y_1^-).We also observed some differences between the two ways of activating the molecule. For internally excited trajectories unimolecular dissociation follows exponential decay while in collision activation the initial population decays in a non-exponential way [3]. Furthermore, the thermal simulations allowed us to compute the temperature dependent rate constants, $k(T)$, and the Arrhenius A en E_a parameters. To complete the information provided by trajectories we compared results with those obtained experimentally. To the best of our knowledge, this is the first time that dynamics simulations are applied to explain the fragmentation of negative peptide ions.

[1] A.Bensimon, A.J.R. Heck, and R.Aebersold, *Annu. Rev. Biochem.,* **81**, 379 (2012).
[2] S.Pratihar, X.Ma, Z.Homayoon, G.L.Barnes, W.L.Hase, *J. Am. Chem. Soc.* **139**, 3570 (2017).
[3] R.Spezia, A.Martin-Somer, V.Macaluso, Z.Homayoon, S.Pratihar and W.L.Hase, Faraday Discuss. **195**, 599 (2016).

Oxidation of metallocenes as external stimuli to enhance the reactivity of catalytically active metal complexes

Stephan Kohaut[1], **Alexander Feyrer**[2], **Frank Breher**[2], **Karin Fink**[1]

[1] *Institut für Nanotechnologie, Karlsruher Institut für Technologie (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

[2] *Institut für Anorganische Chemie, Karlsruher Institut für Technologie (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany*

Hydrosilylation is one of the key catalytic reactions in the synthesis of organosilicon compounds. Depending on the catalytically active metal center two possible reaction paths have been proposed [1]. In contrast to its heavier neighbor platinum it was concluded for rhodium that the hydrosilylation reaction proceeds through a modified Chalk-Harrod mechanism [2]. Recently it was shown that a redox-active, mesityl(Mes)-substituted phosphaferrocenophane (FcPMes) can influence the reactivity of a coordinated transition metal within the proposed modified Chalk-Harrod mechanism [3]. Oxidation of the metal center in the metallocene led to enhanced reactivity and selectivity towards the hydrosilylation of alkynes by a rhodium complex. Thereby it was observed from DFT based calculations, that the positive partial charge from the metallocene was partially shifted to the rhodium atom which led to a significantly lower barrier for the final reductive elimination step. In addition to the previous work we studied the influence of the oxidation of the metal center on the other steps of the catalytic process.

For a detailed understanding of the role of the metallocene unit on the reaction at the rhodium site, we investigated several model systems. The role of the iron center is analyzed by substitution with different 3d elements (Co, Zn) or by removing the metal center completely. This allows to differentiate between cooperative effects between the metal centers and the sterical effect due to the metallocene unit.

[1] A. K. Roy, Adv. *Organomet. Chem.* 2008, **55**, 1 (2008).

[2] S. Sakaki, M. Sumimoto, M. Fukuhara, M. Sugimoto, H. Fujimoto, S. Matsuzaki, *Organometallics* **21**, 3788 (2002).

[3] A. Feyrer, M. K. Armbruster, K. Fink, F. Breher, *Chem. Eur. J.* **23**, 7402 (2017).

We thank the DFG for funding within the collaborative research centre SFB/TRR 88 “Cooperative effects in homo- and heterometallic complexes (3MET)”, projects B1 and B4.

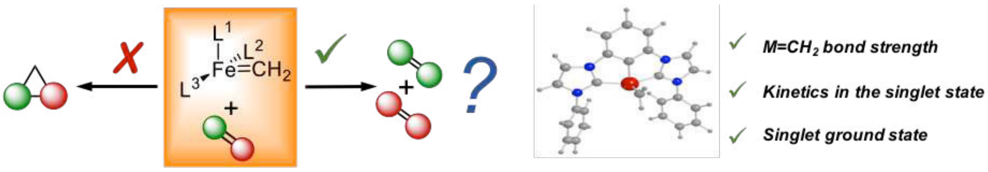
Electronic structure and reactivity with alkenes of iron carbenes complexes: Towards iron-based olefin metathesis.

Xavier Solans-Monfort,[1] **Égil de Brito Sá,**[1,2]**, Luis Rodríguez-Santiago,**[1]
Mariona Sodupe[1]

[1] *Universitat Autònoma de Barcelona, Cerdanyola del Vallès, 080290, Barcelona-Espanya*
[2] *Universidade Federal do Piauí, Campus Ministro Reis Velloso, Parnaíba, 64202-020, Piauí-Brasil*

Olefin Metathesis (OM) is an efficient synthetic tool for carbon-carbon double bond formation. It requires the presence of a metal carbene [M]=CR_2 acting as catalyst to take place. Most of the carbenes used today are based on Mo, W and Ru. These metals are not within the most abundant elements in earth. Therefore, substituting them for cheaper, eco-friendly and less toxic first row transition metal complexes is a desirable goal. In this way, iron appears as the best candidate, since it belongs to the same group as ruthenium. Unfortunately, the synthesis of iron carbenes is challenging and the existing species does not perform metathesis. That is, cyclopropanation is the most common process when reacting first row transition metal carbenes with olefins. Computational chemistry appears as potential technique for determining the suitable combination of ligands, oxidation state and coordination around iron that could favor the olefin metathesis reaction.

In this contribution, we study the reactivity of the existing [Fe]=CR_2, as well as a large set of possible *in silico* designed $L_3M=CH_2$ and $L_4M=CH_2$ carbenes. In a first stage, we calibrated the different DFT methods with the available experimental date. Afterwards, we analyzed which coordination sphere, nature of the ancillary ligands and oxidation state of iron could favor olefin metathesis instead of cyclopropanation. Results show that alkyl-containing σ-donating ligands promotes singlet ground state iron carbenes. However, this is not sufficient for favoring metathesis. In fact, the best combination of ligands is highly sensitive to the geometry around the metal center and coordination number.[1]



[1] E. de Brto Sá, L. Rodríguez-Santiago, M. Sodupe, X. Solans-Monfort, *Organometallics.* **35**, (2016) 3914.

Enhanced sampling methods at the bio-inorganic interface: insights on silica biocompatibility and nanotoxicity

Massimo Delle Piane, Nils Hildebrand, Lucio Colombi Ciacchi

Faculty of Production Engineering and Bremen Center for Computational Material Science, University of Bremen, Am Fallturm 1 28359, Bremen, Germany

The interaction between biomolecules and inorganic materials has become of prominent interest in fields ranging from basic research up to industrial product design, leaving several open challenges. Among inorganic materials, the interaction of silica with biological systems is particularly complex and contradictory, particularly at the nano-level. Indeed, on the one hand, silica is at the basis of several biomineralization processes, on the other hand, the contact of some types of silica nanoparticles with the membrane of erythrocytes is known to cause its rupture.

Molecular dynamics (MD) simulations are a valuable tool in investigating these interactions. However, despite the increase in available computational resources, MD still suffers a debilitating timescale problem that greatly reduces the number of phenomena that can be investigated. Numerous enhanced sampling methods have been introduced to alleviate this problem[1], such as Metadynamics (MetaD) and Replica Exchange with Solute Tempering (REST).

We will here present examples of their applications, to shed light on the interactions between biomolecules and silica. Particularly, recent results will be shown regarding the investigation of silica-induced protein conformational changes[2] and the effects of silica nanoparticles of various size and features on membrane models of different composition (Figure 1).

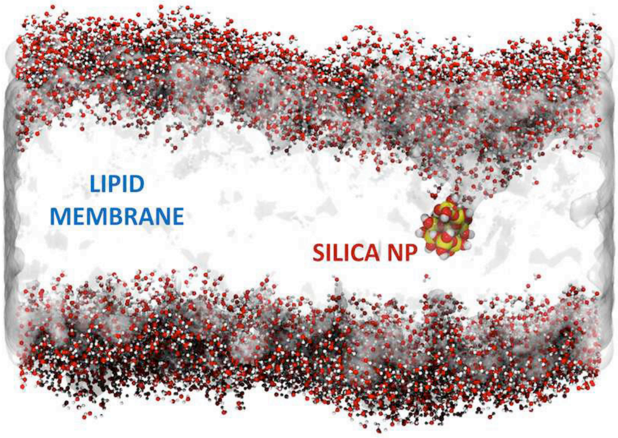


Figure 1: A small colloidal silica particle penetrating a phosphatidylcholine membrane.

[1] T. P. Valson Omar, M. Parrinello, *Annu. Rev. Phys. Chem.* **67**, 159 (2016).
[2] L. Derr, N. Hildebrand, S. Köppen, et al., *Biointerphases.* **11**, 011007 (2016).

Understanding the Gas-phase Fragmentation Mechanisms of Deprotonated L-Cysteine-sulfate via Direct Dynamics Simulations.

Veronica Macaluso[1], **Debora Scuderi**[2], **M. Elisa Crestoni**[3], **E. Martínez-Núñez**[4], **William L. Hase**[5] **and Riccardo Spezia**[1]

[1]*LAMBE, Univ Evry, CEA, CNRS, Université Paris-Saclay, Blvd. F. Mitterrand, Evry, France*
[2]*Laboratoire de Chimie Physique, UMR 8000, Université Paris Sud, Orsay, France*
[3]*Dipartimento di Chimica e Teconologie del Farmaco, Università di Roma La Sapienza, Rome, Italy*
[4]*Department of Physical Chemistry, University of Santiago de Compostela, Spain*
[5]*Department of Chemistry and Biochemistry, Texas Tech University, Lubbock (TX), USA*
veronica.macaluso@univ-evry.fr

Thiolate cystenyl residues of proteins have different roles in different cellular processes, in particular, in combatting the oxidative stress. In fact, Cys-SH functions are known as to be the major targets of perossides species, and the associated oxidation process can induce many different post-translational modifications. The sulfenic acid seems to be the most interesting one, since has been detected in a broad range of signalling cellular mechanisms. [1] Scuderi, Crestoni and co-workers have characterized the L-cysteine-sulphate anion (m/z 200) via tandem mass spectrometry with the purpose of forming the deprotonated sulfenic acid (m/z 136). In particular, coupling IR-MPD spectroscopy with collision induced dissociation (CID), they investigated the structure of these ions. How the *m/z* 136 ion, and other fragment ions obtained in gas phase as a function of collisional conditions, is an open question.

Coupling collisional dynamics simulations based on PM6-D semi-empirical Hamiltonian with DFT calculations, we have elucidated the different products suggesting the corresponding reaction mechanisms. First we were able to explain the selectivity in terms of thermodynamic *vs* kinetic control. Moreover, simulations suggested an initial common mechanism for the formation of *m/z* 136, observed in ion traps, and the ion *m/z* 81, which is the most abundant under linear collisional conditions. The last step is crucial to make the selection between these two ions and a roaming mechanism is at the basis of it. As in previous works [2] on roaming studies, our roaming mechanism product results to be the predominant product when performing IR-MPD experiments on the parent ion.

[1]D. S. Rehder, C. R. Borges, Biochemistry, **49**, 7748–7755 (2010)
[2]J. M. Bowman, Mol Phys, **112**, 2516-2528, (2014)

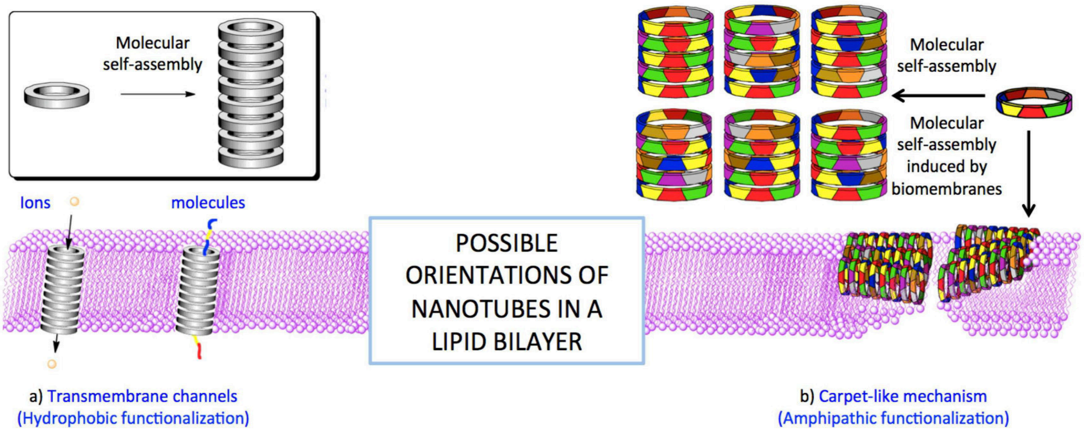
Molecular Dynamics applied to peptide nanotubes in a membrane environment

M. Calvelo,[1] J. R. Granja,[1] R. Garcia-Fandino[1,2]

[1]Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS), University of Santiago de Compostela 15782 Santiago de Compostela, Spain
[2]CIQUP, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, R. Campo Alegre s/n, P-4169-007 Porto, Portugal.

Self-assembling cyclic peptide nanotubes (SCPNs) have attracted a great amount of attention from the scientific community in recent years due to their important applications in biology, chemistry and material science.[1] They are based on cyclic structures that adopt a planar form with the amide groups arranged perpendicular to the plane of the cycle so that they are stacked by the formation of β-sheets. The radial disposition of the side chains outwards the channel modifies the external properties of the nanotube, allowing to control their formation and properties. The modulation of the external properties of SCPNs allows the design of cyclic peptides (CPs) that self-assemble into lipid membranes, changing their permeability and resistance properties.[2] Depending on the sequences the formed SCPNs can be oriented perpendicularly to the lipid membrane (hydrophobic CPs) or in a parallel fashion (amphiphilic CPs). The consequences of this orientation determine the response caused in the lipid membrane and confer them important properties, such as a high antimicrobial activity.

Using Molecular Dynamics simulations (both using atomistic-AA and coarse-grained-CG resolution) we have studied the effect of the inner-functionalization of the SCPNs cavities, as well as the modulation of their external properties when they are inserted into a lipid bilayer. Different examples carried out recently in our research group will be presented, showing the power of combining experimental and computational methods in the field of supramolecular chemistry and demonstrating the power of theoretical calculations when acting as an atomic microscope to analyze the fine details of a complex supramolecular structure.



[1] (a) A. Stavrakoudis, *Peptide,* **92**, 143 (2009). (b) A. Khalfa, *J. Phys. Chem. B*. **114**, 2676 (2010)

[2] D. Seebach, *Helv. Chim. Acta*, **80**, 173 (1997).

[3] (a) M. R. Ghadiri, *Nature*, **412**, 452 (2001). (b) L. Motiei, *Chem. Commun.*, 3693 (2009).

Assemblage of Metal Hydrides Clusters: Theoretical Design of One and Two-Dimensional Structures for Hydrogen Storage.

C. Giraldo[2], C. Z. Hadad[2], W. Tiznado[3], E. Osorio[1] and F. Ferraro[1]

[1]Departamento de Ciencias Básicas, Universidad Católica Luis Amigó, Transversal 51A # 67B-90, Medellín, Colombia
[2]Grupo de Química-Física Teórica, Instituto de Química, Universidad de Antioquia, AA1226, Medellín, Colombia
[3]Departamento de Ciencias Químicas, Facultad de Ciencias Exactas, Universidad Andrés Bello, Av. República 275, Santiago, Chile

Recently we have reported a theoretical design of new metal hydrides clusters based on the high stability of the $Al_4H_7^-$ system [1]. Our results showed that the systems with the higher stability and a high percentage of hydrogen, by weight, correspond to systems where three aluminum atoms have been substituted by three Mg-H and Be-H units, $Be_3AlH_{10}^-$ and $Mg_3AlH_{10}^-$ systems. Interestingly, these flat and tetrahedral conformations persist after being doped with Na^+ as contraion. In this work we report a theoretical study about the use of metal hydride clusters as assembly blocks for the formation a larger system, especially one and two-dimensional structures, in order to be used has hydrogen storage materials. For these purposes, the explorations on the potential energy surfaces (PES) of $(NaAl_4H_7)_n$ and $(NaE_3AlH_{10})_n$ clusters, whit E=Mg-Be and n=2-4 systems were performed, in addition, some larger linear and circular structures were proposed to determine their stability. The results obtained in this work showed that the cluster prefer to interact through contraion, in agreement whit fukui functions regions, which allows maintaining their identity as building blocks; otherwise, its initial building blocks conformation is lost; additionally, it was found that the cluster containing beryllium is the one that more easily retains its conformation as a block. It was also found that H-L gap decreases as the size of the system increase, in agreement with Gemming et al., work on $(Mo_3S_3)_n$ clusters [2]. On the other hand, some linear and circular structures were proposed with the aim of determining their stability; it was found that they are minima in the potential energy surface, but that they are around 30 kcal.mol^{-1} less stable that the global minima.

[1] C. Giraldo, F. Ferraro, C. Z. Hadad, L. Ruiz, W. Tiznado and E. Osorio. *RSC Adv*. **7**, 16069, 2017.

[2] S. Gemming, G. Seifert, N. Bertram, T. Fischer, M. Gotz and G. Gantefor. Chem. Phys. Lett. **474**, 127, 2009.

Alchemical Free Energy Calculations by Ensemble Dynamics: The Conveyor Belt Scheme.

David F. Hahn[1], **Philippe H. Hünenberger**[1]

[1] *Laboratory of Physical Chemistry, Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 2, 8093 Zurich, Switzerland*

Molecular dynamics (MD) simulations are an important tool for studying chemical and biological processes at a molecular level. MD can be used to predict differences between different chemical environments or molecular entities by means of alchemical free energy calculations where two physical end states A and B are connected by a coupling parameter λ along an alchemical pathway. Most commonly these calculations are performed by thermodynamic integration (TI)[1] or Bennett's acceptance ratio (BAR)[2]. We present an alternative method based on λ-dynamics[3][4], which employs several copies of a system (replicas) as parts of an ensemble with an assigned periodic variable Λ and mass m_Λ. This ensemble is propagated in the Λ-space, simultaneously moving each replica accordingly in the mapped λ space. Because of force compensation, the total force on the Λ is significantly lower compared to the forces acting on the λ of a single replica and thus facilitating diffusion of each replica along the alchemical pathway. We apply the method to three model systems and compare it to TI, which reveals several advantages: (i) Instead of multiple simulations as in TI, one simulation with several replicas is sufficient, therefore the set-up is convenient. (ii) The method is easier to automatize because no prior knowledge about the curvature of the pathway is needed. (iii) Since the energy barriers are lowered in comparison to λ-dynamics of one system, a nearly uniform sampling is achieved along the pathway. (iv) Because the pathway is sampled continuously, there is no error due to quadrature. (v) The calculations converge faster than TI calculations, thus they are computationally more efficient.

[1] J.G. Kirkwood, *J*. Chem. Phys. **3**, 300 (1935).

[2] C.H. Bennett, *J*. Comput. Phys. **22**, 245 (1976).

[3] X. Kong, C.L. Brooks III, *J*. Chem. Phys., **105**, 2414 (1996).

[4] N.S. Bieler, R. Häuselmann, P.H. Hünenberger, *J*. Chem. Theory Comput. **10**, 3006 (2014).

Electron correlation from a screened Coulomb formalism

Daniel Kats[1]

[1] *Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany*

Electron correlation is an important concept which can be understood as the missing part in the mean-field treatment. Wavefunction-based approaches are widely used in quantum chemistry to compute the electron correlation. The electron correlation energy can also be calculated as an infinite sum of all possible Feynman diagrams (excluding the diagrams which correspond to the mean-field energy). Taking into account only some classes of diagrams or combinations of diagrams can yield a polynomial-scaling method applicable even to molecular systems for which many wavefunction-based methods fail. [1]

The recently introduced screened Coulomb formalism [2] can be seen as one of the ways to guide the summation of diagrams. It can be used to derive the distinguishable cluster doubles approach [3], which is usually more accurate than the coupled cluster doubles for weakly correlated systems, and gives qualitatively correct description of strongly correlated systems. [3, 4, 5]

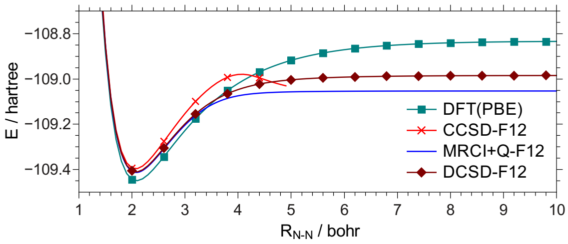


Figure 1: N_2 potential energy curve using aug-cc-pVTZ basis.

In this contribution new developments will be presented which further improve the results of the distinguishable cluster approach.

[1] R. D. Mattuck, *A Guide to Feynman Diagrams in the Many-Body Problem* (1976).

[2] D. Kats, *J. Chem. Phys.* **144**, 044102 (2016).

[3] D. Kats and F. R. Manby, *J. Chem. Phys.* **139**, 021102 (2013).

[4] D. Kats, *J. Chem. Phys.* **141**, 061101 (2014).

[5] D. Kats, D. Kreplin, H.-J. Werner, and F. R. Manby, *J. Chem. Phys.* **142**, 064111 (2015).

Bringing DORI to analyze and understand fluxional molecules

Benjamin Meyer[1], Laurent Vannay[1], Riccardo Petraglia[2], Michele Ceriotti[2] and Clémence Corminboeuf[1]

[1]Laboratory for Computational Molecular Design, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland
[2]Laboratory of Computational Science and Modeling, Institute of Materials, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland
benjamin.meyer@epfl.ch

The Density Overlap Region Indicator[1] (DORI) is a density-based scalar field, which reveals covalent bonding patterns and non-covalent interactions simultaneously (Figure 1). The present work goes beyond the traditional static quantum chemistry use of scalar fields and illustrates the suitability of DORI for analyzing geometrical and electronic signatures in highly fluxional systems. Examples include a dithiocyclophane, which possesses multiple local minima featuring a different extend of π-stacking interactions; DORI is then employed to capture fingerprints of CH-π and π-π interactions throughout the temperature-dependent rotational processes of a molecular rotor. Finally, it serves to examine the fluctuating π-conjugation pathway of a photochromic torsional switch (PTS). Molecular dynamic trajectories are obtained using the REMD@DFTB framework,[2] which combines density functional tight binding in DFTB+ and replica exchange molecular dynamic as implemented in the dynamic driver i-PI.[3] Attention will be placed on post-processing the large amount of generated data and on reducing their dimensionality using DORI.

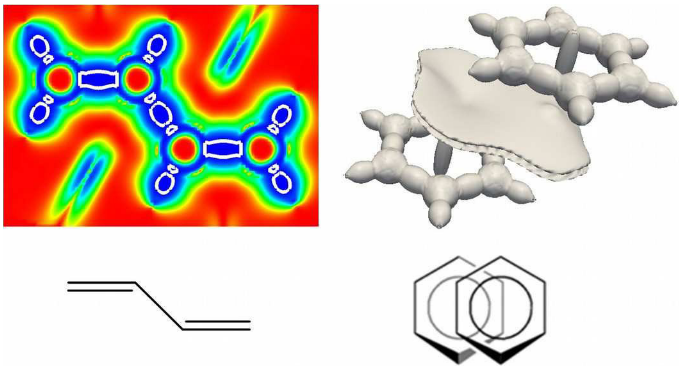


Figure 1: Two-dimensional DORI maps in the σ_h plane of the cyclobutadiene (left) and three dimensional DORI representation of the parallel-displaced benzene dimer (right).

[1] P. de Silva, C. Corminboeuf, *J. Chem. Theory Comput.* ***10***, 3745 (2014).
[2] R. Petraglia, A. Nicolaï, M. D. Wodrich, M. Ceriotti; C. Corminboeuf, *J. Comput. Chem.* ***37***, 83 (2016).
[3] M. Ceriotti; J. More; D. E. Manolopoulos; *Comput. Phys. Commun.* **185**, 1019 (2014).

Combining molecular docking and QM/MM methods for studying ligand binding to metalloproteins

Okke Melse, Antoine Marion, and Iris Antes

Center for Integrated Protein Science Munich at the Department of Biosciences, Technische Universität München, Emil-Erlenmeyer-Forum 8, D-85354 Freising, Germany

Combined Quantum Mechanics/Molecular Mechanics (QM/MM) studies were shown to be a valuable tool in areas of biomolecular simulations in which an explicit description of the system's electronic properties is needed, such as the prediction of spectroscopic properties or the simulation of enzymatic reactions [1]. More recently, QM/MM calculations were also evaluated for the area of computer-aided drug design, predominantly to improve the accuracy of binding free energy calculations and for the refinement of ligand binding poses. For these purposes many different variations in the free energy approaches as well as the QM methods applied were evaluated, with very varying success [2-3]. In the end, in most cases empirical, adjusting parameters were fitted to obtain satisfactory results.

We evaluated and optimized a new, combined molecular docking and QM/MM-based approach for the accurate calculation of ligand binding free energies in metal containing binding sites, which is not dependent on the use of any empirical fitting parameters. We specifically chose metalloenzymes as evaluation case as classical force fields are known to have several shortcomings in the description of metal interactions. Thus, describing the binding site with quantum mechanics should improve the description of potential polarization effects and the metal coordination. We evaluated different combinations such as calculating QM/MM interaction energies directly for optimized docking poses of the ligand or calculations of molecular dynamics-based QM/MMPBSA-based energies. In the presentation we will discuss the results obtained with the different combinations for four different metalloenzymes and present the final approach.

[1] H. M. Senn, W. Thiel, *Angew. Chem. Int. Ed.* **48**, 1198-1229 (2009).
[2] A. Khandelwal, S. Balaz, *Proteins: Struct., Funct., Bioinf.* **69**, 326-339 (2007).
[3] H. Lu, X. Huang, et al., *Bioorg. Med. Chem.* **22**, 2149-2156 (2014).

Vibrational properties of iridium and rhenium complexes in ground and excited states: Interpretation using DFT

Martin Pižl[1,2], **Stanislav Záliš**[1], **Jan Heyda**[1,3], **Antonín Vlček Jr.**[1,4]

[1]J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Dolejškova 3, 182 23 Prague, Czech Republic.
[2]Department of Inorganic Chemistry, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic.
[3] Department of Physical Chemistry, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic
[4] Queen Mary University of London, School of Biological and Chemical Sciences, Mile End Road, London E1 4NS, United Kingdom

Measurements of vibrational properties are often used for characterization of complexes. In excited state, the time-resolved infrared (TRIR) spectroscopy is used for investigations of vibrational properties. In the present study, we focused on complexes containing iridium or rhenium metal atoms.

The binuclear iridium complex - $[Ir_2(1,8\text{-diisocyanomenthane})_4]^{2+}$ - has two "deformational isomers" with different absorption at 470 nm (eclipsed) and 585 nm (twisted). Experimental photophysical data of both isomers were interpreted using DFT calculations in ground and excited states. Geometries of excited states were optimized by time-dependent DFT (TDDFT) for both singlet and triplet states.

In order to understand the character and dynamics of optically excited states DFT calculations were performed on $[Re(X)(CO)_3(L)]^n$ (X = Cl, Br, I, NCS; L = bpy (2,2'-bipyridine) or substituted bpy systems. Vibrational frequencies and intensities were calculated either by harmonic approach or by anharmonic one using the vibrational second order perturbation theory (VPT2) method. Molecular dynamic (MD) simulations on ground and the lowest triplet states followed by time DFT and TDDFT calculations at instant times were used for interpretation of time-dependent experimental data. Vibrational analyses of ground and excited states for both complexes are in good agreement with experimental data.

Acknowledgements This work was supported by the Ministry of Education of the Czech Republic (grant number LTC17052) and the COST Action CM1405.

Molecular excitation energies from the Bethe-Salpeter equation

Xin Gui[1], **Christof Holzer**[1], **Wim Klopper**[1]

[1]*Institute of Physical Chemistry, Karlsruhe Institute of Technology, Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany*

The Bethe-Salpeter equation (BSE) [1] was initially derived in nuclear physics and later imported to the field of computational solid-state physics. Recently, it has been widespread for calculating molecular excitation energies and provided optimistic results in a variety of systems.[2-6] The BSE formalism is very similar to the time-dependent density functional theory (TDDFT) in the language of linear response, and thus has the same scaling with respect to system size as TDDFT. However, BSE can be applied for description of excitations that are particularly problematic for TDDFT, e.g. excitations with charge-transfer character. The BSE approach has recently been implemented in our TURBOMOLE program using a resolution-of-the-identity (RI) approximation for all two-electron integrals that are required to solve the equation.[7] Since BSE normally requires quasiparticle energies from preceding *GW* calculations as input, *GW* and BSE have often emerged together, which is known as the *GW*-BSE formalism. Here we present an extensive assessment of the performances of the *GW*-BSE approach for singlet and triplet valence and Rydberg excitations, charge-transfer transitions, and absorption spectra of transition metal complexes. We also investigate the performances of BSE with different underlying *GW* methods, since the quality of the *GW* energy levels strongly affects the BSE excitation energies.

[1] E. E. Salpeter, H. A. Bethe, *Phys. Rev.* **84**, 1232 (1951).

[2] D. Jacquemin, I. Duchemin, X. Blase, *J. Chem. Theory Comput.* **11**, 3290 (2015).

[3] D. Jacquemin, I. Duchemin, X. Blase, *J. Chem. Theory Comput.* **11**, 5340 (2015).

[4] D. Jacquemin, I. Duchemin, X. Blase, *Mol. Phys.* **114**, 957 (2016).

[5] X. Blase, P. Boulanger, F. Bruneval, M. Fernandez-Serra, I. Duchemin, *J. Chem. Phys.* **144**, 034109 (2016).

[6] D. Jacquemin, I. Duchemin, X. Blase, *J. Phys. Chem. Lett.* **8**, 1524 (2017).

[7] K. Krause, W. Klopper, *J. Comput. Chem.* **38**, 383 (2017).

Modelling the structural and optical properties of supramolecular arrays adsorbed on two-dimensional materials

Anton S. Nizovtsev[1,2], Matteo Baldoni[1,3], Vladimir V. Korolokov[4],
Simon A. Svatek[4], James Kerfoot[4], Alex Summerfield[4],
Nicholas A. Besley[1], Peter H. Beton[4] and Elena Besley[1]

[1]School of Chemistry, University of Nottingham, University Park,
Nottingham NG7 2RD, United Kingdom
[2]Nikolaev Institute of Inorganic Chemistry SB RAS, Academician Lavrentiev Avenue, 3,
Novosibirsk, Russia
[3]ISMN, CNR, via P. Gobetti 101, 40129 Bologna, Italy
[4]School of Physics and Astronomy, University of Nottingham, University Park,
Nottingham NG7 2RD, United Kingdom

Two-dimensional supramolecular assembly of organic molecules, which can be achieved on a wide range of different substrates, provides a highly flexible route to control the spatial organization of adsorbates and the chemical functionality of a surface.

We present an overview of our recent computational studies based on the classical molecular dynamics and density functional theory, which was focused on modelling the structural and optical properties of different molecular arrays adsorbed on graphene and hexagonal boron nitride (*h*BN). The following main findings are highlighted:

(i) supramolecular organization of adsorbed alkane chains induces curvature in a graphene monolayer transferred onto a deformable substrate [1];
(ii) supramolecular heterostructures can be formed on *h*BN surface by sequential deposition of layers with different structural properties [2];
(iii) *h*BN surface influences the optical properties of the network formed by molecules, which are relevant for organic electronics.

We thank the Leverhulme Trust for providing financial support under the grant RPG-2016-104. EB acknowledges ERC Consolidator grant (307755 FIN).

[1] S. A. Svatek *et al.*, *Nano Lett.* **15**, 159 (2015).
[2] V. V. Korolkov *et al.*, *Nature Chem.* (2017), in press.

Leading relativistic corrections for L=1 atomic states calculated with a finite-nuclear-mass approach and all-electron explicitly correlated Gaussian functions.

Monika Stanke[1]

[1]*Institute of Physics, Faculty of Physics, Astronomy, and Informatics, Nicolaus Copernicus University, Grudziądzka 5, Toruń, PL 87-100, Poland*

We report progress in the development and implementation of quantum-mechanical methods for calculating bound ground and excited states of small atomic systems. The work concerns states with the L=1 angular momentum quantum number. The method is based on the finite-nuclear-mass (non-Born-Oppenheimer; non-BO) approach and the use of all-particle explicitly correlated Gaussian functions for expanding the non-relativistic wave function of the system. The development presented here includes derivation and implementation of algorithms for calculating the leading relativistic corrections determined using the standard first-order perturbation theory as expectation values of the operators representing the corrections using the non-BO wave functions. The method is tested in the calculations of the ten lowest ^1P states of the helium atom and the four lowest ^1P states of the beryllium atom.

Excited states with second order approximate internally-contracted multireference coupled-cluster linear response theory

Arne Bargholz[1], **Andreas Köhn**[1]

[1]*Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany*

Based on previous work from e.g. Banerjee and Simmons [1], Hanauer *et. all* [2] have introduced the internally-contracted multireference coupled-cluster theory. Namely the singles-and-doubles method with and without pertubative triples (ic-MRCCSD(T) and ic-MRCCSD) as multireference analoga to the well known single reference CCSD(T) and CCSD methods. The new methods are able to accurately consider strong static correlation while improving upon the treatment of dynamic correlation over standard multireference methods like MRCISD. Yet they share the steep scaling in computational cost with their single reference analoga, ic-MRCCSD scales O(N^6) iteratively and ic-MRCCSD(T) includes an O(N^7) non-iterative step. We present a cheaper O(N^5) second order approximate internally-contracted multireference coupled-cluster theory (ic-MRCC2) which can be used to obtain excitation energies in the framework of linear response theory (compare also [3]).
We will present ground state energies and vertical excitation energies of selected molecules and compare them to CASPT2, NEVPT2 and full ic-MRCCSD and ic-MRCCSD(T) results.

[1] A. Banerjee and J. Simons, *J. Quantum. Chem.* **2**, 207 (1981).

[2] M. Hanauer and A. Köhn, *J. Chem. Phys.* **134**, 204211 (2011).

[3] P. K. Samanta, D Mukherjee, M. Hanauer and A. Köhn, *J. Chem. Phys.* **140**, 134108 (2014).

Molecular dynamics simulation steady-state prediction by electrostatics — applications in supramolecular chemistry

Jean-Noël Grad[1], **Daniel Hoffmann**[1]

[1] *Bioinformatics and Computational Biophysics, Center for Medical Biotechnology,*
University of Duisburg-Essen, Universitätsstr. 7, D-45117 Essen, Germany

Recent improvements in software and hardware have enabled computationally-tractable microsecond molecular dynamics (MD) simulation of large protein complexes, offering new insights into biological processes with slow kinetics. Nonetheless, the MD sampling problem remains a challenging obstacle[1], especially in supramolecular chemistry where the protein–polymer interface is stabilized by a multitude of weak and non-specific interactions, often leading to a combinatorial explosion of the conformational landscape accessible to the polymer. In such a situation, the MD simulation steady-state may never be reached. Two decades ago, a similar computational problem was solved using FFT-driven algorithms for protein–protein recognition based on shape complementarity and electrostatics[2, 3], allowing the exhaustive sampling of protein–protein interface energetic landscapes in a time-efficient manner. The technique was successfully transferred to protein–ligand docking and mapping[4, 5], and was recently adapted by our group into a tool for MD simulation steady-state prediction. Using electrically charged fragments of macromolecular ligands to exhaustively scan a protein surface, we could extract information to narrow down MD starting conditions or assess MD convergence. Two test cases are presented: sonic hedgehog–heparin interactions and 14-3-3/c-Raf stabilization.

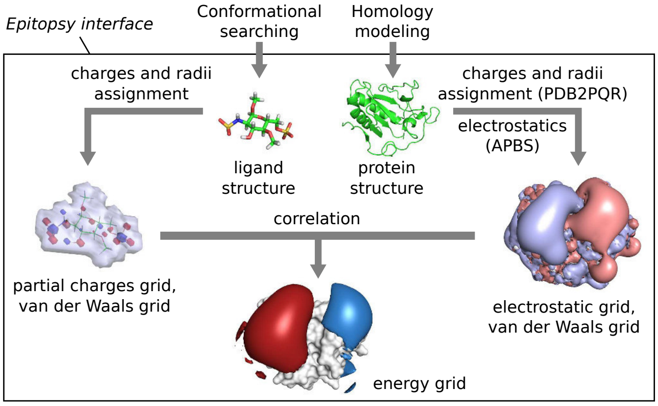


Figure 1: Computation of energy grids with our software Epitopsy. Source code available at: `https://github.com/BioinformaticsBiophysicsUDE/Epitopsy`

[1] D. M. Zuckerman, *Annu. Rev. Biophys.* **2011**, *40*, 41–62.
[2] E. Katchalski-Katzir *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **1992**, *89*, 2195–2199.
[3] H. A. Gabb *et al.*, *J. Mol. Biol.* **1997**, *272*, 106–120.
[4] S. E. Mottarella *et al.*, *J. Chem. Inf. Model.* **2014**, *54*, 2068–2078.
[5] C. H. Ngan *et al.*, *Nucleic Acids Res.* **2012**, *40*, W271–W275.

Using DFT Methods to Understand the Chemistry of Functionalized Binary and Intermetalloid Zintl Clusters

Lukas Guggolz[1], **Stefan Mitzinger**[1], **Armin Eulenstein**[1], **Stefanie Dehnen**[1]

[1]*Philipps-Universität Marburg, Fachbereich Chemie and Wissenschaftliches Zentrum für Materialwissenschaften, Hans-Meerwein-Straße, D-35043 Marburg, Germany*

In the course of our recent studies in the field of Zintl anion chemistry,[1–5] we use density functional theory (DFT) methods[6,7] to better understand this type of clusters. Our focus lies on both binary and intermetalloid Zintl anions. One of the goals of the experimental study is the reduction of the high anionic charges in order to modify the anions' chemical and physical surface properties, and thus to affect their stability and reactivity in common solvents. The calculations support the experimentalists on choosing suitable reactants.

We performed extensive and systematic computational studies on the properties of binary, tetrahedral group 13/14, 13/15, and 14/15 clusters and their possible functionalization with protons, silyl groups, and other (metal)organic substituents.

Additionally, we used DFT calculations to find the most plausible position for each element in binary Zintl clusters, depending on the electronic structure of the anion of choice. In doing so, we were also able to rationalize the protonation, and the respective positions of the hydrogen atoms in various clusters obtained by chemical synthesis.

[1] F. Lips, R. Clérac, S. Dehnen, *J. Am. Chem. Soc.* **133**, 14168 (2011).

[2] F. Lips, M. Hołyńska, R. Clérac, U. Linne, I. Schellenberg, R. Pöttgen, F. Weigend, S. Dehnen, *J. Am. Chem. Soc.* **134**, 1181 (2012).

[3] R. Ababei, W. Massa, K. Harms, X. Xie, F. Weigend, S. Dehnen, *Angew. Chem.* **125**, 13786 (2013); *Angew. Chem. Int. Ed.* **52**, 13544 (2013).

[4] S. Mitzinger, L. Broeckaert, W. Massa, F. Weigend, S. Dehnen, *Chem. Commun.* **51**, 3866 (2015).

[5] S. Mitzinger, L. Broeckaert, W. Massa, F. Weigend, S. Dehnen, *Nat. Commun.* **7**, 10480 (2016).

[6] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **7**, 3297 (2005).

[7] J. M. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.* **91**, 146401 (2003).

Can Coupled Cluster Theory Describe Polyradical Character?

Andrew M. James[1], **T. Daniel Crawford**[1], **Hans Lischka**[2]

[1]*Department of Chemistry, Virginia Tech, Blacksburg, Virginia, United States*
[2]*School of Pharmaceutical Sciences and Technology, Tianjin University, Tianjin, China*

Polycyclic aromatic hydrocarbon (PAH) systems have been the focus of many investigations in recent years. These materials are nano scale analogs to graphene, which has been shown to posses many properties that make it useful for applications in organic electronic devices. While many PAHs have closed-shell ground states, many examples exist of PAH which have open-shell and radical character in the ground state. In this work two classes of PAHs have been investigated to characterize polyradical features of their ground state electronic structure. The triangular non-Kekulé structures phenalenyl, triangulene, and a π-extended triangulene system with high spin ground states, and zethrene, p-quinodimethane-linked bisphenalenyl, and the Clar goblet, which have singlet-polyradical character in the ground state. Unrestricted Hartree-Fock (UHF), Coupled Cluster with singles and doubles (CCSD), and equation-of-motion CCSD (EOM-CCSD) computations have been carried out on these systems. The natural orbital occupation numbers (NOONs) have been computed to quantify the open shell character of their electronic structure in the ground, and lowest excited states. Given the expense associated with high-level CCSD calculations, the agreement between NOONs and singlet-triplet splitting with different orbital freezing schemes has been investigated. A comparison has been made to results of previous studies[1] where multi-reference methods have been used in order to probe the limitations of single-reference coupled cluster methods for chemical systems of this type.

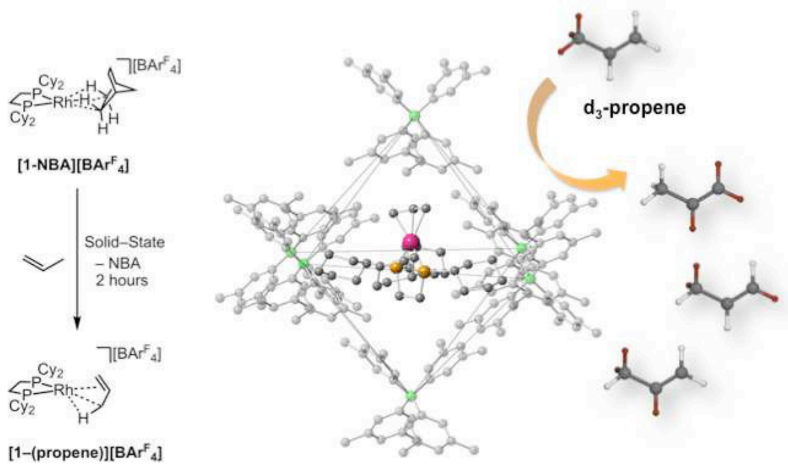
[1] A. Das, T. Müeller, F. Plasser, H. Lischka, *J. Phys. Chem. A.* **120**, 1625 (2016).

Modeling σ-Alkane Complexes as Precursors to Organometallic Catalysis in Solid-State.

Tobias Krämer[1], Stuart A. Macgregor,[1] F. Mark Chadwick,[2]
Alasdair I. McKay,[2] Andrew S. Weller[2]

[1]Institute of Chemical Science, Heriot-Watt University, Edinburgh, EH14 4AS, UK
[2]Department of Chemistry, University of Oxford, Oxford, OX1 3TA, UK

The crystalline solid-state environment is a versatile platform that can enable access to unstable organometallic species whose generation and stabilization might be difficult to achieve otherwise. We recently reported the targeted synthesis of well-defined σ-alkane complexes, e.g. **[1–NBA][BAr$^F{}_4$]** ([Rh($Cy_2P(CH_2)_2PCy_2$)(NBA)][BAr$^F{}_4$]; Cy = cyclohexyl; NBA = norbornane; Ar^F = 3,5–($(CF_3)_2C_6H_3$)), via single-crystal to single-crystal solid/gas transformations [1]. Such complexes feature a labile alkane directly coordinating to the metal center through their C–H σ-bonds, rendering them interesting precursors for onward solid/gas reactivity and catalysis.



Addition of small gaseous molecules such as propene or 1–butene to **[1–NBA][BAr$^F{}_4$]** in a solid/gas reaction results in the formation of the corresponding alkene complexes [2]. We used periodic electronic structure calculations in parallel with experiment in order to characterize these species structurally and spectroscopically, and modeled the processes involved in their solid/gas reactivity and catalysis.

[1] S. D. Pike, A. L. Thompson, A. G. Algarra, D. C. Apperley, S. A. Macgregor, A. S. Weller, *Science* **337**, 1648 (2012)

[2] F. M. Chadwick, A. I. McKay, A. J. Martinez-Martinez, N. H. Rees, T. Krämer, S. A. Macgregor, A. S. Weller, *Chem. Sci.*, submitted (2017)

Molecular Basis of Ligand Interaction of GPR40/GPR120 based on FMO Calculations with Multiple Sequence Analysis

Yuta Yamamoto[1], **Vladimir Sladek**[1, 2], **Sundaram Arulmozhiraja**[1, 2],
Kohsuke Hayamizu[3], **Shogo Nakano**[4], **Sohei Ito**[4], **Yasuo Watanabe**[3],
Shizuo Yamada[5], **Hiroaki Tokiwa**[1, 2]

[1] *Department of Chemistry, Rikkyo University, 3-34-1 Nishi-Ikebukuro, Toshima, Tokyo, 171-8501 Japan*
[2] *Research Center for Smart Molecules, Rikkyo University, 3-34-1 Nishi-Ikebukuro, Toshima, Tokyo, 171-8501 Japan*
[3] *General Health Medical Center, Yokohama College of Pharmacy, 601 Matano, Totsuka, Yokohama,245-0066 Japan*
[4] *Department of Food and Nutritional Sciences, University of Shizuoka, 52-1 Yada, Suruga, Shizuoka, 422-8526 Japan*
[5] *Center for Pharma-Food Research, University of Shizuoka, 52-1 Yada, Suruga, Shizuoka, 422-8526 Japan*

Free fatty acids (FFAs) are nutrients that provide a source of energy and play an important role as signaling molecules in various cellular processes. FFA receptors (FFARs), which belong to the superfamily of GPCRs, are activated by direct binding of FFAs. FFAR1 and FFAR4, (previously designed as GPR40 and GPR120), respectively, have been demonstrated by various pharmacological studies on insulin sensitivity. However, the molecular basis of ligand interactions at the receptors still remains unclear. To elucidate the difference of interactions between carbon chain length and the number of unsaturated bonds in the FFAs, the interaction analysis of FFAR1/FFAR4 complexes with ω-3 and ω-6 FFAs were performed by the first-principles calculations based fragment molecular orbital (FMO) calculations combined with multiple sequence analysis. All FMO calculations were carried out at the correlated RI-MP2/cc-pVDZ level. Consensus and corresponding amino acid residues in the receptors were identified by the multiple sequence alignment analysis using our newly-developed INTMSAlign program [1]. Active site could be found in FFAR4 by the multiple correlation analysis. And Arg183 and Arg258 among the residues in the active site were identified as key residues for stable interactions of FFAs binding to FFAR1 by the interfragment interaction energy (IFIE) analysis for the FFAR1 complex with ω-3/ω-6 FFAs. Similar combined analysis for the FFAR4 complex with ω-3 /ω-6 FFAs could also reveal that Arg99 contributes significantly stable interaction of FFAs to FFAR4 due to attractive electrostatic interaction with carboxyl group.

[1] S. Nakano & Y. Asano, *Sci. Rep.* **5**, 8193 (2015).

Molecular dynamics simulation study of self-organization of carbazole dendrimer

OneMichio Katouda[1], **Motomichi Tashiro**[2], **Yutaka Imamura**[3]

[1]*RIKEN Advanced Institute for Computational Science, 7-1-26 Minatojima-minami-machi, Chuo-ku, Kobe, Japan*

[2]*Department of Applied Chemistry, Toyo University, 2000 Kujirai, Kwagoe, Japan*

[3] *Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Japan*

Dendrimers is the macromolecule consisting of three major architectural components, the central core, branch units, and peripheral end groups. Dendrimers tend to form amorphous aggregation despite of the good symmetric structure, and the tendency is significant as the generation of the dendrimer increases. Only several examples have been reported for crystalline dendrimers consisting the earlier (first- or second-) generation dendrimers. Yamamoto and his coworkers reported recently the crystalline self-assembled π-conjugated dendrimer framework composed of a triazine (TAZ) core and third-generation carbazole (Cz) dendrons. [1] This third-generation triazine (G3TAZ) dendrimer forms different self-assembled structures and/or morphology depending on the concentration of dendrimers and the difference of mixture ratios of chloroform good solvent and acetonitrile poor solvent. In this study, we have performed the molecular dynamics simulation study to investigate the self-organization structures depending on the concentration of dendrimers and mixture ratios of solvents. The results of radial distribution functions (RDFs) indicate that different self-assembled structures are formed depending on the difference of the mixture ratio of chloroform and acetonitrile solvents. When the ratio of chloroform is higher than acetonitrile, the RDF indicates that the self-assembled structure of G3TAZ is crystal-like structure. The RDF when the ratio of acetonitrile is higher than chloroform indicates that the more amorphous-like structure is formed.

[1] S. Nakajima, K. Albrecht, S. Kushida, E. Nishibori, K. Yamamoto, Y. Yamamoto, (private communication).

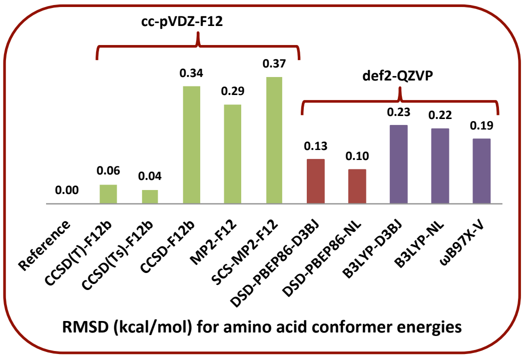
Benchmark *Ab Initio* Conformational Energies for the Proteinogenic Amino Acids and Assessment of DFT Functionals

Manoj K. Kesharvani[1], **Amir Karton**[2], **Jan M. L. Martin**[1,*]

[1]*Department of Organic Chemistry, Weizmann Institute of Science, 76100 Reḥovot, Israel*
Email: gershom@weizmann.ac.il
[2]*School of Chemistry and Biochemistry, The University of Western Australia, Perth, WA 6009, Australia*

The relative energies of the YMPJ [1] conformer database of the 20 proteinogenic amino acids, with N- and C-termination, have been re-evaluated using explicitly correlated coupled cluster methods. Lower-cost *ab initio* methods such as MP2-F12 and CCSD-F12b actually are outperformed by double-hybrid DFT functionals: in particular, the DSD-PBEP86-NL double hybrid performs well enough to serve as a secondary standard. Among range-separated hybrids, ωB97X-V performs well, while B3LYP-D3BJ does surprisingly well among traditional DFT functionals. Treatment of dispersion is important for the DFT functionals: for the YMPJ set, D3BJ generally works as well as the NL nonlocal dispersion functional. Basis set sensitivity for DFT calculations on these conformers is weak enough that def2-TZVP is generally adequate. For conformer corrections to heats of formation, B3LYP-D3BJ and especially DSD-PBEP86-D3BJ or DSD-PBEP86-NL are adequate for all but the most exacting applications. The revised geometries and energetics for the YMPJ database have been made available as electronic supporting information and should be useful in the parametrization and validation of molecular mechanics force fields and other low-cost methods. The very recent dRPA75 method yields good performance, without resorting to an empirical dispersion correction, but is still outperformed by DSD-PBEP86-D3BJ and particularly DSD-PBEP86-NL.

[1] Y. Yuan, M. J. L. Mills, P. L. A. Popelier, F. Jensen, *J. Phys. Chem. A*, **118**, 7876 (2014).

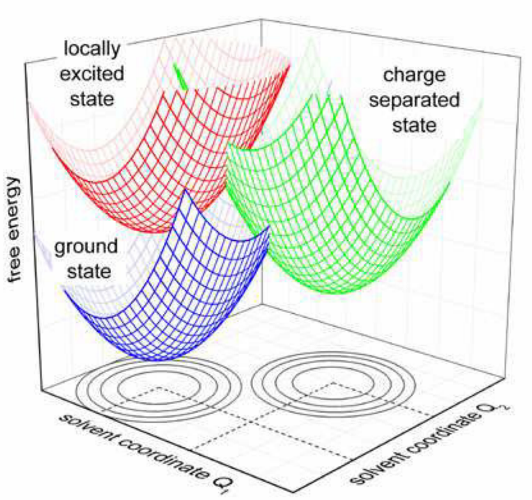


The model of multistage non-equilibrium electron transfer reaction in non-Debye polar solvent

Serguei V. Feskov

Volgograd State University, Universitetskiy pr.,100, Volgograd, Russia

Ultrafast photoinduced electron transfer reactions often proceed in non-equilibrium regime with respect to solvent polarization around the reactants. In non-Debye solvents with several relaxation timescales, a single-step electron transfer (ET) is generally described with a set of solvent "relaxation" coordinates. This approach however cannot be extended to multistage ET, because non-equilibrium polarization, formed at early stages, can affect subsequent photochemical processes in donor-acceptor molecular systems.



We report here a general model of multistage non-equilibrium ET, taking into account both multimode relaxation of solvent and electronic transitions between several molecular centers. The model uses reaction coordinates of two types ("spatial" and "relaxation" polarization coordinates) and a matrix of solvent reorganization energies for construction of parabolic free energy surfaces for electronic states of the molecular system.

Efficient numerical algorithms for solution of the model equations are also proposed. The algorithms are based on the Brownian simulation technique and address the most computationally demanding tasks of the method: 1) detection of the recrossing events for all electronic and vibrational transitions in the course of the reaction; 2) calculation of transient absorption spectra in photoreactions with participation of several intramolecular vibrational quantum modes; 3) simulation of optical excitation of the system by short laser pulses with known spectral and temporal characteristics. The proposed approaches allow reducing computational complexity of the algorithm with respect to some critical parameters (number of solvent relaxation modes, number of active high-frequency vibrational degrees of freedom, etc.) and thus rising performance of computations.

The work is supported by Russian Science Foundation under the project 16-13-10122.

Efficient Parallel Implementation of Exact Exchange for Periodic Systems within Concentric Atomic Density Fitting Approximation

Xiao Wang[1]**, Cannada A. Lewis**[1]**, Edward F. Valeev**[1]

[1]*Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061, United States*

Development of quantum chemistry methods for periodic systems, especially 2-D slabs and 3-D crystals, has been hampered for decades due to the unaffordable scaling with system size.[1] One of the obstacles is the computation of two-electron repulsion integrals, whose near-field interaction can only be computed exactly or approximated using density fitting (DF). In this work, a massively-parallel implementation of an efficient local DF method is presented in which product density is approximated using only auxiliary basis functions with the same centers as atomic orbitals (AOs) in that product. We applied this approach for the exchange term in Hartree−Fock with periodic boundary conditions (periodic HF) based on linear combinations of Gaussian-type AOs, leading to a significant decrease in the computational cost with an accuracy below millihartree per atom. Large computations such as lattice energies of 3-D systems are carried out efficiently using the new periodic HF method.

[1] C. Müller and B. Paulus *Phys. Chem. Chem. Phys.* **14**, 7605 (2012).

[2] D. S. Hollman, H. F. Schaefer, and E. F. Valeev *J. Chem. Phys.* **140**, 064109 (2014).

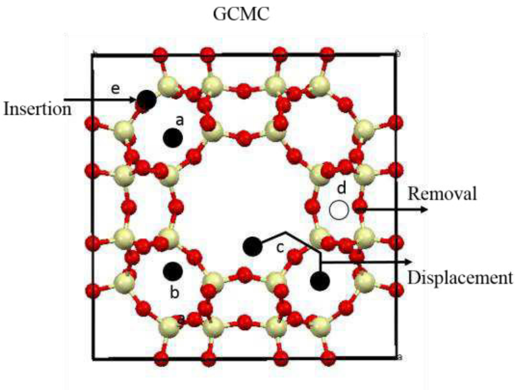
[3] S. Manzer, E. Epifanovsky, and M. Head-Gordon *J. Chem. Theory Comput.* **11**, 518 (2015)

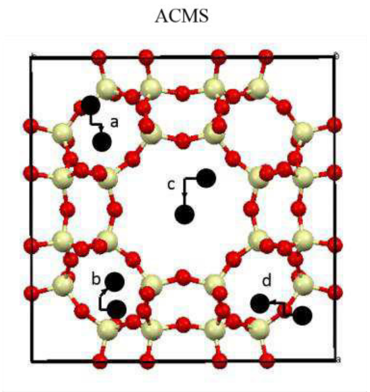
A Novel Method For Recruiting Global Optimization Techniques For Strategically Oriented Molecular Simulation

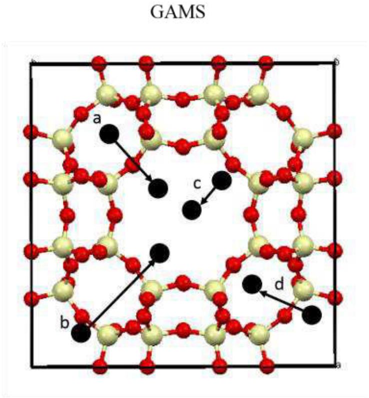
Leila LotfiKatooli[1*], Akbar Shahsavand[1], Fahimeh Nazarikatouli[2]

Chemical Engineering Department, Ferdowsi University of Mashhad, Mashhad, Iran[1]
Chemistry Department, Aliabad Katoul Branch, Islamic Azad University, Aliabad Katoul, Iran[2]
leylaalotfi@gmail.com [*]

Traditional molecular simulation techniques such as Grand Canonical Monte Carlo (GCMC) strictly rely on purely random search inside the simulation box for predicting the adsorption isotherms. This blind search is usually extremely time demanding for providing a faithful approximation of the real isotherm and in some cases may lead to non-optimal solutions. A novel approach is presented in this article which does not use any of the classical steps of the standard GCMC method, such as *displacement*, *insertation* and *removal*. The new approach considers the molecular simulation problem as a global optimization challenge. The proposed approach uses popular global optimazation techniques. Two different algorithms, Molecular simulation via Genetic Algorithm (GAMS) and Molecular Simulation via Ant Colony Algoirithm (ACMS) are introduced to find the optimal configuration for adsorption of any adsorbate on Nano-structured adsorbent under prevailing pressure and temperature. Three various case studies used for validation of new algorithms and results illustrate the superior performances of the proposed method over the standard GCMC technique. The introduced algorithms are more complex while they are more accurate and tremendously faster.







Controlling the Photoexcited Decay of Fe(II)-*N*-Heterocyclic Carbene Complexes Through Structural Modifications

Mátyás Pápai[1,2], Klaus B. Møller[1], György Vankó[2], Tamás Rozgonyi[3], Thomas J. Penfold[4]
[1]Department of Chemistry, Technical University of Denmark, Kemitorvet, DK-2800 Kongens Lyngby, Denmark;
[2]Wigner Research Centre for Physics, Hungarian Academy of Sciences, P.O. Box 49, H-1525 Budapest, Hungary
[3]Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, P.O. Box 286, H-1519 Budapest, Hungary
[4]School of Chemistry, Newcastle University, Newcastle upon Tyne, NE1 7RU, United Kingdom.

Understanding, and subsequently being able to manipulate, the excited-state decay pathways of functional transition metal complexes is of utmost importance in order to solve grand challenges in solar energy conversion and data storage. Herein, we present spin-vibronic quantum wavepacket dynamics simulations [1,2] on two functional Fe-*N*-heterocyclic carbene (NHC) complexes: the first discovered Fe(II)-NHC photosensitizer, $[Fe(bmip)_2]^{2+}$ (bmip = 2,6-bis(3-methyl-imidazole-1-ylidene)pyridine) [3], and its 3-*tert*-butyl (*t*-Bu) functionalized derivative, $[Fe(btbip)_2]^{2+}$ (btbip = 2,6-bis(3-tert-butyl-imidazole-1-ylidene)-pyridine). The results show that relatively minor variations in the molecular structure lead to completely different excited-state relaxation of the initially excited singlet metal-to-ligand charge transfer (^{1}MLCT) state. In $[Fe(bmip)_2]^{2+}$, the ultrafast ^{1}MLCT→^{3}MLCT intersystem crossing is followed by a rather slow ^{3}MLCT→^{3}MC (MC = metal-centred) decay, resulting in a relatively long (>4 ps) simulated ^{3}MLCT state lifetime, in good agreement with the experimental 9 ps value [3]. On the other hand, in the case of $[Fe(btbip)_2]^{2+}$, the initially photoexcited ^{1,3}MLCT state relaxes to MC states on the subpicosecond timescale. This occurs because the *t*-Bu functionalization stabilizes the ^{1}MC states, enabling the ^{1,3}MLCT→^{1}MC population transfer to occur in the near proximity of the Franck-Condon geometry, making the conversion very efficient. These simulations [1,2] demonstrate how the excited-state dynamics of these Fe(II)-NHC complexes can be controlled by comparably small changes in the ligand sphere, thus, paving the way for the design of high-efficiency transition metal-based functional molecules.

[1] M. Pápai, G. Vankó, T. Rozgonyi, T. J. Penfold, *J. Phys. Chem. Lett.*, 2016, **7**, 2009–2014.

[2] M. Pápai, T. J. Penfold, Klaus B. Møller, *J. Phys. Chem. C*, 2016, **120**, 17234–17241.

[3] Y. Liu, V. Sundström, K. Wärnmark, *Chem. Commun.*, 2013, **49**, 6412–6414.

Structure of hyaluronan solvation sphere and its influence on the molecular shape.

Marek Ingr[1,2], Eva Kutálková[1], Roman Witasek[1], Václav Buš[1], Josef Hrnčiřík[1]

[1]*Tomas Bata University in Zlín, Faculty of Technology, Department of Physics and Materials Engineering, Nám. T.G. Masaryka 5555, 76001 Zlín, Czech Republic*
[2]*Charles University, Faculty of Sciences, Department of Biochemistry, Hlavova 8/2030, 12843 Praha 2, Czech Republic*

Hyaluronan (HA), an alternating co-polymer of glucuronic acid and N-acetylglucosamine ([4)-β-D-Glc*p*A-(1→3)-β-D-Glc*p*NAc-(1→]$_n$) is an important biomolecule occurring in the extracellular matrix of the connective tissues, synovial fluid, vitreous fluid of eyes, etc. It has numerous biological functions and is also a promising material for drug delivery systems and tissue engineering. Free macromolecules of HA in aqueous solutions form highly swollen and loosely packed random coils. We have recently developed a molecular-dynamics (MD) based method for modelling HA random coils [1] which revealed the dependencies of the radius of gyration on concentration of dissolved ions, in an apparent agreement with experiment. In order to study the individual interactions governing the macromolecular shape we constructed an averaged plot of the solvation-sphere atoms surrounding the monomeric units of individual types. Analyzing this plot, tiny structural differences of the HA molecule and its solvation shell can be uncovered and correlated with the solution composition and the macromolecular properties. The plot also clearly identifies the hydrophilic and hydrophobic areas on HA molecule and supports the hypothesis of partially hydrophobic behavior of this otherwise strongly hydrophilic molecule [2]. In accord with this, hydrophobic interactions between two HA chains were identified, although the structures are rather unstable. Hence, the detailed description of HA solvation shell may contribute to understanding of the macromolecular shape of this molecule and its interactions with other, especially protein, molecules.

Acknowledgment: Access to computing and storage facilities owned by parties and projects contributing to the National Grid Infrastructure MetaCentrum provided under the program “Projects of Large Research, Development, and Innovations Infrastructures” (CESNET LM2015042), is greatly appreciated. RW was supported by the Internal Funding Agency of Tomas Bata University in Zlín, project IGA/FT/2016/011.

[1] M. Ingr, E. Kutálková, J. Hrnčiřík, *Carbohyd. Polym.* **170**, 289 (2017).
[2] J. Necas, L. Bartosiková, P. Brauner, J. Kolar, *Vet. Med.-Czech* **53**, 397 (2008).

Carbon-Chlorine Multiple Bonding in Doubly and Triply Charged Chlorobenzene

Felipe Fantuzzi[1]**, Benedikt Rudek**[2]**, Wania Wolff**[3]**, Marco A. C. Nascimento**[1]

[1]*Instituto de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ 21941-909, Brazil.*
[2]*Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany.*
[3]*Instituto de Física, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ, 21941-972, Brazil.*

In free-radical halogenation of aromatics, singly-charged ions are usually formed as an intermediate. We used a proton beam to ionize chlorobenzene (C_6H_5Cl, $^1\mathbf{1}$) and investigate its stability by means of time-of-flight mass spectroscopy. However, apart from the singly-charged parent-ion and its fragments, we find a significant yield of doubly- and triply-charged parent-ions. We used high-level theoretical methods based on Density Functional Theory (DFT) at the PBE0/cc-pVTZ(-f) level and Generalized Valence Bond (GVB) to calculate the structure, relative stabilities and bonding of these chlorobenzene dications and trications. The most stable isomers (Figure 1) are distonic and exhibit unusual carbon-chlorine multiple bonding: a terminal C=Cl double bond in a formyl-like CHCl moiety ($^1\mathbf{2}^{2+}$), and a cumulene-like C=C=Cl species ($^1\mathbf{3}^{2+}$). The GVB calculations also revealed an excited state of $^1\mathbf{3}^{2+}$ with a nitrile-like C≡Cl triple bond structure. This study paves the way for the synthesis of novel chlorine-containing compounds with multiple C-Cl bonds [1].

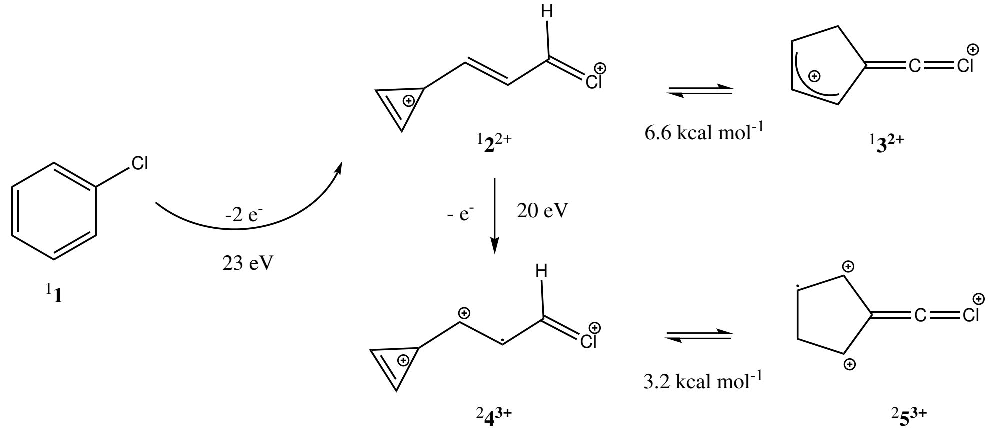


Figure 1: Most stable structures of doubly- and triply-charged C_6H_5Cl.

[1] F. Fantuzzi, B. Rudek, W. Wolff, M. A. C. Nascimento. *In preparation* (2017).

Towards Improved Machine Learning and Semiempirical Quantum Chemical Methods

Pavlo O. Dral and Walter Thiel

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

Many areas of research require fast methods for computing quantum mechanical (QM) properties. Particularly useful for this purpose are semiempirical QM (SQM) methods and machine learning (ML). Because of the underlying physical model, SQM methods can be general-purpose and reasonably accurate for many molecules quite far outside the training set, while ML is generally a special-purpose technique and only as good as its training set. In our lab we improve and combine both QM and ML methods.

We introduced improvements for training and applying kernel ridge regression-based ML to generate very accurate molecular potential energy surfaces that can be used to calculate rovibrational spectra of small molecules with spectroscopic accuracy (error less than 1 cm^{-1} relative to the reference *ab initio* spectrum)[1]. We also proposed two hybrid QM/ML approaches. The first one (an automatic parameterization technique) uses ML to improve the SQM Hamiltonian by adjusting semiempirical parameters[2] while the second one (Δ-ML) employs ML to correct low-level QM methods (SQM or DFT) using reference data from high-level QM calculations[3].

Moreover, we currently develop new general-purpose orthogonalization- and dispersion-corrected SQM methods (ODM*x*)[4] based on the robust OM*x* framework[5,6]. Our validation of preliminary parameterizations shows that the new ODM*x* methods are more accurate than the OM*x* methods for many ground- and excited-state properties and for noncovalent interactions[4]. They are essentially as fast as the OM*x* methods.

[1] P. O. Dral, A. Owens, S. N. Yurchenko, W. Thiel, *J. Chem. Phys., accepted.*

[2] P. O. Dral, O. A. von Lilienfeld, W. Thiel, *J. Chem. Theory Comput.* **11**, 2120 (2015).

[3] R. Ramakrishnan, P. O. Dral, M. Rupp, O. A. von Lilienfeld, *J. Chem. Theory Comput.* **11**, 2087 (2015).

[4] P. O. Dral, X. Wu, W. Thiel, *in preparation.*

[5] P. O. Dral, X. Wu, L. Spörkel, A. Koslowski, W. Weber, R. Steiger, M. Scholten, W. Thiel, *J. Chem. Theory Comput.* **12**, 1082 (2016).

[6] P. O. Dral, X. Wu, L. Spörkel, A. Koslowski, W. Thiel, *J. Chem. Theory Comput.* **12**, 1097 (2016).

CASPT2 on-the-fly surface hopping dynamics

Jae Woo Park[1], **Toru Shiozaki**[1]

[1]Department of Chemistry, Northwestern University, 2145 Sheridan Rd., Evanston, IL 60208, USA.

We present the development of theory and algorithms that enable the efficient evaluations of the analytical nuclear gradient and derivative coupling in the framework of extended multistate complete active space second-order perturbation theory (XMS-CASPT2). With this implementation, on-the-fly condensed phase surface hopping dynamics on the XMS-CASPT2 surfaces in large systems are now routine. As an example, the nonadiabatic dynamics simulations of GFP chromophore in water will be presented.

Insights into the Excited State Chemistry of Lanthanoid(III) Motexafins

Norah Heinz, Nils Herrmann, Michael Dolg, Xiaoyan Cao

Institute for Theoretical Chemistry, University of Cologne, Greinstr. 4, 50939 Köln, Germany

Texaphyrins, which can be understood as expanded porphyrins, localise at cancerous lesions and are considered to be promising drugs in treatments as radiation therapy or photodynamic therapy. Especially certain texaphyrins called motexafins containing trivalent lanthanoid ions in the center – e.g. Gadolinium, Gd-Tex^{2+} – are considered to posess very promising attributes. In the presence of ascorbic acid they are expected to catalyse the generation of reactive oxygen species (ROS). When stimulated by visible light, texaphyrins are believed to play an important role as catalysts in this process. With the help of the texaphyrin an electron is transfered from the ascorbate to O_2 forming $O_2^{\bullet-}$. This species is then used to generate H_2O_2 which is known to be a potent apoptosis trigger. During the catalysis the texaphyrin – Gd-Tex^{2+} – is reduced by the ascorbate species. The electron is then transfered to O_2 and the catalyst is regained [1].

To understand the process of the electron transfer in detail, several properties of lanthanide(III) motexafins are analysed. Electron affinities and ionisation potentials in gas phase as well as in aqueous environment are calculated and discussed in detail. The first water coordination sphere and its effects on the molecular properties are considered. Reduction potentials are determined in order to explain the effectiveness of texaphyrin species as catalyst [3]. The results are discussed in the context of the autoxidation of ascorbic acid [2], which accounts for the uncatalysed formation of ROS in the postulated mechanism.
On the other hand emphasis is being placed on the description of the excited states of the Gd-Tex^{2+} species, in order to analyse the primary step of the catalysis, namely the activation of the compound by visible light. Since the electronic structure of texaphyrins resembles the one of porphyrins and several electronic excitations in porphyrins are known to display charge transfer character, this is also expected in the case of texaphyrins. A detailed study of the excitation spectra of texaphyrins at the level of TD-DFT is presented applying different density funcionals and energy-consistent scalar relativistic pseudopotentials for lanthanoids. Also the aqueous environment is taken into account to simulate *in vivo* conditions. Special focus is set on the treatment of long range correlation effects and the identification of charge transfer excitiations.

[1] D.J. Magda, Z. Wang, N. Gerasimchuk, W. Wei, P. Anzenbacher, Jr. and J.L. Sessler *Pure Appl. Chem.* **76**, 365 (2004).

[2] N. Herrmann, N. Heinz, M. Dolg and X. Cao *J. Comput. Chem.* **37**, 1914 (2016).

[3] X. Cao, N.Heinz, J. Zhang and M. Dolg. *submitted.*

Orbital Locality Landscapes

Charles J. C. Scott[1] , **David J. Wales**[1] , **Alex J. W. Thom**[1]

[1]*Department of Chemistry, University of Cambridge, Cambridge*

We consider the optimisation of orthonormal molecular orbitals according to various localisation conditions[1] using techniques developed to treat potential energy landscapes.[2] We categorise the stationary points and connectivity of the landscapes resulting from different penalty functions in various molecules. We consider the chemical significance of the solutions obtained and the implications for reliably obtaining localised orbitals. While multiple stationary points and minima have been previously acknowledged as a problem in localisation procedures,[3, 4] we believe this to be the first study of the structure of the corresponding landscapes. Understanding this structure is required to obtain well-localised orbitals for general molecular systems, and hence facilitate the development of high-level local correlation methods.

[1] B. Jansík, S. Høst, K. Kristensen, P. Jørgensen, *J. Chem. Phys.* **134**, 194104 (2011).

[2] D. J. Wales, *Energy Landscapes*, Cambridge University Press, (2003).

[3] J. E. Subotnik, A. Sodt, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **9**, 5522 (2007).

[4] S. Lehtola, H. Jónsson, *J. Chem. Theory and Comput.* **9**, 5365 (2013).

Hybrid Approach to Fermi Operator Expansion: Towards Langevin Dynamics with Linear System-Size Scaling

H. Wiebeler[1], **S. Mohr**[2], **Thomas D. Kühne** [1]

[1]*Dynamics of Condensed Matter, Department of Chemistry, University Paderborn,*
Warburgerstr. 100, 33098 Paderborn, Germany
[2]*Department of Computer Applications in Science and Engineering, Barcelona*
Supercomputing Center (BSC-CNS), c/ Jordi Girona 29, 08034 Barcelona, Spain

In our recent work, we introduced an improved field-theoretic approach to the grand-canonical potential suitable for linear scaling molecular dynamics using forces from self-consistent electronic structure calculations [1, 2]. This approach does not rely on the ability to localize the electronic wavefunction, so even metals can be treated.

In this work, we present an implementation of this approach into a DFT electronic structure calculation code, which is using a localized Daubechies wavelet basis [3, 4]. In particular, we investigate the possibility to substantially accelerate the computation of the interatomic forces by computing them approximately at the expense of white noise. The noisiness of the forces can then be compensated by means of a modified Langevin dynamics scheme [5].

For the purpose of demonstrating our novel approach, we also performed some tests in order to proof the linear scaling behavior of our approach with respect to Hamiltonian matrices from DFT-calculations. Furthermore, we are testing the white noise criterion by calculating the auto-correlation of the noise in the forces.

[1] M. Ceriotti, T. D. Kühne and M. Parrinello, *J. Chem. Phys.* **129**, 024707 (2008).

[2] D. Richters and T. D. Kühne, *J. Chem. Phys.* **140**, 134109 (2014).

[3] S. Mohr, L. E. Ratcliff, P. Boulanger, L. Genovese, D. Caliste, T. Deutsch and S. Goedecker *J. Chem. Phys.* **140**, 204110 (2014).

[4] S. Mohr, L. E. Ratcliff, L. Genovese, D. Caliste, P. Boulanger, S. Goedecker and T. Deutsch *Phys. Chem. Chem. Phys.* **17**, 31360 (2015).

[5] T. D. Kühne, M. Krack, F. R. Mohamed and M. Parrinello, *Phys. Rev. Lett.* **98**, 066401 (2007).

Esterase-2 as a fluorescent biosensor for the detection of organophosphates: electronic insights from molecular dynamics

Ingrid G. Prandi[1,2], **Teodorico C. Ramalho**[1], **Tanos C. C. França**[2]

[1]Department of Chemistry, Federal University of Lavras, Av. Doutor Sylvio Menicucci, 1001, Lavras, Brazil

[2] Laboratory of Molecular Modeling Applied to the Chemical and Biological Defense, Military Institute of Engineering, Praça Gen. Tibúrcio, 80, Rio de Janeiro, Brazil

Organophosphorus (OP) pesticides began to be employed on large scale during the World War II in order to protect soldiers from insects that transmit infectious diseases like malaria. Specifically synthesized to be toxic molecules, most OPs pesticides are not specific to a target organism, and the indiscriminate use of these substances poses a great risk to many species including humans [1]. Unfortunately, despite of some strong restrictions about the use of OP pesticides by the Food Quality Protection Act, they are still in clandestine use because of their low cost and, consequently the number of people intoxicated by OP pesticides is still high worldwide. [2,3] The first step to cure a patient that is intoxicated by an OP molecule is to identify the specific infecting compound. In the literature, previous studies show that OPs are great inhibitors of the acetylcholinesterase enzyme (AChE) [3,4]. Thus, for patient diagnostics, it may be possible to use an esterase enzyme as a biological sensor to detect OP compounds. In particular, the presence of the Esterase 2 (EST2) from *Alicyclobacillus acidocaldarius* in an environment that contains OP is able to change the fluorescence signal when light of the right wavelength falls on the sample. Indeed, experimental results show signs that the variation in the fluorescence signal is able to quantitatively identify these compounds [5,6]. In this work, we apply docking analyses, molecular dynamics simulations and quantum-mechanics-based calculations in order to study structural and fluorescence properties of four different OPs (chlorpyriphos, diazinon, paraoxon and parathion) as EST2 inhibitors. Finally, theoretical predictions are compared with experimental results in order to validate the methodology and enable its employment on other OP compounds.

[1] L. Perezgasga, L. Sánchez-Sánchez, S. Aguila, R. Vazquez-Duhalt. *Appl Biochem Biotechnol.* **166**, 1236–1247 (2012)

[2] R. Iyer, B. Iken, A. Leon. *Toxicol Lett.* **233**, 200–206 (2015)

[3] B. Hileman. *Chem. Eng. News.* **78**, 34–36 (2000)

[4] N. Bunya, K. Sawamoto, H. Benoit, S. B. Bird. *J Toxicol.* **2016**, 1-5 (2016)

[5] P. Carullo, G. P. Cetrangolo, L Mandrich, G. Manco, F. Febbraio. *Sensors.* **15**, 3932-3951 (2015)

CYLview: A Free Molecular Analysis and Representation Program for Chemists.

Claude Y. Legault[1]

[1]Department of Chemistry, Université de Sherbrooke, 2500 boul. De l'Université,
Sherbrooke (Québec), J1K 2R1, Canada

The efficient analysis and communication of scientific results is a vital portion of the work of any chemist. This aspect is even more important for computational chemists, due to the amount and complexity of the results obtained. Tools to maximize the efficiency of this process are thus critical. The present major challenge with the preparation of publication quality representations of structures is the need to use multiple programs to achieve the desired result. In this regard, CYLview [1] was specifically created to accelerate the evaluation and analysis of computed structures, as well as to generate in the same program high quality representations, containing all the information (e.g. bond distances, angles, atom numbering) needed for professional publications and presentations. The steady increase in computing resources has led to the study of ever larger structures that are inherently more difficult to depict; static two dimensional images of three dimensional structures over a certain size lead to a loss of spatial orientation and distracting clutter. CYLview overcomes these issues by using powerful visual cues, such as fog and focal blur. This free software has grown in popularity over the years, with now more than 2500 registered users. The current features of the program will be presented. New developments will be presented to stimulate feedback and suggestions from the researchers.

[1] C. Y. Legault, *CYLview*, *1.0b*; Université de Sherbrooke (Québec), Canada; http://www.cylview.org (2009)

Range-separated hybrid scheme combining AP1roG with density-functional theory

Odile Franck[1]

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

The antisymmetric product of one-reference orbital geminals (AP1roG) [1] is a geminal-based method that can be rewritten as a general pair-coupled-cluster-doubles (PCCP) wave-function. However, AP1roG, as other geminal-based methods, misses a large fraction of dynamical correlation effects. To overcome this limitation *a posteriori* corrections have been proposed such as linear coupled-cluster based methods [2] or perturbation theory based methods [3]. Another approach to include dynamical correlation to PCCD that has been proposed recently is to combine PCCD with density-functional theory (DFT) [4][5]. In this study, we combine DFT and AP1roG in a range-separated hybrid and compare this method to other *a posteriori* corrections.

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

[2] K. Boguslawski, P. W. Ayers, *J. Chem. Theory Comput.* **11**, 5252 (2015).

[3] P. Limacher, P. W. Ayers, P. Johnson, S. De Baerdemacker, D. Van Neck, P. Bultinck, *Phys. Chem. Chem. Phys.* **16**, 5061 (2014).

[4] A. J. Garza, I. W. Bulik, T. M. Henderson, G. E. Scuseria, *Phys. Chem. Chem. Phys.* **17**, 33523 (2015).

[5] A. J. Garza, I. W. Bulik, T. M. Henderson, G. E. Scuseria, *J. Chem. Phys.* **142**, 044109 (2015).

Electrode effects in molecular electronics: a computational perspective

Manuel Smeu

Department of Physics, Binghamton University – SUNY, 4400 Vestal Parkway East,
Binghamton, NY 13902, United States

Molecular electronics offers a means of achieving next generation of electronic devices, beyond semiconductor technologies, due to the high tunability and relatively inexpensive manufacturing costs of molecules. The field is now at a point where molecular junctions can be routinely fabricated and their conductance measured in the lab. From the computational perspective, the state-of-the-art is the non-equilibrium Green's function technique combined with density functional theory (NEGF-DFT) approach that provides the transmission function, $T(E)$, from which the conductance characteristics of the molecular junction can be obtained. The prototypical system is composed of two Au electrodes bridged by a molecule with some anchoring groups (e.g. thiol, amine). However, using a different metal (e.g. Cu, Pt, Al), or other material (e.g. carbon nanotube, graphene nanoribbon), for the electrodes results in a different alignment between the molecular orbitals and the Fermi level of the electrodes, thus yielding different transport properties. Additionally, the exact atomic configuration at the electrode/molecule interface can play a dramatic role. In this presentation, the effects on molecular conductance of different metal electrodes, their atomic orientation and configuration will be discussed, and some insights into how to obtain control over these parameters will be offered.

The Methylsulfinyl Radical and Its Reaction with Ozone

Marissa L. Estep[1], **Henry F. Schaefer**[1]

[1] *Center for Computational Quantum Chemistry, University of Georgia, 1004 Cedar Street, Athens, GA, USA*

The methylsulfinyl radical (CH_3SO) serves as a key intermediate in the sulfur chemistry of the remote marine atmosphere, with its reactions leading to production of sulfuric acid and sulfates [1]. The methylsulfinyl radical is typically oxidized by either NO_2 or ozone, but we focus our efforts on its reaction with ozone. We have studied the structures and fundamental modes of the ground and first excited states of the methylsulfinyl radical using coupled cluster methods, and have examined the adiabatic excitation energy of the first excited state using methods as complete as CCSDT(Q) [2]. With this background, we examine the reaction of the methylsulfinyl radical with ozone. This reaction has been the object of experimental [1, 3] and theoretical [4] studies, with the theoretical work entailing treatment of the reaction with the MP2/6-311++G(2df,p) method. Given the multiconfigurational nature of ozone, we build upon this available work by considering the possibility that the reaction complex may require treatment of both static and dynamic correlation. We examine metrics of multireference character to determine whether application of multireference methodology is appropriate for this system.

[1] D. Borissenko, A. Kukui, G. Laverdet, G. Le Bras, *J. Phys. Chem. A* **107**, 1155 (2003).

[2] M. L. Estep, H. F. Schaefer, *Phys. Chem. Chem. Phys.* **18**, 22293 (2016).

[3] A. A. Turnipseed, S. B. Barone, A. R. Ravishankara, *J. Phys. Chem.* **97**, 5926 (1993).

[4] X. Li, Y. Meng, S. Zheng, *J. Mol. Struct. THEOCM* **847**, 52 (2007).

Computational Studies of Substituted Porphyrin-Squaraine Dyads as Chromophores for Solar Cells based on TiO_2

Merlys Borges-Martínez[1], Raúl Mera-Adasme[1], Gloria Cárdenas-Jirón[1]

[1]Theoretical Chemistry Laboratory, Faculty of Chemistry and Biology,
University of Santiago de Chile (USACH), Casilla 40, Correo 33, Santiago, Chile

Since the discovery of dye-sensitized solar cells (DSSC), the search for efficient dyes for the devices has been an active area of research. Porhyrin-based dyes have produced excellent results so far [1]. The porphyrin macrocycle can efficiently inject electrons to a semiconductor but it has a poor absorption in the visible light region [2]. Linking porphyrin with a second chromophore is expected to enhance the light-absorption properties [3]. In the present work, we studied the light-absorption properties of a dyad formed by the combination of porphyrin and squaraine (SQ), which we modified by adding of electron-donor (push) groups to porphyrinic moiety. The modifications aimed to improve electron injection properties of the chromophores toward to a semiconductor, like TiO_2, and induce a panchromatic light absorption.

Optimized molecular geometries were obtained at the density functional theory (DFT) using hybrid functional B3LYP and double- and triple-zeta polarized Ahlrichs basis set. Vibrational frequencies were obtained for the minimum-energy structures. The absorption spectra of the chromophore dyads and their isolated fragments were obtained using Time-Dependent DFT. Solvent effects of tetrahydrofuran (THF) were modeled with Conductor Polarizable Continuum Model (CPCM). Fourteen density functionals were evaluated in order to choose the method that better reproduced the experimental spectra. Using the chosen functional, dyads were analyzed in terms of the electronic absorption properties and parameters of photovoltaic cells.

The changes in the UV-vis spectra upon substitution of the porphyrinic ring were fundamentally in the relative intensities of absorption bands. Stronger and red-shifted SQ bands were observed for substituents with amine groups, favouring the panchromatic absorption of the dyads. Of the four models of TiO_2 studied, the band gap of the semiconductor was best described by the clusters with 15 and 16 TiO_2 units. The photovoltaic parameters and chemical potential of donor groups of dyads bonded to TiO_2 cluster indicated that, dyads with aromatic amines are more suited to inject electrons to a semiconductor.

Acknowledgments. GCJ thanks FONDECYT/CONICYT by Project N°1131002 and 1171719 for financial support. MBM thanks CONICYT-PCHA/Doctorado Nacional/2015-21150093 for PhD scholarship. RMA thanks CONICYT for financial support under Proyecto de Atracción e Inserción de Capital Humano Avanzado en la Academia PAI N° 79150043.

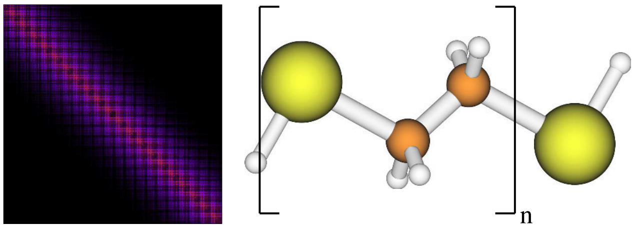
[1] M. Urbani, M. Grätzel, M.K. Nazeeruddin, T. Torres, Chem. Rev., **114**, 12330 (2014).
[2] G.I. Cárdenas-Jirón, T. Baruah, R.R. Zope, Handbook of Porphyrin Science, **42**,233 (2016).
[3] J. Warnan, F. Buchet, Y. Pellegrin, E. Blart, F. Odobel. Org. Lett., **13**, 3944 (2011).

Laplace-transformed atomic and active orbital-based formulations of relativistic and multireference perturbation theories for large molecules

Benjamin Helmich-Paris[1], **Lucas Visscher**[1], **Michal Repisky**[2], **Stefan Knecht**[3]

[1]*Section of Theoretical Chemistry, VU University Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands*
[2]*CTCC, Department of Chemistry, UIT The Arctic University of Norway, N-9037 Tromø, Norway*
[3]*Laboratory of Physical Chemistry, ETH Zürich, Vladimir-Prelog-Weg 2, CH-8093 Zürich, Switzerland*

We present a formulation of Laplace-transformed atomic orbital-based second-order Møller–Plesset perturbation theory (MP2) energies for two-component Hamiltonians in the Kramers-restricted formalism.[1] This low-order scaling technique can be used to enable correlated relativistic calculations for large heavy element-containing molecules. We show that the working equations to compute the relativistic MP2 energy differ by merely a change of algebra (quaternion instead of real) from their non-relativistic counterparts and feature an overhead factor of at most 16 due to inclusion of spin-orbit coupling. Our current implementation computes on 16 CPUs the Coulomb energy of a tellurium polyethylene glycol (Te-PEG-20) within 4.5 h by using 6500 and 8409 spherical Harmonic orbital and auxiliary basis functions, respectively.



(a) (b)

Figure 1: Real occupied pseudo-density matrix $\underline{\mathbf{P}}^0$ (a) of Te-PEG-20 (b)

Following similar lines, Laplace transformation of energy denominators is employed to express the partially contracted n-electron valence second-order perturbation theory (NEVPT2) energies in the atomic and active molecular orbital basis.[2] As AO basis functions are inherently localized and the number of active orbitals is comparatively small, our formulation is particularly suited for a linearly scaling NEVPT2 implementation that may calculate accurate energies and properties of large open-shell molecules.

[1] B. Helmich-Paris, M. Repisky, and L. Visscher *J. Chem. Phys.* **145**, 014107 (2016).

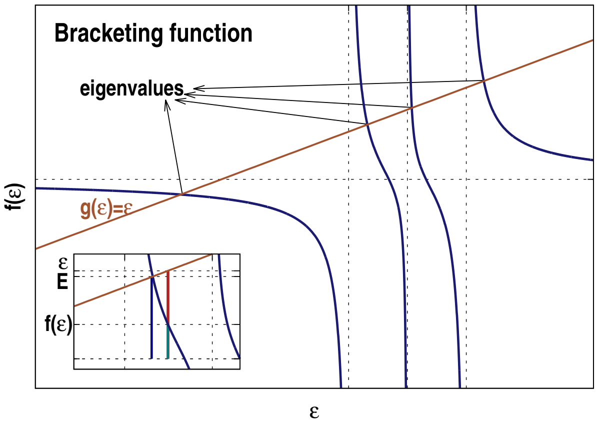
[2] B. Helmich-Paris and S. Knecht *J. Chem. Phys.* **146**, 224101 (2017).

Calculating lower bound to the energy eigenvalues of the Hamiltonean

Zsuzsanna Tóth[1], **Ágnes Szabados**[2]

[1]*Doctoral School of Chemistry, Faculty of Science, ELTE Eötvös Loránd University, Budapest, Hungary, tzsuzsi@lowdin.chem.elte.hu*
[2]*Laboratory of Theoretical Chemistry, Faculty of Science, ELTE Eötvös Loránd University, Budapest, Hungary*

In quantum chemistry the usage of upper bounds to the energy is common. 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.

In a previous publication[2] we proved, that the bracketing function has variational nature, which means that maximising the lower bound leads to exact wavefunction and energy. It leads to the idea of calculating the lower bound with better and better wavefunction in steps of a full CI iteration[3]. In each step of the iteration we get closer and closer lower and upper bounds to the full CI energy.

In my presentation I will show an improvement over our pervious method of calculating approximate but reliable lower bound. The new technique is based on the closed formula for the inverse of a block partitioned matrix[4]. This allows efficient calculation of the expansion of the lower bound, utilizing a more sophisitcated zero order matrix.

[1] P.-O. Löwdin, *Phys. Rev.* **139**, A357 (1965).

[2] Á. Szabados, Zs. Tóth, *J. Math. Chem.* **52**, 2210 (2014).

[3] Zs. Tóth, Á. Szabados *J. Chem. Phys.* **143**, 084112 (2015).

[4] Zs. Tóth, P. R. Nagy, P. Jeszenszki, Á. Szabados *Theor. Chem. Acc.* **134**, 100 (2015).

Holomorphic Hartree–Fock Theory: Beyond the Coulson–Fischer Point

Hugh G. A. Burton[1], **Hamish G. H. Hiscock**[1, 2], **James D. Farrell**[1, 3],
Alex J. W. Thom[1]

[1]*Department of Chemistry, University of Cambridge, Cambridge, UK*
[2]*Department of Chemistry, University of Oxford, Oxford, UK*
[3]*Institute of Physics, Chinese Academy of Sciences, Beijing, China*

The disappearance of unrestricted Hartree–Fock (UHF) solutions at certain geometries is well studied for many molecular systems, preventing the use of UHF states as a basis for non-orthogonal Configuration Interaction (NOCI) calculations.[1] We propose a new holomorphic energy functional constructed by removing the complex conjugation of orbital coefficients from the expectation value of the Hartree-Fock energy.[2, 3] The holomorphic Hartree–Fock energy functional is complex analytic and we believe it has a constant number of stationary points across all molecular geometries. Using a revised self-consistent field (SCF) method we find a constant number of solutions for H_2 and LiH; where standard UHF states coalesce and disappear, their holomorphic UHF counterparts extend into the complex direction. Finally, we use the holomorphic UHF solutions of LiH as a basis for NOCI to calculate size-extensive, smooth binding curves.

[1] A. J. W. Thom and M. Head–Gordon, *J. Chem. Phys.* **131**, 124113, (2009).

[2] H. G. Hiscock and A. J. W. Thom, *J. Chem. Theory Comput.* **10**, 4795, (2014).

[3] H. G. A. Burton and A. J. W. Thom, *J. Chem. Theory Comput.* **12**, 167, (2016).

The Prototypical Transition Metal Carbenes: $(CO)_5Cr{=}CH_2$, $(CO)_4Fe{=}CH_2$, and $(CO)_3Ni{=}CH_2$

Jared D. Weidman, Marissa L. Estep, and Henry F. Schaefer III

Center for Computational Quantum Chemistry, University of Georgia, 140 Cedar St., Athens, GA, USA

Transition metal carbene complexes have received interest in the field of organometallic chemistry due to their demonstrated ability to catalyze various carbon-carbon bond forming reactions. Here, we present a theoretical study of the most prototypical of such carbenes, these methylene-substituted transition metal carbonyls. These particular complexes have not been synthesized experimentally, though some similar complexes with larger carbene ligands have been synthesized. Five functionals (B3LYP, BP86, M06-L, ωB97X, and ωB97X-D3) were utilized along with a cc-pVTZ basis to obtain equilibrium geometries and bond dissociation energies. In addition, bonding analysis was performed to gain insight into the nature of the metal-carbene double bond.

Contributions for the Combustion Model of Dimethyl Ether from Theoretical Calculations

Rodrigo R. V. Castro [1], Vinicius N. Rocha [1], Gladson de S. Machado [1], Glauco Favilla Bauerfeldt[1]

[1] Departamento de Química, Instituto de Ciências Exatas, Universidade Federal Rural do Rio de Janeiro, Rodovia Br 465 km 47, Seropédica, Rio de Janeiro, Brazil

Dimethyl ether (DME) has been pointed out as a potential alternative fuel for compression ignition engines and the understanding of the combustion profile is fundamental for this discussion. In this work, a contribution for this issue is proposed by: (1) the evaluation of the combustion mechanism and identification of the key steps for the DME consumption; (2) re-evaluation of the rate coefficients for these most important reactions, on the basis of a quantum mechanical description and variational transition state theory calculations and (3) reassessment of the combustion mechanism adopting the predicted rate coefficients. The analysis of the DME combustion mechanism suggests that DME unimolecular dissociation (the only unimolecular reaction included in the original mechanism) and DME + OH bimolecular reaction are the steps with major contribution to the DME consumption, at different time scales. Since DME shows four unimolecular steps, namely dissociation ($CH_3OCH_3 \rightarrow CH_3O + CH_3$), H_2 elimination (E11, $CH_3OCH_3 \rightarrow CH_3OCH + H_2$ and E12, $CH_3OCH_3 \rightarrow CH_2OCH_2 + H_2$) and decomposition ($CH_3OCH_3 \rightarrow CH_2O + CH_4$), the possible competition and contribution of the other unimolecular channels were quantified. The dissociation step has been described at the MRPT2/cc-pVTZ level, whereas elimination and decomposition channels have been calculated at the M06-2X/aug-cc-pVTZ level. The dissociation limit for the $CH_3OCH_3 \rightarrow CH_3O + CH_3$ channel has been predicted as 81 kcal mol^{-1}. Critical energies for elimination reactions, E11 and E12, and decomposition are 85.58, 82.58 and 101.7 kcal mol^{-1}, respectively. Barrier values suggest that E12 reaction may compete with the unimolecular dissociation channel, contributing to the formation of H_2 specie, which are very important in the combustion mechanism. The bimolecular, DME + OH reaction, is also shown to be important for the consumption of the fuel and proceeds by a hydrogen abstraction mechanism, leading to methoxymethyl radical and H_2O. For such reaction, theoretical calculations have also been performed at the M06-2X/aug-cc-pVTZ level. Concerning the available literature on this bimolecular reaction, new stationary points have been located and connected to reactants and products via reaction paths, whose contribution to the global kinetics has been proved to be significant. Pre-barrier complexes have been located, stabilized by 0.76, 4.81 and 5.05 kcal mol^{-1}. These intermediates are connected to corresponding saddle points, which lie 0.29, -0.34 and 1.57 kcal mol^{-1}, respectively, also with respect to reactants. Canonical variational rate coefficients have been calculated for each reaction path and summed up to predict the global rate coefficients, in the range from 200 – 1500 K, in good agreement with the experimental data. The proposed kinetic data finally represent a great contribution to the literature, concerning the combustion chemistry of dimethyl ether.

Multistructure and Multipath Kinetics Test Study: Reaction of 1-pentene + OH

Tatiane Nicola Tejero[1], **Glauco Favilla Bauerfeldt**[1]

[1] Departamento de Química, Instituto de Ciências Exatas, Universidade Federal Rural do Rio de Janeiro, Rodovia Br 465 km 47, Seropédica, Rio de Janeiro, Brazil

Alkenes + OH reactions are important in the field of atmospheric chemistry and, despite all devoted efforts, several points remain yet to be explored. Here, the 1-pentene + OH reaction is described by a mechanism taking into account the reversible formation of a π-type prebarrier complex (π-PC), followed by the addition steps, which can lead to different products, considering the addition of the OH radical to each carbon atom at the double bond [1]. Moreover, several conformers of the reactants are observed. Then, the single mechanism described above should be attributed to each single conformer and the collection of the distinct mechanisms composes the so-called multipath case [2]. σ-type intermediates can also be located and their role in the dynamics of these reactions could be clarified through a detailed and complete description of this problem. Theoretical procedures have been performed at the Density Functional Theory level, adopting the M06-2X functional along with the aug-cc-pVDZ basis set and canonical variational rate coefficients have been predicted. At the M06-2X/aug-cc-pVDZ level, π-PCs, σ-PC and saddle points lie on the ranges: -3.54 – -3.63, -2.55 – -3.59 and -2.12 – 0.12 kcal mol^{-1}, respectively. The contributions of each different reaction channel (of each reactant conformer) to the overall kinetics have been calculated, leading to the conclusion that the inclusion of all conformers and the corresponding paths is very important to improve the final kinetic results. It has also been noted that the contributions of the intermediate π type for the dynamics of the reaction are the most important. This model could also explain the non-Arrhenius behavior. Global rate coefficients have been finally calculated, as a function of the temperature, by summing up individual rate coefficient weighted by the Boltzmann population of the conformer. The global rate coefficient, predicted at 298 K is 1.54×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, in good agreement with the experimental value [3], 2.74×10^{-11} cm^3 $molecule^{-1}$ s^{-1}.

[1]Barbosa, T. S. et al. *PCCP* **2015**, *17*, 8714.
[2] Yu, T.; *et al. Faraday Discuss.* **2012**, *157*, 59.
[3] Miller, W. H.; The Journal Chemical Physics, **1976**, 65, 2216.

Computational Study of Isolated Glycine, Alanine and Solvated Glycine Zwitterion and Contribution to ISM Behavior

Neubi F. Xavier Junior[1], Diego N. Jesus[1], Gabriel S. S. Brites[1], Leonardo Baptista[2], Cristiane M. Cardoso[1], Glauco F. Bauerfeldt[1]

[1]*Departamento de Química. Instituto de Ciências Exatas. Universidade Federal Rural do Rio de Janeiro. Rodovia Br km 7, Seropédica, RJ, Brasil*

[2]*Departamento de Química e Ambiental, Faculdade de Tecnologia, Universidade do Estado do Rio de Janeiro, Rodovia Presidente Dutra Km 298, Resende - RJ, Brazil*

The presence of glycine in interstellar medium (ISM) is still controversial[1]. Although gas phase glycine has not been detected in ISM, some fragments associated to its formation and decomposition have already been identified. The solid phase (icy) glycine is, on the other hand, predominant in the ISM. In this work, the main goal is the description of the structure and reactivity of glycine in different media (gas phase and aqueous solution) aiming the contribution to the Astrochemical knowledge about the formation and decomposition of amino acids in the ISM. All calculations have been performed at the CCSD(T)/6-311++G(2d,2p)//B3LYP//6-311++G(2d,2p) level. Conformational analysis of the glycine in its neutral and radical cation forms, revealing spectra of eight and four conformers of neutral and glycine radical cation, respectively. In each case, one conformer has been shown to prevail. The study of the unimolecular reactions show that the deamination is the dominant channel among all possibilities, including decarboxylation and dissociation paths. Rate coefficients have been calculated as a function of the temperature and the energy, adopting the canonical and microcanonical variational transition state theories, respectively. The barrier energies are predicted as: 69,36 kcal/mol for decarboxylation and 44,76 kcal/mol for deamination on neutral form glycine. On glycine radical cation the barrier height estimated was 56,00 kcal/mol. A similar study has been performed for alanine. To simulate the icy medium, calculations for glycine in aqueous solution have been performed using CPCM and IEF-PCM methods. PCM parameters have been tested and chosen as those which allowed the best description of a global chemical property: the pKa´s values. These results finally contribute to the understanding of the role of glycine in the ISM and the possible paths leading to its formation and decomposition in the prebiotic atmosphere and primitive Earth.

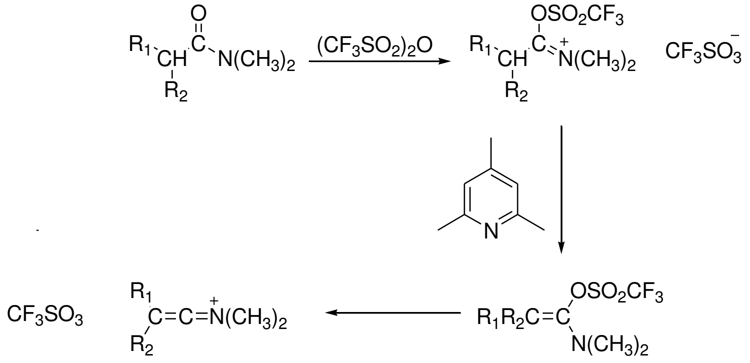
[1] Sergio Pilling et al., *Astrobiology* **13**, 79-91 (2013).

KETENIMINIUM SALT FORMATION AND THEIR ELECTROCYCLIZATION REACTIONS

Ulfet Karadeniz,[1] **Gamze Tanriver,**[1] **Amandine Kolleth,**[2] **Alexandre Lumbroso,**[2] **Sarah Sulzer,**[2] **Alain De Mesmaeker,**[2] **and Saron Catak**[1]*****

[1]*Bogazici University, Department of Chemistry, Bebek 34342 Istanbul, Turkey*
[2]*Syngenta Crop Protection AG, Crop Protection Research, Research Chemistry, Schaffhauserstrasse 101, CH-4332, Switzerland*

Keteniminium salts are an improved alternative to their ketene analogues due to their higher electrophilicity, regioselectivity and reactivity properties. We use a DFT approach to elucidate the formation of keteniminium salts by referring to the mechanism proposed by Ghosez in 1981 (Scheme 1).[1] Depending on a previous study by E. Villedieu-Percheron et al.[2] we recently described an efficient access to 3-amino-benzothiophenes through the 6π electrocyclization of keteniminium intermediates.[3] As a continuation of this study, we examine the reactivity of keteniminium salts in electrocyclization reactions resulting in different heterocyclic systems. In addition to the effect of the heteroatom, the effect of the substituents on the keteniminium salt is also rationalized by the study.



Scheme 1. Ghosez's Mechanism for the Formation of Keteniminium Salts.[1]

[1] J. B. Falmagne, J. Escudero, S. Taleb-Sahaoui, L. Ghosez, *Angew. Chem. Int. Ed. Engl.* **20** (1981).

[2] E. Villedieu-Percheron, S. Catak, D. Zurwerra, R. Staiger, M. Lachia, A. De Mesmaeker, *Tetrahedron Lett.* **55** (2014).

[3] A. Lumbroso, J. Behra, A. Kolleth, P. Y. Dakas, U. Karadeniz, S. Catak, S. Sulzer-Mossé, A. De Mesmaeker, *Tetrahedron Lett.* **56** (2015).

Fermionic PEPS for finite two-dimensional Hubbard models

Jheng-Wei Li[1], **Toru Shiozaki**[1]

[1]*Department of Chemistry, Northwestern University, 2145 Sheridan Rd., Evanston, IL 60208, USA*

We study the finite two-dimensional Hubbard model using fermionic projected entangled pair states (fPEPS). A general procedure to account for the anti-commutative relation of fermions in tensor network states has been proposed. We demonstrate that the fPEPS ansatz is an efficient numerical approximation to explore the ground state phase diagram of the two-dimensional Hubbard model.

Electron Delocalization in Infinite σ-Bonded One-dimensional Chains $(\mathrm{MMe}_2)_\infty$, M = Si, Ge, Sn, Pb

Milena Jovanovic[1,2], **Josef Michl**[1,2]

[1]Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309, United States
[2]Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, 16610 Prague 6, Czech Republic

σ-Electron delocalization in σ-bonded systems affects their optical properties, ionization potentials, charge and energy transfer, conductivity, and chemical reactivity. The presence or absence of σ delocalization is often dictated by chain conformation. We investigate σ delocalization in linear saturated infinite chains of atoms of silicon, germanium, tin, and lead, from the planar all-anti limit with a backbone dihedral angle $\omega = 180°$ toward the highly twisted all-syn limit $\omega = 0°$. To describe σ delocalization we use band theory within the tight-binding Ladder C model, which includes only those hybrid orbitals that are involved in backbone bonding. This model has three distinct hopping integrals that describe primary, geminal, and vicinal interactions. Only the vicinal integral depends on the backbone dihedral angle. We investigate the effects of parameter values and chain conformation on electron delocalization.

Structural characterization of hydrogen adsorbed ruthenium clusters - toward an atomistic understanding of ammonia synthesis

Dennis Bumüller[1], Anna-Sophia Hehn[2], Eugen Waldt[1], Reinhart Ahlrichs[2],
Manfred M. Kappes[1,2], Detlef Schooss[1,2]

[1]*Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT),*
Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
[2]*Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 2,*
76131 Karlsruhe, Germany

Structural characterization of ruthenium nanoparticles is essential when aiming to elucidate the catalyst's role in ammonia synthesis. In particular, the examination of small ruthenium clusters is significant and indispensable as cluster structures often differ from the bulk lattice motif. We present a combined experimental and theoretical study using trapped ion electron diffraction and density functional theory calculations to determine the structure of Ru_{19}^- clusters and to analyze the effect of hydrogenation [1, 2]. Cluster structure computations are obtained from a genetic algorithm search procedure [3]. Results reveal that bare Ru_{19}^- has a closed-shell octahedral fcc structure in contrast to the hcp geometry of the bulk. Adsorption of hydrogen causes the octahedral cluster to rearrange toward a bi-icosahedral motif once a load of 20 to 30 hydrogen atoms is reached. Calculations furthermore predict that hydrogen is preferentially atomically bound and favors two-fold bridge configurations. A linear dependence between adsorption energies and the relative position of the d-band centers to the Fermi level is found, confirming the bi-icosahedral cluster structure as favorable motif for hydrogen adsorption.

[1] E. Waldt, A.-S. Hehn, R. Ahlrichs, M. M. Kappes, D. Schooss, *J. Chem. Phys.* **142**, 024319 (2015).

[2] D. Bumüller, A.-S. Hehn, E. Waldt, R. Ahlrichs, M. M. Kappes, D. Schooss, *J. Phys. Chem. C* **121**, 10645 (2017).

[3] C. Neiss, D. Schooss, *Chem. Phys. Lett.* **532**, 119 (2012).

DFT Study of the Chemical-Physics Properties of a Series of New Benzoxazole Derivatives

Hayat Ayache[1,2], **Fazia Derridj**[3], **Aziz Elkechai**[1], **Dalila Hammoutène**[2]

[1] *LPCQ, Faculté des Sciences, UMMTO, Tizi-Ouzou, Algeria*
[2] *LTMM, Faculté de Chimie, USTHB, 16111, Algiers, Algeria*
[3] *LPCM, Faculté des Sciences, UMMTO, Tizi-Ouzou, Algeria*

A new series of benzoxazole derivatives have been recently synthesized. They constitute an interesting class of chelating agents capable of coordinating metal ions such as zinc and cadmium, by giving complexes of biological interest, and which can serve as models for metallic depollution.

Structural parameters, vibrational spectra (IR, ^{1}H NMR, ^{13}C NMR and UV-Visible absorption) of these benzoxazole derivatives were performed by DFT and TD-DFT, to have an insight into their photophysical properties.

Reactivity descriptors such as ionization energy, electronic affinity, global hardness, global softness, electrophilicity, nucleophilicity and condensed Fukui functions were also determined. The calculated geometrical parameters are in good agreement with those of similar benzoxazole derivatives and the theoretical frequencies assignments confirmed the experimental measurements [1-5].

References

[1] C. T. Zeyrek, H. Unver, Ö. Temiz-Arpaci, K. Polat, N. O. İskeleli, M. Yildiz, *J. Mol. Struct.* **1081**, 22 (2015).
[2] C. N. Sundaresan, S. Dixit, P. Venugopalan, *J. Mol. Struct.* **693**, 205 (2004).
[3] H. Unver, O. T. Arpaci, M. Zengin, T. N. Durlu, *J. Mol. Struct.* **609**, 205 (2002).
[4] A. E. H. Machado, J. A. Miranda, S. Gualardi, D. E. Nicodem, D. Severino, *Spectrochim. Acta A* **59**, 345 (2003).
[5] F. Derridj, J. Roger, F. Geneste, S. Djebbar, H. Doucet, *J. Organomet. Chem.* **694**, 455 (2009).

Development of *In Silico* Drug Design Techniques Based on the Fragment Molecular Orbital Method

Kaori Fukuzawa

School of Pharmacy and Pharmaceutical Sciences, Hoshi University, 2-4-41 Ebara,
Shinagawa-ku, Tokyo 142-8501, Japan

The Fragment molecular orbital (FMO) method is one of the high-potential approach for protein - ligand interaction energy analysis in structure based drug design. By using the FMO method, detailed information on the interaction between the ligand and the target protein can be obtained based on a quantum mechanical calculation. Interaction between a ligand and each amino acid residue can also be quantitatively evaluated using the inter fragment interaction energy (IFIE). The FMO method has been applied to many protein-ligand systems, and recent activities that have evolved these research have been rapidly progressing. Here we will introduce the recent research on the development in "FMO Drug Design Consortium (FMODD)" through industry-academia-government collaboration.

By using K-computer since 2015, FMO calculation of protein-ligand complex exceeding 1,000 structures have been done so far. Correlation between calculated binding energies and IC_{50} activity values was investigated on various types of target proteins using X-ray crystal structures from Protein Data Bank. We are preparing to store these calculation results in the IFIE database and plan to release it widely as basic data of FMO based drug design. In the future, we would like to enable rational drug design with high reliability for targets for which electronic effects are important, which cannot be solved by conventional classical approaches.

Acknowledgement

This research has been carried out by cooperation of many collaborators involved in FMODD. A part of this research was done in activities of the FMODD, and the results were obtained using the K computer (project ID: hp170183). This work was also supported by JSPS KAKENHI Grant Number JP15K05397.

References

[1] "The Fragment Molecular Orbital Method" ed. Fedorov, D. G. & Kitaura K.: (Taylor & Francis/ CRC Press, Boca Raton, FL, 2009).

[2] Fedorov, D. G., Nagata, T., Kitaura, K., *Phys. Chem. Chem. Phys.* **14**, 7562 (2012).

[3] Tanaka, S., Mochizuki, Y., Komeiji, Y., Okiyama, Y. and Fukuzawa, K., *Phys. Chem. Chem. Phys.*, **16**, 10310 (2014).

Construction of IFIE-database with semi-automated FMO calculation protocol

Chiduru Watanabe[1], Yoshio Okiyama[1], Daisuke Takaya[1], Shunpei Nagase[1], Kikuko Kamisaka[1], Hirofumi Watanabe[2], Kaori Fukuzawa[3], Teruki Honma[1]

[1]*RIKEN Center for Life Science Technologies, 1-7-22 Suehiro-cho, Tsurumi-ku, Yokohama, Kanagawa 230-0045, Japan,*

[2] *Education Center on Computational Science and Engineering, Kobe University, 7-1-48, Minatojimaminamimachi, Chuo-ku, Kobe 650-0047, Japan*

[3]*Department of Physical Chemistry, School of Pharmacy and Pharmaceutical Sciences, Hoshi University, 2-4-41 Ebara, Shinagawa, Tokyo 142-8501, Japan*

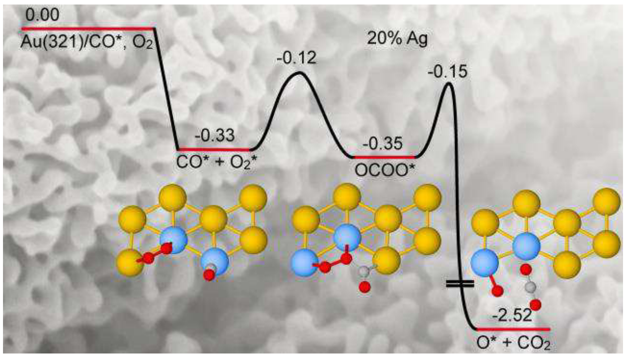
The fragment molecular orbital (FMO) method proposed by Kitaura *et al.* enables us to efficiently perform *ab initio* quantum mechanical calculations for large biomolecules by many-body expansion technique with fragmentation. Inter-fragment interaction energy (IFIE) analysis based on FMO is able to reveal important interactions in molecular recognition such as protein-ligand binding in units of amino acid residues and a ligand. Moreover, the information of important interactions estimating from decomposed electronic energy terms (e.g. electrostatic and dispersion interactions) is quite useful for drug design. On the other hand, it is not easy to perform FMO calculations for not experienced researchers in the matter of structure preparation and FMO setting. To publicly disclose the IFIE data, we have started to comprehensively collect IFIE data and construct IFIE-database (Figure 1). However, there are limits to prepare huge amount of various protein structure data (e.g. PDB having ca. 40,000 entries of protein-ligand complex) by manual labor. Thus, we developed "semi-automated FMO calculation protocol" to efficiently carry out structure preparation and subsequent FMO calculations for multiple X-ray crystal structures. To validate the FMO protocol, we manually prepared protein structure and carry out FMO calculations using the same crystal structures. As a result, IFIE values of the FMO protocol data showed good agreement with those of manual labored data. Therefore, we confirmed that this protocol can be used for structure preparation and FMO calculations of massive protein structures. There are at present the IFIE data of 300 complexes obtained from the FMO protocol. They were registered in newly developed IFIE-database with GUI. This research was done in activities of the FMO drug design (FMODD) consortium [http://eniac.scitec.kobe-u.ac.jp/fmodd/index.html]. The results of FMO calculations were obtained using the K computer (project ID: hp170183).

Figure 1 IFIE-database

New Insights Into Oxygen Activation On Nanoporous Gold - A Selective Catalyst For Methanol Oxidation

Wilke Dononelli[1], Lyudmila Moskaleva[2], Thorsten Klüner[1]
1 IfC, Carl von Ossietzky Universität Oldenburg, 26111 Oldenburg, Germany
2 IAPC, Universität Bremen, 28359 Bremen, Germany

Au-based catalysts can be used for fuel cells, the synthesis of esters or the selective oxidation of alcohols. [1] There is a high interest in this metal based catalysts because the selectivity of gold to partial oxidation products is higher than the selectivity of other metals. Especially nanoporous gold (np-Au), an unsupported form of catalytically active gold, has recently attracted considerable interest due to its potential use in the selective oxidation of alcohols like methanol. [2] Although these oxidation reactions have been investigated by several groups during the past decade, the origin of the catalytic activity of np-Au has not been understood completely. The main remaining question that we try to answer is the nature of the active sites of the np-Au. Within DFT (density functional theory) calculations, using the PBE functional as implemented in the Vienna ab initio simulation package (VASP) [3], we describe the influence of residual silver atoms in the material and try to explain possible pathways for the activation of oxygen, which is the most essential step of these oxidative coupling reactions. [1,4] Therefore a kinked Au(321) surface introduced by Moskaleva [5] represents one of the reactive surfaces of the nanoporous gold in this study. Since Zielasek *et al.* [6] experimentally found atomic oxygen at the surface of the np-Au for the reaction of CO and O_2 to CO_2, it was estimated that first molecular oxygen is dissociated and then the atomic oxygen reacts with CO. In earlier studies, we were able to demonstrate, that this reaction only occurs if a high amount of residual silver is present at the surface. The activation barrier for the dissociation can be lowered form 1.1 eV on pure gold to 0.7 eV with silver impurities. [5] For this study, we considered a direct reaction of CO and O_2, where the activation barrier can be lowered to 0.4 eV without and 0.2 eV with silver impurities (see fig., reprinted from ref. [1]). [1,4] In addition, we are able to show, that comparable reaction pathways via the direct reaction of O_2 with either H_2O [4] or CH_3OH are possible and that the role of the residual silver has not been discussed entirely correct for the last decade, since no ag is needed to activate these reactions.



[1] W. Dononelli, L. V. Moskaleva and T. Klüner, in Encyclopedia “Interface Chemistry: Surface Science and Electro-chemistry”, Elsevier (2017).
[2] A. Wittstock, V. Zielasek, J. Biener, C. Friend and M. Bäumer, *Science* **327**, 319 (2010).
[3] G. Kresse and J. Hafner, Phys. Rev. B, **49**, 14251 (1994).
[4] W. Dononelli, M. V. Moskaleva, M. Bäumer and T. Klüner, submitted (2017).
[5] L. V. Moskaleva, V. Zielasek, T. Klüner, K. Neyman and M. Bäumer, *Chem. Phys. Lett.* **525**, 87 (2012).
[6] V. Zielasek, B. Jürgens, C. Schulz *et al.*, *Ang. Che. Int. Ed.* **45**, 8241 (2006).

Mechanism of Nakamura's Bisphosphine Iron-Catalyzed Asymmetric C(sp2)-C(sp3) Cross-Coupling Reaction .

Wes Lee[1], Jun Zhou[1], Osvaldo Gutierrez[1]

[1] *Department of Chemistry and Biochemistry,* University of Maryland, College Park, MD 20742 (USA)

Quantum mechanical calculations are employed to investigate the mechanism and origin of stereoinduction in asymmetric iron-catalyzed C(sp^2)-C(sp^3) cross-coupling reaction between Grignard reagents and a-chloroesters. A coherent mechanistic picture of this transformation is revealed. These results have broad implications for understanding the mechanisms of iron-catalyzed cross-coupling reactions and rational design of novel iron-based catalysts for asymmetric transformations.

Theoretical Study on the Origin of the Enantioselectivity of Flexible Catalytic Systems

Miho Hatanaka[1,2]

[1]*Institute for Research Initiatives, Division for Research Strategy, Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama-cho, Ikoma, Nara, Japan, 630-0192*
[2]*PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan*

Highly stereoselective reactions have been achieved by using chiral catalysts, and the computational chemistry contributed to better understanding of the mechanism of such reactions. Conventional chiral catalysts usually have rigid structures and bulky side chains on chiral centers to restrict the approach directions of reactants. Therefore, only a few transition states (TSs) of stereo-determining step need to be computed to elucidate the origin of the enantioselectivity. Recently, a number of catalytic systems having flexible structures have been reported. There could be a large number of TSs that may contribute to the stereoselectivity, and a few selective TSs may not be enough. To overcome this problem, an automated exploration method called the Global Reaction Route Mapping (GRRM) is one of the most suitable strategies. [1]

We focus on aqueous C-C bond formations catalyzed by two independent metal complexes having flexible structures. [2] Unlike conventional rigid and bulky chiral catalytic systems, the approach directions of reactants were not restricted by the catalysts and we could not predict the enantioselectivity from the geometries of the prereaction complexes. Therefore, we exhaustively gathered the TSs of the stereo-determining C-C bond formation step by using the artificial force induced reaction (AFIR) method, which is one of the methods of the GRRM strategy, and succeeded in reproducing the experimental enantio excesses quantitatively. In both two catalytic systems, the origin of the enantioselectivity was not the structural bulkiness nearby the chiral centers but the asymmetric structure of the coordination sphere.

[1] (i) S. Maeda, K. Ohno, K. Morokuma, *Phys. Chem. Chem. Phys*. **15**, 3683 (2013). (ii) S. Maeda, Y. Harabuchi, M. Takagi, T. Taketsugu, K. Morokuma, *Chem. Rec*. **16**. 2232 (2016).

[2](i) M. Hatanaka, S. Maeda, K. Morokuma, *J. Chem. Theory Comput.* **9**, 2882 (2013). (ii) M. Hatanaka, K. Morokuma, *J. Am. Chem. Soc*. **135**, 13972 (2013). (iii) M. Hatanaka, K. Morokuma, *ACS Catal.* **5**, 3731 (2015).

Proton Transfer in Cytochrome c Oxidase - Calculation and Prediction of Transition Networks.

Marco Reidelbach[1], **Marcus Weber**[2], **Petra Imhof**[1]

[1] *Physics Department, Free University Berlin, Arnimallee 14, 14195 Berlin, Germany*
[2] *Computational Molecular Design, Zuse Institute Berlin, Takustrasse 7, 14195 Berlin, Germany*

In Cytochrome c Oxidase protons are transferred from the complex surface towards the interior via two distinct channels. How the proton transfer occurs inside the channels, however, is unclear. The Transition Network Approach allows the identification of such proton transfer pathways without introducing any bias. Thereby, a pathway displaying several experimental characteristics was identified. To circumvent numerous Transition Network recalculations, e.g. for different redox-states of the enzyme complex, the Transition Network prediction using Minimum Spanning Tree sensitivities was tested and proved to be efficient.

The Effects of Lewis acid Complexation on Type I Radical Photoinitiators

Benjamin B. Noble[1], Adam C. Mater[1], Leesa M. Smith[1] and Michelle L. Coote[1]*

[1] *Australian Research Council Centre of Excellence for Electromaterials Science, Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia*

In the present work, we examine the effects of zinc chloride ($ZnCl_2$) and aluminium chloride ($AlCl_3$) complexation on the photochemistry of two well-known type I photoinitiators, methyl-4′-(methylthio)-2-morpholinopropiophenone (MMMP) and 2,2-dimethoxy-2-phenylacetophenone (DMPA). High-level *ab initio* calculations and experimental results demonstrate that Lewis acid complexation has a significant effect on the individual processes that comprise radical photoinitiation. Theoretical calculations predict that both Lewis acids form solution stable chelates with MMMP and DMPA. Moreover, we found experimentally that addition of $ZnCl_2$ and $AlCl_3$ significantly alters the UV-Vis spectra of both MMMP and DMPA. Time dependent density functional theory (TD-DFT) calculations demonstrate that Lewis acid complexation blue shifts the $n\pi^*$ excitations of both DMPA and MMMP, while concurrently red shifting the $\pi\pi^*$ transitions. Complexation also significantly alters the stability and reactivity of the photoinitiator fragment radicals. Lewis acid binding localizes and destabilizes acyl radicals, resulting in significantly increased reactivity towards methyl methacrylate (MMA). In contrast, complexation of Lewis acids dramatically reduces the reactivity of the morpholine substituted isopropyl radical and the dimethoxyphenyl radical towards MMA. Alternative complexation at the methyl ester side-chain of MMA has a beneficial effect on the reactivity of all fragments, increasing addition rate coefficients by 2–4 orders of magnitude. Some of the important implications of these findings for pulsed laser polymerization (PLP), and acetophenone photochemistry more generally are outlined.

Advanced artificial neural network approaches to prediction of pharmacokinetic properties and toxicity of drug compounds

Eugene V. Radchenko, Vladimir A. Palyulin, Nikolay S. Zefirov

Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory, 1/3, Moscow 119991 Russia

The pharmacokinetic properties and toxicity of potential drug compounds (ADMET properties: absorption, distribution, metabolism, excretion, toxicity) critically affect their efficacy, pharmacological profile, administration protocol and safety. Thus, the optimization of these properties is an important aspect of drug discovery and development, and the ability to predict them for new structures can substantially improve the speed and efficiency of such optimization.

The artificial neural networks are a powerful nonlinear machine learning method applicable to a broad range of chemistry problems, including the QSAR/QSPR modeling. We have developed a general methodology for the prediction of ADMET parameters based on the application of artificial neural networks and fragmental descriptors to extensive and verified experimental data sets. The fragmental descriptors for a structure are the occurrence counts of the paths, cycles and branches of varied size using an hierarchical atom type classification, providing a 'holographic' representation of a molecule. During the model construction, the GPU-based deep learning and double cross-validation are used to achieve optimal performance and model predictivity. During the prediction, a graphic map highlighting the parts of a molecule that make positive or negative contributions to the predicted property is generated as an additional guidance for the ADMET optimization.

The models built by us are implemented in an integrated online service available on the Internet (http://qsar.chem.msu.ru/admet/). It supports convenient prediction of important properties (in particular, lipophilicity, blood-brain barrier permeability [1], human intestinal absorption [2], plasma protein binding, mutagenicity, hERG-mediated cardiac toxicity [3], aromatic hydrocarbon receptor binding, cytotoxicity, etc.) as well as qualitative and semi-quantitative estimation of their suitability for drug-like compounds. This integrated prediction system may be used in the research in various areas of medicinal chemistry and pharmacology.

This work was supported by the Russian Foundation for Basic Research (grant #15-03-09084).

References

[1] A.S. Dyabina, E.V. Radchenko, V.A. Palyulin, N.S. Zefirov, *Dokl. Biochem. Biophys.*, **470**, 371 (2016). **[2]** E.V. Radchenko, A.S. Dyabina, V.A. Palyulin, N.S. Zefirov, *Russ. Chem. Bull.*, **65**, 576 (2016). **[3]** E.V. Radchenko, Yu.A. Rulev, A.Ya. Safanyaev, V.A. Palyulin, N.S. Zefirov, *Dokl. Biochem. Biophys.*, **473**, 128 (2017).

How many electrons are excited in an electronic transition?

G. M. J. Barca[1], **A. T. B. Gilbert**[1], **P. M. W. Gill**[1]

[1]*Research School of Chemistry, Australian National University, ACT 2601, Australia*

What am I asserting if I claim that a "singly-excited state" resulted from an electronic transition? Or, for that matter, a doubly- or a triply-excited state? In other words, what if I ask: *how many electrons are excited in an electronic transition?*

In this Poster, we address this fundamental question by introducing the excitation number, η, as a metric for characterising multiply excited states. We show that calculated η values lie very close to positive integers, leading to unambiguous assignments of the number of excited electrons. This contrasts with previously defined quantities, such as the promotion number,[1] which can lead to misassignments. We consider several examples where η can provide improved characterisation of excited states.[2]

[1] M. Head-Gordon, A. M. Graña, D. Maurice, and C. A. White, *J. Phys. Chem.* **99**, 14261 (1995).

[2] G. M. J. Barca, A. T. B. Gilbert, and P. M. W. Gill, *submitted*

Photoisomerisation and electronic spectroscopy of XC_3N ($X=-CH_3$, $-H$). The TD-DFT perspective.

Marcin Gronowski[1], **Thomas Custer**[1], **Robert Kołos**[1]

[1]*Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland*

Photochemical transformations of cyanoacetylene (HC_3N) and methylcyanoacetylene (CH_3C_3N) dispersed in noble gas matrices were the subject of intense experimental studies. For both molecules, UV irradiation leads to formation of several isomers. In spite of the fact that both molecules have the same chromophore, their photolysis products are significantly different. We try to explain the mechanisms for photochemical transformation of these molecules using quantum chemical computations.

In the first step, we studied ground state potential energy surfaces. We found transition states on them and applied IRC computations in order to determine the minimum energy path between the transition states and minima. Then, we applied time-dependent density functional theory in the Tamm-Dancoff approximation to describe excited state potential energy surfaces. The study was carried out using the vertical approximation meaning that the energies of excited states were calculated for each of the geometries obtained during ground state IRC calculations. In the final step, we optimized geometries for minima on triplet and singlet excited states.

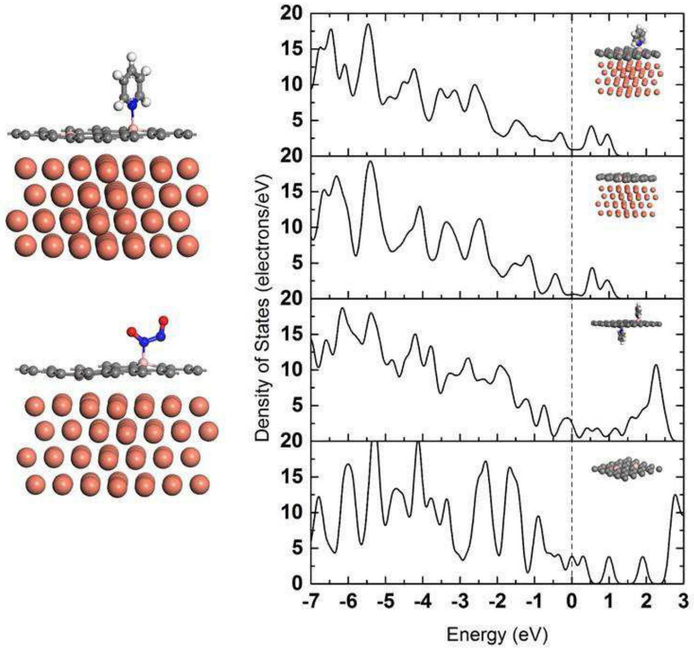
The ground and singlet excited state potential energy surfaces do not cross each other during most unimolecular transformations discussed here. This suggests that most of the chemical transformations take place on the first triplet potential energy surface. Our computations show that energies of first triplet excited states of isocyanide species are higher than for the respective cyanides. This hinders the formation of isocyanides if any other reaction channel is open, as is the case for CH_3C_3N.

Boron-Doped Graphene for multifunctional coating – A DFT study

Valentina Cantatore and Itai Panas

Chalmers University of Technology, Department of Chemistry and Chemical Engineering, Energy and Materials, Gothenburg, Sweden

We describe a route to achieve multi-functional graphene coating through DFT calculations. To start with we show how chemical bonding between a copper substrate and a graphene layer can be obtained if the graphene is a priori boron doped. [1] Utilizing the well-known epitaxy between graphene and Cu(111) [2] and pair-wise binding to the Cu(111) surface through boron sites,[3] we can observe co-existence of pseudo-gap property in the graphene subsystem and, at the same time, a metallic density of states in the Cu subsystem at the common Fermi energy. Apparently a paradox is that the two subsystems, the doped graphene and the Cu surface, preserve and even recover their individual integrities upon formation of surface chemical bonds. Employing pyridine as test molecule, conditioned ability of a nucleophile to offer competitive dative bonding with the substrate for boron sites is demonstrated. It is shown also that the adsorption of small molecules on the BBG@Cu system occurs for the case of half coverage and for adsorption to boron atoms originally bound to the on-top site of Cu(111). The ability of complementary boron sites to compensate for loss of binding between on-top site and boron, resulting from said bonding to the incoming nucleophile, is emphasized. Based on these observations, the possibility to study infinite layered systems comprising FeSe monolayer and boron doped graphene is inferred and first insights on the peculiar magnetic structure of the system are showed.



[1] V. Cantatore and I. Panas, *Carbon*, **115**, 375 (2017).

[2] L. Ferrighi, M. I. Trioni and C. Di Valentina, *J. Phys. Chem. C*, **119**,6056 (2015).

[3] V. Cantatore and I. Panas, *Carbon*, **104**, 40 (2016).

Theoretical design of boron nitride based electrocatalysts for oxygen reduction and hydrogen evolution reactions

Andrey Lyalin[1], **Kohei Uosaki**[1], **Tetsuya Taketsugu**[1,2]

[1]*Global Research Center for Environment and Energy based on Nanomaterials Science (GREEN), National Institute for Materials Science (NIMS), Tsukuba 305-0044, Japan*
[2]*Department of Chemistry, Hokkaido University, Sapporo 060-0810, Japan*

It is demonstrated that chemically inert and insulating hexagonal boron nitride (h-BN) supported on the inert gold surface can be functionalized by interaction with the metal support and become active electrocatalysts [1,2]. It is shown that small gold clusters deposited on h-BN/Au(111) surface can provide active sites for oxygen adsorption promoting effective 4e$^-$ pathway of oxygen reduction reaction (ORR) via dissociation mechanism of OOH intermediate at the perimeter interface between the supported Au cluster and h-BN/Au surface [3]. It is also demonstrated that hydrogen evolution reaction (HER) proceeds very efficiently at the interface between Au surface and h-BN nanosheets [2]. Theoretical evaluation suggests that edge atoms of h-BN nanosheets on Au provide energetically favored sites for adsorbed hydrogen, i.e., the intermediate state of HER. Therefore it is suggested that increase in the interface area between Au and h-BN would result in increase of ORR and HER activity. This study opens a new route to develop ORR and HER catalysts based on the materials never been considered as catalytically active.

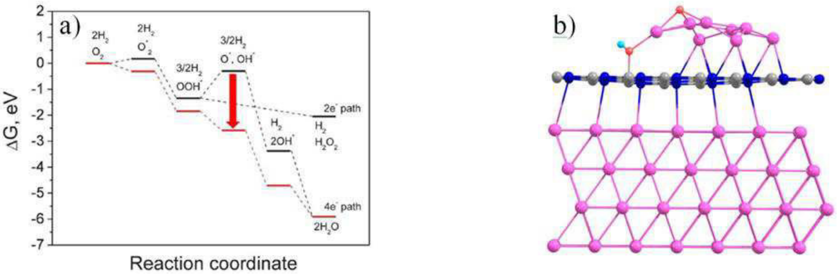


Figure 1: Energy diagram for ORR at BN/Au(111) (black line) and Au$_8$@BN/Au(111) (red line) (a); optimized geometry of dissociated OOH on Au$_8$@BN/Au(111) (b).

[1] K. Uosaki, G. Elumalai, H. Noguchi, T. Masuda, A. Lyalin, A. Nakayama, T. Taketsugu, *J. Am. Chem. Soc.* **136**, 6542-6545 (2014).

[2] K. Uosaki, G. Elumalai, H. C. Dinh, A. Lyalin, T. Taketsugu, and H. Noguchi, *Sci. Rep.* **6**, 32217 (2016).

[3] G. Elumalai, H. Noguchi, A. Lyalin, T. Taketsugu, K. Uosaki, *Electrochem. Commun.* **66**, 53-57 (2016).

Analysis of hyperfine structure in Dirac theory: anomalous increase of relativistic contraction of outer orbitals

Ayaki Sunaga, Minori Abe, Masahiko Hada

Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji-city, Tokyo, Japan

Hyperfine interaction is a magnetic interaction between an electron spin $\hat{\mathbf{S}}$ and a nuclear spin $\hat{\mathbf{I}}$, and the coupling constant of the interaction is referred to as the hyperfine coupling constant (HFCC). In the framework of four-component relativistic theory, the formula of the HFCC is defined by Arratia-Perez *et al.* [1] and Malkin *et al.* [2] and so on. However, the inner product $\hat{\mathbf{S}}\cdot\hat{\mathbf{I}}$ does not clearly appear in their definitions.

In this work, we derive a formalism which apparently includes $\hat{\mathbf{S}}\cdot\hat{\mathbf{I}}$ when the potential of the system is spherical symmetric. Our expression of the 1st order perturbation energy due to the hyperfine interaction is as follows.

$$E = \frac{2}{3}\mu_0 g_{\mathrm{e}} \beta_{\mathrm{N}} g_{\mathrm{N}} \beta_{\mathrm{e}} \frac{1}{\alpha r_{\mathrm{B}}} \frac{\hat{\mathbf{S}}\cdot\hat{\mathbf{I}}}{\hbar^2} \int_0^\infty g^\dagger\left(r_{\mathrm{N}}\right) f\left(r_{\mathrm{N}}\right) dr_{\mathrm{N}} , \tag{1}$$

where $g(r_{\mathrm{N}})$, $f(r_{\mathrm{N}})$ are radial functions of large and small components.

By using Eq. (1) and the nonrelativistic formula of HFCC, we calculated the contribution of the relativistic effect to HFCC for Hydrogen like atom. FIG. 1 show the relativistic effect x (%), where $x = 100(a_{\mathrm{Rel}} - a_{\mathrm{NR}})/a_{\mathrm{NR}}$. a_{Rel} and a_{NR} are the HFCC, which are obtained by using the solutions of Dirac and Schrödinger equation for Hydrogen-like atom, respectively. From FIG. 1, the values of x of 2s ~ 6s orbitals are clearly larger than 1s orbital. The reason for this is that Dirac's solution includes a term which contributes to only the relativistic contraction of the outer orbitals. The increase of the relativistic effect is accompanied by the penetration of the outer orbitals into the region of 1s orbital. This tendency can be observed in the HFCC of many-electron systems too, which will be discussed in my poster.

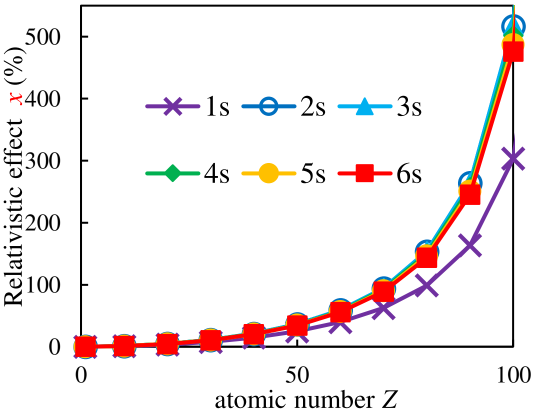


FIG. 1. Comparison of x for 1s ~ 6s orbitals for Hydrogen-like atom.

[1] R. Arratia-Perez and D. A. Case, *J. Chem. Phys.* **79**, 4939 (1983).

[2] E. Malkin, M. Repiský, S. Komorovský, P. Mach, O. L. Malkina, and V. G. Malkin, *J. Chem. Phys.* **134**, 044111 (2011).

An Open-Source Framework for Analyzing N-Electron Dynamics. Capabilities and Applications of DETCI@ORBKIT

Gunter Hermann[1], Vincent Pohl[1], Jean Christophe Tremblay[1]

[1] *Institut für Chemie und Biochemie, Freie Universität Berlin, Takustraße 3, Berlin 14195, Germany*

We present the capabilities of our recently published open-source framework DETCI@ORBKIT [1, 2] which is able to analyze and visualize correlated N-electron dynamics of molecular systems. In general, the program evaluates transition moments and expectations values of one-electron operators, e.g., the electron density or the electronic flux density, for explicitly time-dependent electronic wave packets that are represented as linear combinations of multi-determinantal wave functions. The wave functions are directly extracted from the output of standard Configuration-Interaction (CI) calculations at various levels of theory. Our procedure can be used to unravel the mechanistic features of a broad range of ultrafast charge migration processes in different molecular systems. To assess the robustness of the qualitative and quantitative statements concerning the dynamical details of a charge migration simulation, we investigated its convergence with respect to the electronic structure theory level and basis set size for a few benchmark systems.

Since CI calculations are not always feasible for extended systems, we extend our procedure to a non-variational hybrid method, where multi-determinantal eigenstates are obtained from linear-response time-dependent density functional theory (TDDFT). These build up a space of pseudo CI singles basis functions, which can be used to perform many-electron dynamics in strong laser fields. This combination of electronic structure methods also confers great scalability to the approach with respect to the system dimension. To validate this hybrid TDDFT/CIS scheme, we conduct a comparison of different CI methods for the laser-driven state selective excitation in a test system. The mechanistic features of the electron dynamics quantitatively coincide with the results from the higher-level electronic structure methods. In addition, the scalability of our scheme is demonstrated at the example of the broadband laser excitation in an moderate sized organic dye.

[1] V. Pohl, G. Hermann, J. C. Tremblay, *J. Comput. Chem.* **38**, 1515 (2017).

[2] G. Hermann, V. Pohl, J. C. Tremblay, *J. Comput. Chem.* **accepted**, (2017).

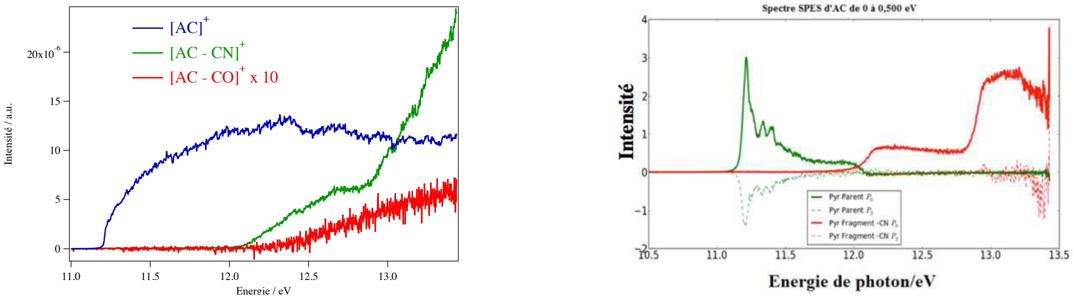
Structural and spectroscopic investigation of acetyl cyanide: theory and experience

A.Bellili[1*], M. Hochlaf[2],R. Linguerri[2], M. Schwell[3], L. Poisson[4], C. Puzzarini[5]

[1] ENS de Lyon Laboratoire de Chimie UMR 5182, 46, allée d'Italie 69364 LYON, FRANCE
[2] Université Paris-Est, Laboratoire Modélisation et Simulation Multi Echelle, MSME UMR 8208 CNRS, 5 bd Descartes, 77454 Marne-la-Vallée, FRANCE.
[3] Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR CNRS 7583, Université Paris Est Créteil and Université Paris Diderot, Institut Pierre Simon Laplace, 61 Avenue du Général de Gaulle, 94010 Créteil, FRANCE
[4] Laboratoire Francis Perrin, URA 2453, CEA, IRAMIS, SPAM, Laboratoire Interactions Dynamique et Lasers, F-91191 Gif-sur-Yvette, FRANCE.
[5]Dipartimento di Chimica "Giacomo Ciamician", Università di Bologna, Via F. Selmi, Bologna, ITALY.

In this combined theoretical and experimental work [1,2], we are interested in the photoionization, the spectroscopy and dynamics of acetyl cyanide molecule (H_3CCOCN denoted AC) cations and neutral [3]. The molecule is prebiotic and relevant for astrochemistry. It is one product of Streker reaction [4], which is originally a realistic scenario for the formation of amino acids in interstellar medium (ISM).

We present the results of measurements performed in the synchrotron SOLEIL (DESIRS beamline) [5], where we measured the photoelectron photoion coincidence (PEPICO) spectra and the SPES spectra of acetyl cyanide. In-vacuum temperature-controlled oven was applied to promote the intact neutral species into the gas phase. The PIPICO and SPES spectra of AC are given below.



(a) (b)

Figure1: (a) PIPICO **(b)** SPES spectra of acetyl cyanide obtained with 500 meV threshold electron resolution.

The SPES spectrum present rich structures corresponding to the population of the vibrational levels of the cations in their ground and the electronic excited states. The assignment of these features was investigated with the help of state-to-the-art ab initio calculations. In addition, we explored the potential energy surface (PES) of acetyl cyanide and its cation using standard CCSD(T) and explicitly correlated CCSD(T)-F12 methods and more precise methods as CCSD(T)/CBS+CV. A set of specific spectroscopic parameters (vibration and rotation) was also calculated. The performed calculations included enolic tautomers which can be formed within the covered excitation energies was studied in this work. This study allowed us to provide high resolution spectroscopic data which are essential for the interpretation of astrophysical observations.

[1] Bellili et al , The Journal of Chemical Physics 141, 134311 (2014)
[2] Bellili et al, The Journal of Chemical Physics 143, 184314 (2015)
[3] Danger et al, ApJ 535, A47, 1 (2011).
[4] Poully et al., Phys Chem Chem Phys. 12, 3566 (2010)
[5]http://www.synchrotronsoleil.fr/portal/page/portal/Recherche/LignesLumiere/DESIRS

*The calculations was realized at Université Paris-Est Marne-La-Vallée, Laboratoire Modélisation et Simulation Multi Echelle, MSME UMR 8208 and Dipartimento di Chimica "Giacomo Ciamician", Università di Bologna.

Exciton relaxation dynamics in photoexcited cycloparaphenylenes

Ljiljana Stojanović[1], Felix Plasser[2], Thomas Niehaus[3], Rifaat Hilal[4], and Mario Barbatti[1]

[1]Aix Marseille Univ, CNRS, ICR, Marseille, France (ljiljana.stojanovic@univ-amu.fr)
[2]Instutute for Theoretical Chemistry, University of Vienna, Vienna, Austria
[3]Univ Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, Lyon, France
[4]Chemistry Department, Faculty of Science, KAU, Jeddah, Saudi Arabia

Cycloparaphenylenes (CPPs) are the shortest subunits of the single-walled armchair carbon nanotubes. In the last several years, they have received a significant attention due to potential applications in bottom-up synthesis of nanotubes. They have unusual photophysical properties, markedly distinct from linear paraphenylenes. For example, they are characterized by broad, featureless, size-independent absorption spectra, unusual size impact on photoluminiscence spectra, and relaxation lifetimes in nanosecond time domain.

We studied the 3-ps relaxation dynamics of [8]CPP and [10]CPP in the gas phase using surface hopping simulations based on the TD-DFTB potential energy surfaces. The properties of excitons occurring during dynamics are analyzed based on transition density matrices.

The relaxation dynamics of [8]CPP is featured by a series of delocalized charge-transfer excitons, whereas in the case of [10]CPP localized “self-trapping” excitons also occur. The localization of excitons is accompanied by significant dihedral angle distortions around sequences of rings on which they are localized. In the case of [8]CPP, significant ring strain prohibits formations of localized excitons.

The simulated emission spectra from the dynamics results confirm its experimentally found multi-peaked structures. We find that the relaxation from the S_1 state, which is a dark state in the Frank-Condon region, becomes allowed due to symmetry breaking induced by electron-phonon couplings. The specific multi-peaked emission spectra arise from the relaxation processes from different local minima on the S_1 surfaces.

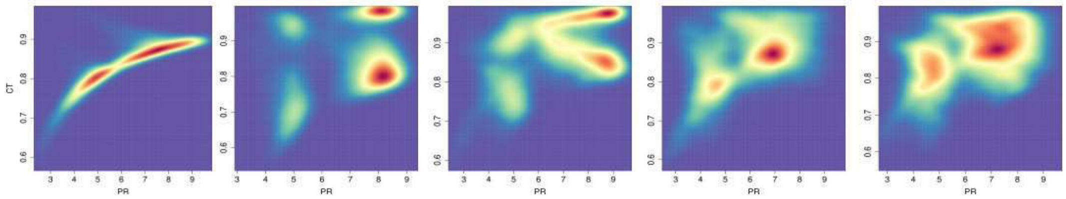


Figure 1. The correlation plots of participation ratio and charge transfer number distributions in different adiabatic states of [10]CPP.

Water Adsorption On Gold Nanoparticles: A Theoretical Study

Chen Hui CHAN[1], **Elise DUMONT** [1], **David LOFFREDA**[1]

[1]*Laboratoire de Chimie, Ecole Normale Supérieure de Lyon and CNRS, 46 allée d'Italie,*
69364 Lyon Cedex 07, FRANCE.

The applications of Gold Nanoparticles for enchancing hadrontherapy performance is very promising. This success have been demonstrated by highly active *in vivo* and *in vitro* experimental studies. High Z-AuNPs contribute to radiosensitization effect, making tumor cells more responsive to ionizing radiation. Upon water radiolysis, AuNPs generate secondary electrons and reactive oxygen species (ROS) which favor hadrontherapy by amplifying the damages and improving local dose enchancement.

In this work, we use theoretical approaches to study the mechanism of generation of ROS by AuNPs and provide atomic level insight into water/AuNPs interface. In particular, we aim at rationalizing the interaction of water molecule with AuNPs as a function of the size, and to determine the most stable positions of water on these nanoparticles. By using Density Functional Theory (DFT), we computed adsorption energies of single water molecule on AuNPs. To do so, we have considered metallic clusters having a truncated octahedron structure, with a diameter ranging from 0.9 to 3.3nm. The interaction energy of water on AuNPs has been decomposed into covalent and dispersive (Van der Waals forces) contributions. Out preliminary results show that the most competitive adsorption sites for water are top positions, essentially at the corners of the clusters. The adsorption strength of water progressively decreases inversely with respect to the nanoparticle size. The stability loss is significant since the adsorption energy is roughly reduced by a factor of two. This suggests weaker solvation effects at larger nanoparticle sizes.

Apart from this interesting DFT analysis, those interaction energies between water and AuNPs are key parameters for future theoretical developments related to radiochemistry in collaboration with colleagues from Institut de Physique Nucléaire in Lyon.

This project is funded by Labex PRIMES (ANR 11-LABX-0063, PhD fellowship awarded to C.H.Chan).

Knockout driven reactions in porphyrin molecules and butadiene clusters

Giovanna D'Angelo[1,2,3], **Michael Gatchell**[1], **Linda Giacomozzi**[1], **Henrik Cederquist**[1], **and Henning Zettergren**[1]

[1]Department of Physics, Stockholm University, Stockholm, SE-106 91, Sweden
[2]Facultade de Ciências, Universidade do Porto, Porto, 4169-007, Portugal
[3]Departamento de Química, Universidad Autónoma de Madrid, Madrid, 28049, Spain

Recent studies on collisions between energetic ions/atoms and PAHs, fullerenes or their clusters have demonstrated the importance of prompt atom knockout in Rutherford-like scattering for molecular processing [1]. Such processes may lead to molecular growth, due to the formation of highly reactive fragments that very efficiently form new covalent bonds with surrounding molecules [1]. This type of energetic processing can be of importance for, e.g., the origin and evolution of complex molecules in space [2].

Here we present the modeling of keV-ion impact on butadiene clusters [3] and of collisions between tetraphenyl-porphyrin (TPP) ions and Ne or He atoms at 50-80 eV center-of-mass collision energies [4]. We have performed classical Molecular Dynamics simulations to model entire collision sequences, i.e. the initial knockout event and the subsequent fragmentation or molecular growth processes inside molecular clusters. Figure 1 shows a comparison between experimental and simulated mass spectra for collisions with butadiene clusters. The spectra clearly suggest the presence of molecular growth within the clusters and that this is driven by prompt carbon knockouts. We are currently investigating possible secondary fragmentation pathways, specific to collisions with atoms or ions, by means of density functional theory based methods.

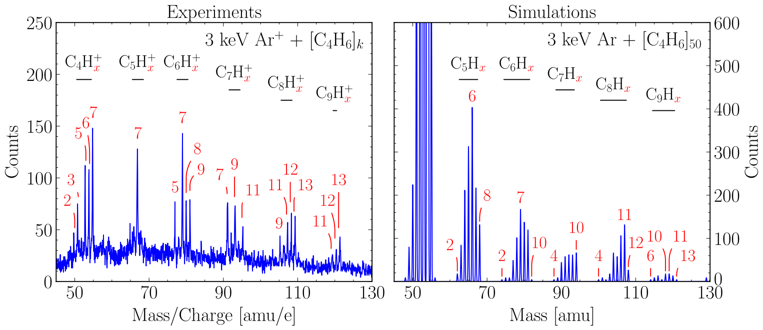


Fig.1 Experimental (left) and simulated (right) mass spectra for collision of C_4H_6 cluster with Ar^+.

[1] M. Gatchell and H. Zettergren, *J. Phys. B,* **59**, 162001 (2016).
[2] A. G. G. M. Tielens, *Rev. Mod. Phys.* **85**, 1021-1081 (2013).
[3] M. Gatchell et al., *Phys. Chem. Chem. Phys.* (in press) (2017).
[4] L. Giacomozzi et al., *Phys. Chem. Chem. Phys.* (in press) (2017).

QM/MM Studies of Reactive Intermediates in Solution: Diphenylcarbene in Solvent Mixtures

Pandian Sokkar[1,2], **Walter Thiel**[1], **Elsa Sanchez-Garcia**[1,2]

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

[2] *Universität Duisburg-Essen, 45117 Essen, Germany*

Abstract: Carbene chemistry is a multifaceted research area by virtue of the highly spin-dependent reactivity of carbenes. In particular, the reactivity of diphenylcarbene (Ph_2C) intrigues researchers owing to the variety of possible reaction pathways depending on whether the spin-configuration is either a singlet or a triplet state. Singlet carbenes are assumed to insert into O-H bonds, whereas triplet carbenes insert into C-H bonds. In this work, we investigate singlet Ph_2C reaction pathways in different solvent environments (acetonitrile, methanol, 2-butanol and the binary mixtures of acetonitrile and methanol), using QM/MM molecular dynamics simulations and optimizations. Our results indicate that H-bonding in protic solvents stabilizes the singlet over the triplet state of Ph_2C (Figure). We identify two mechanisms by which the singlet Ph_2C inserts into the O-H bond of alcohols in explicit solvent environment. Transient absorption spectroscopy studies further confirm our findings. [1]

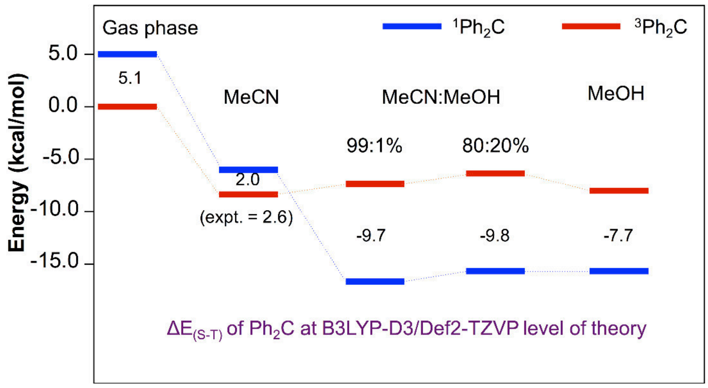


Figure. Relative energies of $^1Ph_2C$ and $^3Ph_2C$ in different solvent environments

[1] J. Knorr, P. Sokkar, S. Schott, P. Costa, W. Thiel, W. Sander, E. Sanchez-Garcia, P. Nuernberger, *Nat. Commun.* **7** (2016).

Time-dependent extension of the long-range corrected density functional based tight-binding method

J.J. Kranz[1], V. Lutsker[2], A. Dominguez[3], B. Aradi[4] , T. Frauenheim[4] , M. Elstner[1], T. A. Niehaus[5]

[1]*Institute of Physical Chemistry, Karlsruhe Institute of Technology, Germany*
[2]*Department of Theoretical Physics, University of Regensburg, Germany*
[3]*Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany*
[4]*BCCMS, University of Bremen, Germany*
[5]*Institut Lumière Matière, Université de Lyon, France*

Although time-dependent density functional theory usually provides a good compromise between accuracy and computational performance for excited state properties, there are still many applications for which a further reduced computational cost is desirable. Such applications include, for example, quantum molecular dynamics simulation in excited states or calculations on large extended nano structures. The time-dependent density functional tight-binding[1] (TD-DFTB) semi-empirical method has been used successfully over years to tackle such problems. The conventional DFTB method is based on an approximation to DFT with an underlying GGA functional, and it thus inherits all shortcomings of such functionals. While a change of functional is straightforward in DFT, in DFTB it requires considerable alternations if the mathematical form deviates from that of a GGA functional.

Recently, a version of DFTB with a long-range corrected functional has been brought forward[2]. It is based on a tight-binding kind of approximation of the Hartree-Fock exchange integrals and a self-consistent determination of the one particle density matrix, rather than merely of atomic charges. We present a formulation and implementation of linear response TD-DFTB derived from this ground-state theory[3]. The resulting theory is similar in form to other recent empirical extension of TD-DFTB[4] to include HF exchange, but fully consistent, with HF exchange included in both ground state and the linear response calculation.

Results of benchmark calculations are presented to assess the performance of the method. It is shown that, as for full DFT, range separated functionals can solve problems, such as an incorrect description of excitations involving charge-transfer or spatially extended states.

[1] Niehaus T. A., Suhai S., Della Sala F., Lugli P., Elstner M., Seifert G. and Frauenheim T. *Phys. Rev. B*, *63(8)*, 085108 (2001).

[2] Lutsker, V., Aradi B., and Niehaus T. A. *J. Chem. Phys.*, *143(18)*, 184107 (2015).

[3] Kranz J. J., Elstner M., Aradi B., Frauenheim T., Lutsker V., Dominguez Garcia A. and Niehaus T. A. *J. Chem. Theory Comput.*, 13(4), 1737 (2017)

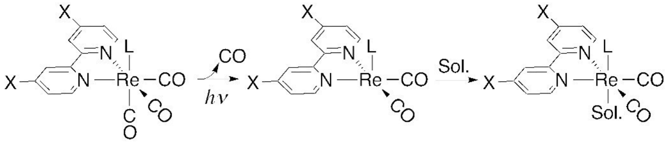
[4] Humeniuk A. and Mitrić R. *J. Chem. Phys.*, *143(13)*, 134120 (2015).

Mechanism of the photochemical ligand substitution of *fac*-[$\mathrm{Re^I(bpy)(CO)_3(PR_3)]^+}$ complex

Kenichiro Saita[1], **Satoshi Maeda**[1]

[1]*Department of Chemistry, Faculty of Science, Hokkaido University, Kita 10 Nishi 8, Kita-ku, Sapporo, 060-0810, Japan*

The mechanism of the CO ligand dissociation of *fac*-$[\mathrm{Re^I(bpy)(CO)_3P(OMe)_3}]^+$ has theoretically been investigated [1], as the dominant process of the photochemical ligand substitution (PLS) reactions of *fac*-$[\mathrm{Re^I(bpy)(CO)_3PR_3}]^+$, by using the (TD-)DFT method. The PLS reactivity can be determined by the topology of the T_1 potential energy surface, since the photoexcited complex is able to decay into the T_1 state by internal conversions (through conical intersections) and intersystem crossings (via crossing seams) with sufficiently low energy barriers [2]. The T_1 state has a character of the metal-to-ligand charge-transfer (^{3}MLCT) around the Franck-Condon region, and it changes to the metal-centered (^{3}MC) state as the Re-CO bond is elongated and bent. The equatorial CO ligand has a much higher energy barrier to leave than that of the axial CO, so that the axial CO ligand selectively dissociates in the PLS reaction. The single-component artificial force induced reaction (SC-AFIR) search [3] reveals the CO dissociation pathway in photostable *fac*-$[\mathrm{Re^I(bpy)(CO)_3Cl}]$ as well, however, the dissociation barrier on the T_1 state is substantially higher than that in *fac*-$[\mathrm{Re^I(bpy)(CO)_3PR_3}]^+$ and the minimum-energy seams of crossings (MESXs) are located before and below the barrier. The MESXs have also been searched in *fac*-$[\mathrm{Re^I(bpy)(CO)_3PR_3}]^+$ and no MESXs were found before and below the barrier.



Scheme 1. Photochemical ligand substitution (PLS) reaction of *fac*-$[\mathrm{Re^I(bpy)(CO)_3L}]^{n+}$.

[1] K. Saita, Y. Harabuchi, T. Taketsugu, O. Ishitani, S. Maeda, *Phys. Chem. Chem. Phys.* **18**, 17557 (2016).

[2] Y. Harabuchi, J. Eng, E. Gindensperger, T. Taketsugu, S. Maeda, C. Daniel, *J. Chem. Theo. Comp.* **12**, 2335 (2016).

[3] S. Maeda, Y. Harabuchi, M. Takagi, T. Taketsugu, K. Morokuma, *Chem. Rec.* **16**, 2232 (2016).

Vibrational Density Matrix Renormalization Group

Alberto Baiardi[1], **Christopher J. Stein**[2], **Vincenzo Barone**[1], **Markus Reiher**[1]

[1]*Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy*
[2]*ETH Zürich, Laboratorium für Physikalische Chemie, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland*

Variational approaches for the calculation of vibrational wave functions and energies are a natural route to obtain highly accurate results with controllable errors. However, the unfavorable scaling and the resulting high computational cost of standard variational approaches limit their application to relatively small molecules. Here, we demonstrate how the density matrix renormalization group (DMRG) can be exploited to optimize vibrational wave functions (vDMRG)[1] expressed as matrix product states. We study the convergence of these calculations with respect to the size of the local basis of each mode, the number of renormalized block states, and the number of DMRG sweeps required. We demonstrate the high accuracy achieved by vDMRG for small molecules that were intensively studied in the literature. We then proceed to show that the complete fingerprint region of the sarcosyn-glycin dipeptide can be calculated with vDMRG.

[1] A. Baiardi, C.J. Stein, V. Barone, M. Reiher, arXiv:1703.09313 [physics.chem-ph] (2017).

Molecular Response to Strong Magnetic Fields: Excitation Energies and Anapole Moments

Sangita Sen[1], **Erik Tellgren**[1]

[1] *Centre for Theoretical and Computational Chemistry/University of Oslo, Sem Sælands vei 26, 0371 Oslo, Norway*

The response of a molecule to weak external magnetic fields is well characterized by the perturbative definition of its magnetic moments, susceptibilities, etc. In the regime of strong magnetic fields, of the order of 10^5T, the Coulombic and magnetic interactions become competitive and neither can be considered a perturbation on the other. Rare early studies include those on He and Li atoms[1, 2] but molecules remain largely unexplored. Such situations are often encountered under astrophysical conditions such as in highly magnetised white-dwarfs and neutron stars. The spectroscopic signatures of atoms and molecules under such extreme conditions is important to astrophysicists for studying these celestial bodies. In this work, we investigate the modulation of molecular excitation energies by external magnetic fields of this order of magnitude. The excitation energies are computed by linear response using the Random Phase Approximation on a mean field wave-function optimized in the presence of a finite magnetic field. Moreover, while electric and magnetic moments and susceptibilities are commonly computed and measured, moments which couple to the curl of the magnetic field, have been largely neglected ever since they were first considered by Zel'dovich[3] and named "anapoles". They are distinct from the usual magnetic moments arising out of a perturbative expansion in the magnetic field and can be visualised instead as arising from a toroidal dipole[4, 5]. We have studied the orbital and spin effects on the anapole susceptibilities of molecules at the SCF level. The RHF theory is used to investigate the orbital effects[6] while the 2-component General Hartree-Fock (GHF) theory is used to study the spin and orbital effects in conjunction. We believe that a thorough study of the microscopic interactions affecting the anapole susceptibilities will throw significant light on the quantum mechanism of intramolecular interactions involving toroidal molecular structures in nature.

[1] Becken, W., Schmelcher, P. and Diakonos, F. K., *J. Phys. B* **32**, 1557 (1999).

[2] Al-Hujaj, O.-A. and Schmelcher, P., *Phys. Rev. A* **70**, 33411 (2004).

[3] Zel'dovich, I. B., *J. Exptl. Theor. Phys.* **33**, 1531 (1957).

[4] Lazzeretti, P., *Theor. Chim. Acta* **87**, 59 (1993).

[5] Faglioni, F., Ligabue, A., Pelloni, S., Soncini, A. and Lazzeretti, P., *Chem. Phys.* **304**, 289 (2004).

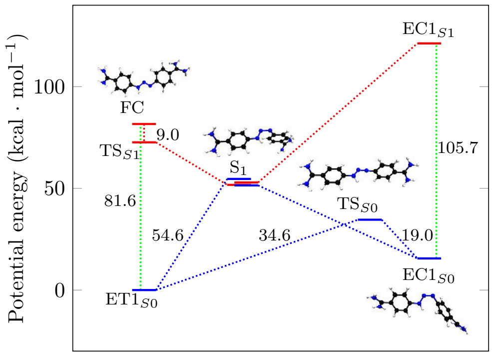
[6] Tellgren, E. I. and Fliegl, H., *J. Chem. Phys.* **139**, 164118 (2013).

QM/MM Polarizable Embedded RI-CC2 analytical gradients: Deexcitation Pathways of a Triazene Compound in Complex Environments

Alireza Marefat Khah[1], **Christof Hättig**[1]

[1]*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Universitätsstraße 150, D-44801 Bochum, Germany*

Berenil (diminazene aceturate) is a DNA minor groove binder with an extremely low fluorescence quantum yield. We have studied the electronic excited state pathways of berenil using the *ab initio* ADC(2) method in combination with Conductor-like screening model (COSMO) in order to include the solvent effect within the continuum approximation. With analyzing the Natural Transition Orbitals (NTOs) and the Intrinsic Reaction Coordinate (IRC) paths, a bicycle-pedal type deexcitation mechanism and a conical intersection between ground and the S1 excited states could be identified [1]. Furthermore, the QM/MM Polarizable-Embedding which partitions the molecular environment to polarizable point multipoles has been combined with the HF, the TDDFT [2] and the Coupled Cluster theory [3]. Within an undergoing project, the PERI-CC2 implementation of excitation energy is extended for molecular gradients for ground and excited states. The latter development would make it possible for us to study the excited state relaxation of berenil when it binds to DNA and/or proteins and would help us to understand the solvent role on the deexcitations with atomistic resolution.



[1] L. Grimmelsmann, et. al. J. Phys. Chem. Lett., 2017, 8, 1986.

[2] J. M. Olsen, et. al.; J. Chem. Theory Comput., 2010, 6, 3721.

[3] K. Sneskov, et. al.; J. Chem. Phys., 2011, 134, 104108.

On-the-fly ab initio semiclassical dynamics of floppy molecules: Resonance Raman spectra of ammonia

Sébastien Reynaud[1], **Sergey V. Antipov**[1], **Jiří Vaníček**[1]

[1]Laboratory of Theoretical Physical Chemistry, Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015, Lausanne, Switzerland

We investigate the performance of on-the-fly *ab initio* dynamics combined with the thawed Gaussian approximation for computing vibrationally resolved resonance Raman spectra and excitation profiles of ammonia [1]. The employed approach does not require any a priori knowledge of the potential energy surface and, contrary to the popular global harmonic approximations, can account for the anharmonicity of the potential. Ammonia is chosen as a well-known example of a floppy molecule, which exhibits a large amplitude motion. Comparing the results with the experiment [2], we show that despite the strong anharmonicity of the potential, the on-the-fly *ab initio* thawed Gaussian approximation captures the main features of the resonance Raman spectrum. Moreover, within the employed approach the intensities of the combination bands are in a better agreement with experimental ones than those based on the global harmonic approximation [3].

[1] S. Reynaud, S. V. Antipov, and J. Vaníček, *In preparation*.

[2] L. D. Ziegler and B. Hudson, *J. Phys. Chem.* **88**, 1110-1116 (1984).

[3] D. W. Silverstein and L. Jensen, *J. Chem. Phys.* **136**, 064110 (2012).

A Novel Correlation between the Activity of Candida antarctica Lipase B and Differences in Binding Free Energies of Organic Solvent and Substrate

S. D. Banik[1], M. Nordblad[2], J. M. Woodley[2], G. H. Peters[1]

[1]*Department of Chemistry, Technical University of Denmark*
[2]*Department of Chemical and Biochemical Engineering, Technical University of Denmark*

The ability of enzymes to operate in organic solvent is now widely accepted. The selection of solvent medium is challenging which allows the modulation of enzyme activity. For rational selection of organic medium, it is important to understand the effect of organic solvent molecules on enzyme structure and the enzymatic reaction on a molecular level. To gain such insight, we combined experimental kinetics studies with full atomic molecular dynamics simulations and found a novel correlation between the activity of Candida antarctica lipase B (CALB) and the binding of the solvent/substrate molecules in the active site region of CALB. We have investigated the influence of four organic solvents hexane (HEX), methyl tertiary butyl ether (MTBE), acetonitrile (ACN) and tertiary butanol (TBU) on the catalytic activity of CALB for the esterification reaction. Our study shows that these organic solvents do not alter the conformation of CALB. Rather the solvent effects ascribed by binding of solvent molecules to the enzyme active site region and the solvation energy of substrate molecules in the different solvents. Polar solvent molecules compete with the substrate to bind to the active site of region CALB resulting in an inhibitory effect which is also confirmed by the binding free energies for the solvent and substrate molecules estimated from the simulations. Consequently, the catalytic activity of CALB decreases in polar solvents. This effect is significant, and CALB is over 10 orders of magnitude more active in nonpolar solvents (HEX and MTBE) than in the polar solvents (ACN and TBU). TBU molecules show an exceptional behavior since the solvent molecule forms an extensive hydrogen bond network within the CALB active site suggesting that solvent molecules rich on hydrogen acceptors and donors are poor solvents when used for lipase-catalyzed esterification reactions.

[1] Q. Wu, P. Soni, M. T. Reetz, J. Am. Chem. Soc. 135, 1872 (2013).

[2] P. Adlercreutz, Chem. Soc. Rev. 42, 6406 (2013).

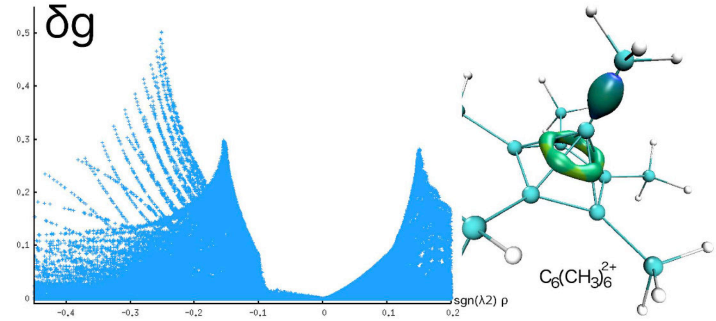
[3] S. Dutta Banik, M. Nordblad2, J. M. Woodley2, G. H. Peters, ACS Catalysis. 6, 6350 (2016).

The Independent Gradient Model: a tool derived from the NCI approach to analyze molecular interactions.

C. Lefebvre[1], G. Rubez[1,2,3], H. Khartabil[1], J-C. Boisson[2], J. Contreras-García[4,5], E. Hénon[1]

[1]ICMR UMR CNRS 7312, URCA, Moulin de la Housse, Reims, France
[2]CReSTIC EA 3804, URCA, Moulin de la Housse, Reims, France
[3]ATOS/BULL company, 1 rue de Provence, Echirolles, France
[4]Sorbonnes Universités, UPMC Univ. Paris 06, UMR CNRS 7616, Laboratoire de Chimie Théorique, Paris, France
[5]CNRS UMR 7616 Laboratoire de Chimie Théorique, Paris, France

An electron density (ED)-based methodology has been developed for the identification and visualization of molecular interactions using either pro-molecular density or ED derived from a single-determinant wave function. The expression of the ED gradient in terms of atomic components furnishes the basis for the Independent Gradient Model (IGM). This model leads to a density reference for non interacting atoms/fragments where the real density is preserved whilst ED gradient interaction turns off. Founded on this ED reference function that features an exponential decay also in interference regions, IGM model provides a way to identify and quantify the net ED gradient attenuation due to interactions. A new descriptor δg is derived to extract the signature of interactions present in an NCI plot, the parent NCI methodology developed by W. Yang *et al.* in 2010 [1]. Using an intra/inter uncoupling scheme, a descriptor *(δg^{inter})* is proposed that uniquely defines interfragment interaction regions. Then, an attractive feature of the IGM methodology [2] is to provide a workflow that automatically generates data composed solely of interfragment interactions for drawing the corresponding 3D isosurface representations.



[1] E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen and W. Yang, *J. Am. Chem. Soc.* **132**, 6498 (2010).

[2] C. Lefebvre, G. Rubez, H. Khartabil, J-C. Boisson, J. Contreras-García and E. Hénon, *PCCP*, submitted

Replica-Exchange Enveloping Distribution Sampling (RE-EDS): Parallel Energy-Offset Estimation and Efficient Local Round-Trip Time Optimisation

Dominik Sidler[1], **Arthur Schwaninger**[1], **Michael Cristofol-Clough**[1], **Sereina Riniker**[1]

[1]*Laboratory of Physical Chemistry, ETH Zurich, Vladimir-Prelog-Weg 2, 8093 Zurich, Switzerland*

Replica-exchange enveloping distribution sampling (RE-EDS) allows the efficient estimation of free-energy differences between multiple end-states from one molecular dynamics (MD) simulation [1]. In EDS, a reference state is sampled, which can be modified by two kinds of parameters, i.e. smoothness parameter and energy offsets, such that all end-states are sufficiently sampled [2]. It can be shown in practise that the choice of the energy offsets can be decoupled from the smoothing parameter distribution problem [3]. As a result, the development of a parallel energy-offset estimation (PEOE) algorithm became possible, which allows the highly efficient determination of the energy offsets [3]. In order to address the smoothness parameter distribution problem, a local round-trip time optimisation (N-LRTO) algorithm is introduced [4]. It is specially designed to deal with highly complex potential energy surfaces. This situation typically occurs for challenging real world applications, e.g. the slowly adapting environment in a protein pocket. Applying PEOE and N-LRTO to a RE-EDS system consisting of nine small-molecule inhibitors, in a complex with phenylethanolamine N-methyltransferase (PNMT), allows the accurate calculation of 36 free-energy differences in parallel [4].

[1] J. Lee, B. T. Miller, A. Damjanovic, B. R. Brooks, *J. Chem. Theory Comput.* **10**, 2738-2750 (2014).

[2] C. D. Christ, W. F. van Gunsteren, *J. Chem. Phys* **126**, 184110 (2007).

[3] D. Sidler, A. Schwaninger, S. Riniker, *J. Chem. Phys* **145**, 154114 (2016).

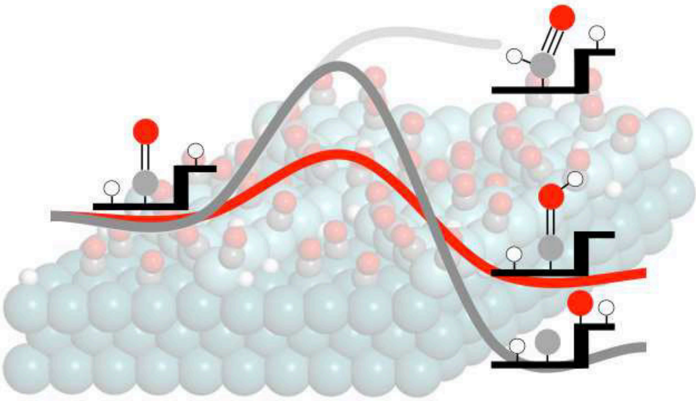
[4] D. Sidler, M. C. Clough, S. Riniker, *J. Chem. Theory Comput.* (online) DOI: 10.1021/acs.jctc.7b0028 (2017).

Carbon Monoxide Activation on Ru Surfaces under Reaction Conditions from *Ab Initio* Molecular Dynamics Simulations

Lucas Foppa[1], Marcella Iannuzzi[2], Christophe Copéret[1] and Aleix Comas-Vives[1]

[1]Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir Prelog Weg 1, CH-8093 Zürich, Switzerland.
[2]Institute of Physical Chemistry, University of Zurich, Winterthurerstrasse 190 CH-8057 Zurich, Switzerland.

The first elementary step of Fischer-Tropsch Synthesis (FTS), the conversion of syngas (CO/H_2 mixture) to hydrocarbons used in the gas-to-liquid chain, consists in the activation of carbon monoxide triple bond on CO-covered surfaces of metallic catalysts (Ru, Co, Fe) [1,2]. Since FTS activity and selectivity depend on CO cleavage, the elucidation of reaction mechanisms and active sites for this transformation has been an active research topic in computational chemistry, with static DFT approaches playing a central role [1-4]. Nevertheless, it remains challenging to evaluate multiple reaction pathways simultaneously while capturing co-adsorbate interactions and entropic effects at reaction temperatures (> 300°C), acknowledged to affect the choice of activation mechanism [3,4]. Herein, we use an *ab initio* molecular dynamics (AIMD) approach to study the direct and hydrogen-assisted CO activation on Ru surface models representing flat and stepped terminations of metal catalysts. Our results point out to the previously unrecognized role of step-edges in hydrogen-assisted mechanisms and illustrate how AIMD can be used to study complex surface reaction networks.



[1] L. Foppa, C. Copéret, A. Comas-Vives, J. Am. Chem. Soc. **138**, 16655 (2016). [2] B. T. Loveless, C. Buda, M. Neurock, E. Iglesia, J. Am. Chem. Soc. **135**, 6107 (2013). [3] G. T. K. Gunasooriya, A. P. van Bavel, H. P. C. E. Kuipers, M. Saeys, ACS Catal. **6**, 3660 (2016). [4] S. Liu, Y.-W. Li, J. Wang, H. Jiao, Catal. Sci. Technol. **6**, 8336 (2016).

Refined approach to the cellularization of the semiclassical Herman-Kluk propagator

Sergey V. Antipov[1], **Jiří Vaníček**[1]

[1]*Laboratory of Theoretical Physical Chemistry, Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015, Lausanne, Switzerland*

The semiclassical Herman-Kluk Initial Value Representation (HK-IVR) is a well-established approximation to the quantum evolution operator. The approximation is based on classical trajectories and incorporates quantum effects, such as tunneling, coherence, and zero-point energy, into the dynamics. However, the direct application of the HK-IVR approach to large scale systems is computationally unfeasible due to the oscillatory nature of the integrand involved. A common way of dealing with this problem is based on application of the Filinov filtering (cellularization) [1, 2] technique to smooth out the oscillatory behavior of the integrand.

Here we present a refined cellularization scheme for the HK-IVR propagator [3], which employs the inverse Weierstrass transform and optimal scaling of the cell size with the number of cells, and was previously only used in the context of the dephasing representation [4]. In the new methodology the size of the sampling weight for the cell centers correlates with the size of cells, allowing for effective sampling of the phase space covered by the initial state of the system. The main advantage of the presented approach is that, unlike the standard Filinov filtering, it converges to the original HK-IVR result in the limit of an infinite number of trajectories. We illustrate the performance of the refined cellularization scheme by calculating autocorrelation functions and spectra of both integrable and chaotic model systems.

[1] N. Makri and W. H. Miller, *J. Chem. Phys.* **89**, 2170-2177 (1988).

[2] E. J. Heller, *J. Chem. Phys.* **94**, 2723-2729 (1991).

[3] S. V. Antipov and J. Vaníček, *In preparation*.

[4] E. Zambrano, M. Šulc, and J. Vaníček, *J. Chem. Phys.* **139**, 054109 (2013).

Local control theory with an approximate treatment of the molecule-field interaction

Julien Roulet[1], **Jiří Vaníček**[1]

[1]Laboratory of Theoretical Physical Chemistry, Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015, Lausanne, Switzerland

The advance of pulse shaping technology has opened the field of laser control of chemical reactions. The local control theory [1] belongs among the most efficient approaches to control since this technique does not require an iterative procedure. Instead, the control field is computed on the fly, using the instantaneous dynamics of the system, and guarantees an increase (or decrease) of a target observable that commutes with the system Hamiltonian. In our case, this observable is the population of a selected electronic state.

Recently, Patoz and Vaníček have implemented [2] geometric integrators of arbitrary order of accuracy for treating the nonadiabatic quantum dynamics of a molecule interacting with a time-dependent electromagnetic field. In particular, this suite of algorithms allows both an exact treatment of the interaction as well as an arbitrary combination of the time-dependent perturbation theory, Condon, rotating wave, and ultrashort pulse approximation.

Here we present an implementation of the local control theory using the above four approximations for the molecule-field interaction, since the exact treatment of the interaction with the electromagnetic-field can be computationally expensive. We investigate the validity of these approximations to the local control on several model systems, and analyze the influence of the approximations on the dynamics of the studied systems as well as on the computational cost of the local control simulation.

[1] V. Engel, C. Meier, and D. J. Tannor, Adv. Chem. Phys. **141**, 29 (2009)
[2] A. Patoz and J. Vaníček, in preparation.

Probing the orientation of recombinant protein A on a membrane using computational infrared spectroscopy.

Ana V. Cunha[1], **Thomas L.C. Jansen**[1]

[1]*Zernike Institute for Advanced Materials, University of Groningen*
Nijenborgh 4, 9747 AG, Groningen, The Netherlands

Homologous recombination is the primary mediator mechanism in DNA repair and thus essential for the survival of cells. Recombinant proteins (RecA) are the molecular motors involved in this process, intervening in numerous processes in eukaryotic cells. However, *in vitro* experiments show that RecA may become inactive when interacting with phospholipids [1]. Our goal is to make use of computational spectroscopy techniques to probe the orientation of such protein (RecA, see Fig. 1(a) and 1(b)) on a membrane. The infrared spectra in the amide I region are calculated by combining classical molecular dynamics simulations with quantum mechanical response function calculations [2-3]. In this study, we examine recombinant protein A (RecA) oriented in two directions [1], one parallel to the membrane (active, Fig. 1(a)), and another perpendicular to the membrane (inactive, Fig. 1(b)). The theoretical linear spectra show that the parallel oriented protein is slightly redshifted compared to the perpendicularly oriented one, see Fig. 1(c). This difference arises as a consequence of the interaction between the protein and the phospholipid membrane, potentially enabling the experimental distinction between the active and inactive configurations.

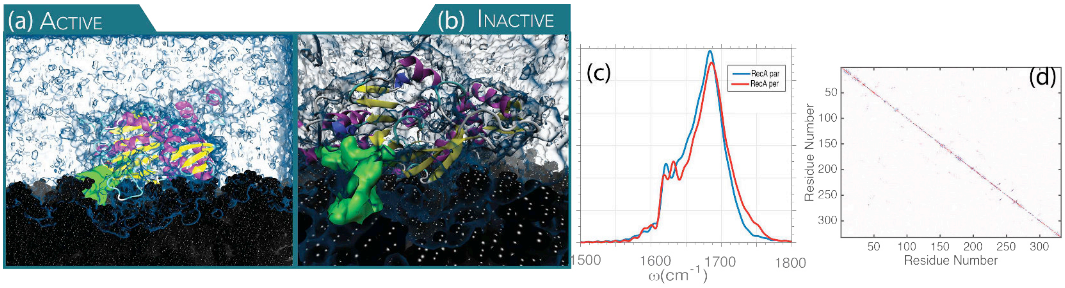


Fig. 1. (a) RecA protein with parallel orientation to the membrane. (b) RecA protein with perpendicular orientation to the membrane. (c) Predicted linear infrared spectra of RecA in both orientations. (d) Map of the difference energies of the vibrational Hamiltonian.

[1] M. Rajendram, *et. al.*, *Mol. Cell.*, **60**,374–384 (2105).
[2] C. Liang, T.L.C. Jansen, *J. Chem. Theo. Comp.*, **8,** 1706 (2012).
[3] T.L.C. Jansen, J. Knoester, *J. Chem. Phys.*, **124,** 044502 (2006).

Color-tuning mechanism in vision from a theoretical perspective

B.B. Kamorzin, A.V. Scherbinin, A.V. Bochenkova

Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Russia

A single chromophore, retinal in the protonated Schiff base form (PSBR), is responsible for absorption of light of different wavelength in visual Opsin proteins. Currently, the wavelength-tuning mechanism and the color span of the individual photoreceptors are far from being understood. This is largely due to the fact that the intrinsic photophysical properties of the bare chromophore, *i.e.*, its 'color' and photoabsorption spectral shape, remain to be resolved and the important reference for the so-called Opsin shift is still missing. Here, we aim at correlating a remarkably broad absorption profile of the isolated PSBR chromophore (450–650 nm) found experimentally [1] with a wide range of absorption energies observed in visual (425–560 nm) and archaeal (480–590 nm) Rhodopsins, as well as at providing a benchmark value for the most intense vibronic transition in the isolated chromophore that will help to understand the origin of the protein "Opsin" shift.

A highly accurate multiconfiguration quasi-degenerate perturbation theory, XMCQDPT2 [2], has been used for constructing a geometry-relaxed adiabatic potential that hinders intra-molecular internal rotation of the β-ionone ring of the isolated PSBR chromophore. The S_0-S_1 photoabsorption profile has been calculated by explicitly taking into account large-amplitude, highly anharmonic ground-state nuclear motion of the β-ionone ring. A rather flat topography of the ground-state potential energy surface along this soft mode is shown to be responsible for substantial non-equilibrium contributions to the gas-phase spectrum, which is found to be very sensitive to temperature variations. Our results potentially lead to a disclosure of one of the wavelength-tuning mechanisms operational in color vision.

This work has been supported by the Russian Science Foundation (project no. 17-13-01276). We thank the Supercomputing Center of the M.V. Lomonosov Moscow State University for providing high performance computing resources.

[1] Rajput, J., Rahbek, D. B., Andersen, L.H., Hirshfeld, A., Sheves, M., Altoè, P., Orlandi, G., and Garavelli, M., *Angew. Chem., Int. Ed.* **49**, 1790 (2010).

[2] Granovsky, A. A., *J. Chem. Phys.* **134**, 214113 (2011).

Accurate prediction of protein-ligand binding using molecular dynamics-based docking and QM/MM methods

Manuel Glaser, Okke Melse, Chen Zheng, Antoine Marion, and Iris Antes

Department of Life Sciences and Center for Integrated Protein Science, Technical University of Munich, Emil-Erlenmeyer-Forum 8, 85354 Freising

Protein-ligand interactions are crucial for many important biological processes and thus the selective inhibition of disease relevant proteins is one of the major strategies for drug design in pharmaceutical industry. In this context computer-based methods are routinely used to screen large compound libraries for the identification of potential drug candidates. Thus many sampling and scoring methods have been developed for this purpose over the last two decades, which perform very well for „classical" drug design applications, namely predicting the binding of non-covalently bound small molecule-based ligands to specific target proteins [1, 2]. Nevertheless, these approaches experience considerable limitations for the prediction of covalently bound inhibitors, ligands binding to metal containing binding sites, and very flexible ligands like peptides or macrocycles. In addition, the calculation of quantitatively accurate ligand binding affinities is still a challenge in the field. We are developing new and optimizing existing approaches for these areas of applications [3-7]. Thereby our focus is on the improvement of classical molecular docking approaches by the use of biophysical sampling methods and QM/MM approaches. We will present several case studies, which show how the accuracy of protein-ligand binding predictions can be improved considerably by the new, combined approaches for e.g. covalently bound inhibitors or metal-containing binding sites.

References:

[1] S.M. Song, S.J. Lim, J.C. Tong, Brief. Bioinform. **10**(5), 579 (2009)
[2] X. Huang, S.Z. Grinter, X. Zou, Phys. Chem. Chem. Phys. **12**(40), 12899 (2012).
[3] C. Hartmann, I. Antes, T. Lengauer, Proteins **74**(3), 712 (2009).
[4] I. Antes, I., Proteins **78**(5), 1084 (2010).
[5] M. Marcinowski, M., M. Rosam, M., C. Seitz, J. Elferich, J. Behnke, C. Bello, M.J. Feige, C.F. Becker, I. Antes, I., J. Buchner, J. Mol. Biol. **425**(3), 466 (2013).
[6] M. Zachmann, G. Mathias, I. Antes, ChemPhysChem **16**(8), 1739 (2015).
[7] M. Schneider, M. Rosam, M. Glaser, A. Patronov, H. Shah, K.C. Back, M.A. Daake, J. Buchner, I. Antes, Proteins **84**(10), 1390 (2016).

Symmetric Proton Transfer Routes in the Membrane Domain of Respiratory Complex I.

Andrea Di Luca, Ana P. Gamiz-Hernandez, Ville R. I. Kaila

Department of Chemistry, Technical University of Munich, Lichtenbergstr. 4, Garching, Germany

Complex I (NADH:quinone oxidoreductase) of the respiratory chain has a fundamental role in the energy conversion of living organisms, contributing to the generation of the proton motive force across membranes. By using the energy from quinone reduction, it catalyses the pumping of four protons. Recently resolved structure from different organisms revealed new details of the enzyme structure, but access points of protons and mechanism of pumping are still elusive. Structural features of the membrane domain, as the long horizontal axis of charged residues or internal symmetry of the antiporter-like subunits, are likely to play a role in the proton transfer (pT) process. We perform large-scale classical MD simulation of transient putative states of the enzyme to identify proton transfer routes in the antiporter-like subunit of complex I, and suggest a possible mechanism of pumping [1]. Steps of the proposed mechanism are investigated with MD replica-exchange umbrella sampling (REUS), QM/MM dynamics and continuum electrostatic calculation for one antiporter-like subunit. Our results suggest that the position of the proton channels are similar for the three antiporter-like subunits and symmetry-related, accordingly to the internal symmetry of the subunits. We also show how a conserved Lys-Glu pair in each antiporter-like subunit forms a key element in the proton pumping mechanism.

[1] A. Di Luca, A. P. Gamiz-Hernandez, V. R. I. Kaila, *PNAS* (submitted)

Aggreagates of quadrupolar dyes: the role of intermolecular interactions.

O. Uranga, D. Casanova*, F. Castet*

[1]Department of Science and Technology of Polymers/ Facultad de Química/ University of the Basque Country (UPV/EHU)
Paseo Manuel Lardizabal 4, 20009, Donostia, Spain

Recently, it has been shown that supramolecular aggrgates provide a wide range of photophysical properties such as aggregation-induced fluorescence or phosphorescence, which can be optimized for use in a large number of applications: optoelectronics, detection of biochemical process, imaging, lightening or photovoltaic energy conversion. Optimizing these propertioes in view of designing devices with increased performances requires a fundamental understanding of properties of the isolated molecules together with a detailed characterization of intermolecular interactions. We present a theoretical investigation of small aggreagtes of quadrupolar (D-π-A-π-D) charge-transfer dyes, with attention focused on the role of intermolecular interactions in determining their optical properties. We takcle the theoretical issue by adopting a localized diabatic model, which describe an isolated molecule in terms of a minimal number of electronic states. The approach is applied to curcuminoid dyes, a family of chromophores with weak quadrupolar character. The method is validated against experiment. Time dependent density theory rationalize the strong ultra-excitonic effects recurrently observed in the experimental optical spectra of aggregates of highly polarizable quadrupolar dyes, offering a valuable tool to exploit the supramolecular design of material properties.

Theoretical Study of the BrO + ClO Cross Reaction

Adam S. Abbott, Kevin B. Moore III, Henry F. Schaefer III

Center for Computational Quantum Chemistry, 1004 Cedar St., University of Georgia, Street Address, Athens, GA, USA

Pathways stemming from the reaction of BrO and ClO radicals are of great interest due to their integral role in stratospheric ozone depletion. An abundance of free halogen radicals, which readily convert ozone to diatomic oxygen, are produced through three pathways:

$$\begin{aligned} \mathrm{BrO} + \mathrm{ClO} &\longrightarrow \mathrm{BrCl} + \mathrm{O_2} \\ &\longrightarrow \mathrm{ClOO} + \mathrm{Br} \\ &\longrightarrow \mathrm{OClO} + \mathrm{Br} \end{aligned}$$

Detailed mechanisms of the above reactions have hitherto been insufficiently characterized in the literature. In this work, optimized geometries and harmonic vibrational frequencies for key stationary points on the potential energy surface have been obtained with high level coupled cluster theory. In the future, these findings will be used to reduce the current uncertainty in regard to the rate constants and branching ratios through theoretical kinetic treatments.

Structural Distortions Accompanying Non-Covalent Interactions

Herzain I. Rivera-Arrieta[1,2], **Justin M. Turney**[2] **and Henry F. Schaefer III**[2]

[1]*Instituto de Física, Universidad Nacional Autónoma de México, Ciudad de México 04510, México*
[2]*Center for Computational Quantum Chemistry, Department of Chemistry, The University of Georgia, Athens, Georgia 30602-2556, U.S.A.*

Non-covalent interactions can be seen as one of the most important forces in nature, as they domain many fundamental phenomena in chemistry and biology. The nature of these weak forces makes difficult to study them for both, theoretically and experimentally [1]. Neglect of the structural distortions suffered by the constituent molecules, as a result from these weak interactions, is a common practice when examining a potential energy surface (PES).

The methane-water complex, which can be seen as the simplest hydrophobic interaction, is a remarkable model system that has been widely studied [2-4]. Unfortunately, none of these studies had quantified the magnitude of the intramolecular distortions for each molecule, nor the energy associate with them.

Herein, in order to obtain the definite answer about the magnitude of the distortions and their energetic effects, focal point analyses (FPAs), which already have shown to be able to achieve subchemical accuracy [5], were performed on the minima structures of the PES. For the FPAs calculations, coupled cluster methods up to perturbative quadruples [CCSDT(Q)] level of theory were considered.

Our results indicate that the difference in the interaction energies (ΔD_e) between fully optimized and monomer fixed structures, always lies in the order of 0.02 kcal mol^{-1} [6]. This study showed beyond any reasonable doubt, that neglect of the monomer relaxation while scanning a weakly bound noncovalent system, is a reasonable approximation for points other than the minima.

[1] K. Müller-Dethlefs, P. Hobza, *Chem. Rev.* **100**, 143 (2000).
[2] K. Patkowski, *J. Chem. Phys.* **138**, 154101 (2013).
[3] C. Qu, R. Conte, P. L. Houston, J. M Bowman, *Phys. Chem. Chem. Phys.* **17**, 8172 (2015).
[4] D. Cappeletti, A. Bartocci, F. Frati, L. F. Roncatti, L. Belpassi, F. Tarantelli, P. Aiswarya, E. Arunan, F. Pirani, *Phys. Chem. Chem. Phys.* **17**, 30613 (2015).
[5] M. S. Schuurman, S. R. Muir, W. D. Allen, H. F. Schaefer, *J. Chem. Phys.* **120**, 11586 (2004).
[6] H.I. Rivera-Arrieta, J.M. Turney, H.F. Schaefer, *J. Chem. Theory Comput.* **13**, 1478 (2017).

Solubility of diclofenac in water: interplay between intra- and intermolecular hydrogen bonds

Mariana Kozlowska[1,2], **Pawel Rodziewicz**[1], **Anna Kaczmarek-Kedziera**[3]

[1] *Institute of Chemistry, University of Bialystok, Ciolkowskiego 1K, 15-245 Bialystok, Poland*
[2] *Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany*
[3] *Faculty of Chemistry, Nicholas Copernicus University, Gagarina 7, 87-100 Torun, Poland*

Diclofenac (DCL) is a widely known and commonly used nonsteroidal anti-inflammatory drug with the best inhibition activity of the COX-2 (cyclooxygenase) enzyme [1]. Due to its simple, but specific, structure, DCL is similar to the original COX-2 substrate, i.e. arachidonic acid, therefore, provides a good fit to the enzyme pocket to inhibit the inflammation process [2,3]. On the one hand, DCL possesses an excellent inhibition ability, but on the other hand, diclofenac has low solubility in water in its unionized form [4]. The latter fact causes the usage of higher doses of the drug for a desirable anti-inflammatory effect, which is connected with undesirable side effects in the gastro-intestinal tract after its oral administration. Therefore, different modifications of DCL are made, nowadays, to increase its water solubility [5].

Why diclofenac has poor solubility in water? Is it due to the strong solute-solute interactions, which prevent the solvation of the drug, or low water affinity? There is no direct answer on this important question in the current literature. It all depends on the nature of the interactions between the drug and the solvent. The understanding of these interactions opens a new perspective for effective drug modifications that increase the diclofenac solubility and decrease the drug intake, therefore, undesirable side effects. In the present work, we focus on understanding the interplay between DCL-DCL and DCL-solvent interactions, based on different intra- and intermolecular interactions in water, including hydrogen bonds. For this purpose, we use a model of the solvated monomer and dimer of diclofenac and first principles molecular dynamics simulations, performed using the Car-Parrinello scheme at the finite temperature corresponding to water ambient conditions.

The authors gratefully acknowledge the financial support of National Science Centre, Poland, grant number UMO-2014/13/B/ST8/04342. Computations were carried out at the Computer Center of University of Bialystok.

[1] B. Cryer, M. Feldman, *Am. J. Med.* **104**, 413 (1998).
[2] A.R. Sallmann, *Am. J. Med.* **80** (4B), 29 (1986).
[3] S. W. Rowlinson et al., *J. Biol. Chem.* **278**, 45763 (2003).
[4] A. Fini, G. Fazio, G. Feroci, *Int. J. Pharm.* **126**, 95 (1995).
[5] R. Altman, B. Bosch, K. Brune, P. Patrignani, C. Young, *Drugs* **75**, 859 (2015).

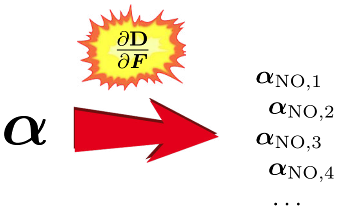
Can orbital–based decomposition of nonlinear optical properties unveil the role of electron correlation?

<u>Sebastian P. Sitkiewicz</u>[1,⋆], **Josep M. Luis**[4], **Eduard Matito**[1,2,3]

[1]*Donostia International Physics Center (DIPC), Euskadi, Spain*
[2]*Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU), Euskadi, Spain*
[3]*IKERBASQUE, Basque Foundation for Science, Bilbao, Euskadi, Spain*
[4]*Institut de Química Comp. i Catàlisi, Depart. de Química, Univ. Girona, Catalonia, Spain*
⋆*sebastian.p.sitkiewicz@gmail.com*

Traditionally, the nonlinear optical properties (NLOPs) are defined as the contributions to the energy in terms of Taylor expansion with respect to the external electric field [1]. While most development studies devoted to higher–order dipole properties focus in finding the best methodology for their computations, the number of tools to analyze their nature is limited. Within this small group, the most popular are based on the Mulliken–type [2] and real–space electron density partitioning [3]. Although very useful for experimentally oriented studies, the atomic partitioning of NLOPs has not showed yet their utility for comparison of performance of quantum chemical methodologies. The role of electron correlation in NLOPs is usually analyzed from the sum over states (SOS) methodology, that represents the electrical response in terms of excited states of the system using the perturbational theory [1, 4]. Unfortunately, the SOS methodology is known to provide wrong estimates of NLOPs, except for FCI computations.

In this talk, a new orbital decomposition scheme of NLOPs is presented. Based on the derivatives of the reduced one-particle density matrix with respect to the magnitude of external electric field, the partitioning combines the informational aspects of SOS and the fully coupled description of the NLOP. We will analyze two systems that suffer from different electron correlation types: singlet diradicals (static correlation) and polymeric/conjugated systems (dynamic correlation).



[1] J. O. Hirschfelder, W. Brown, S. T. Epstein, *Adv. Quant. Chem.* **1964**, 1, 255

[2] M. Nakano, I. Shigemoto, S. Yamada, K. Yamaguchi *J. Chem. Phys.* **1995**, 103, 4175

[3] N. Otero, C. Van Alsenoy, C. Pouchan, P. Karamanis *J. Comput. Chem.* **2015**, 36, 1831

[4] B. Champagne, D. H. Mosley, *J. Chem. Phys.* **1996**, 105, 3592

Excited State Gradients for a State-Specific Continuum Solvation Approach: a Lagrangian TDDFT formulation of VEM.

C. A. Guido[1,2*], **G. Scalmani**[3], **B. Mennucci**[4] , **D. Jacquemin**[1,5]

[1]*Laboratoire CEISAM - UMR CNRS 6230, Université de Nantes, 2 Rue de la Houssinière, 44322 Nantes Cedex 3, France.*

[2]*Laboratoire MOLTECH - UMR CNRS 6200, Université de Angers, 2 Bd Lavoisier49045 Angers Cedex, France.*

[3]*Gaussian, Inc., 340 Quinnipiac Street, Building 40, Wallingford, Connecticut, 06492, USA.*

[4]*Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Moruzzi 13, 56124 Pisa, Italy.*

[5]*Institut Universitaire de France, 103, bd Saint-Michel, F-75005 Paris Cedex 05, France.*

[*]*ciro.guido@univ-nantes.fr*

The accurate modeling of the environment response is a fundamental challenge for accurately describing the photophysics and photochemistry of molecules both in solution and in more complex embedding. [1] When large rearrangements of the electron density occur after an electronic transition, state-specific formulations, such as the Vertical Excitation Model [2], are necessary to achieve a proper modeling of the processes. Such a state-specific model is fundamental not only to obtain accurate energies, but also to follow the geometrical relaxation accompanying the evolution of the excited-states. [3] This study presents the analytical expression of the gradients of the Vertical Excitation Model approach by a Lagrangian formulation in the TD-DFT framework. [4] Representative organic chromophores in solution are used to test the reliability of the implementation and provide comparisons with the linear response description.

[1] B. Mennucci, S. Caprasecca, and C. A. Guido, in *Advances in Physical Organic Chemistry,* edited by I. H. Williams and N. H. Williams (Academic Press), Vol. **50**, pp. 203-241 (2016); J. Tomasi, B. Mennucci, and R. Cammi, *Chem. Rev.* **105**, 2999 (2005).

[2] A. V. Marenich, C. J. Cramer, D. G. Truhlar, C. A. Guido, B. Mennucci, G. Scalmani, and M. J. Frisch, *Chem. Sci.* **2**, 2143 (2011).

[3] C. A. Guido, D. Jacquemin, C. Adamo, and B. Mennucci, *J. Chem. Theory Comput.* **11**, 5782 (2015).

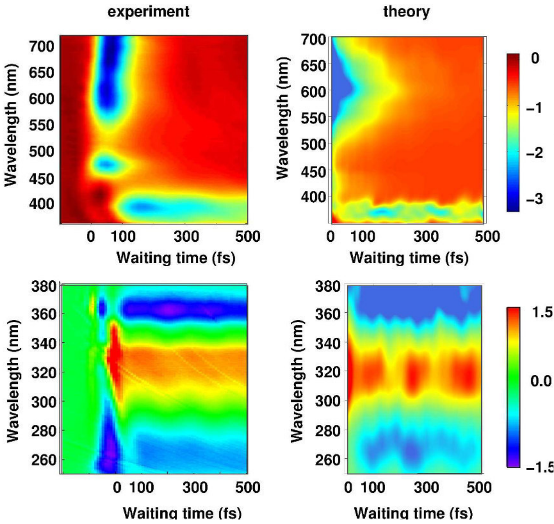
[4] C. A. Guido, G. Scalmani, B. Mennucci, D. Jacquemin, *J. Chem. Phys.* **146**, 204106 (2017).

Coherent Dynamics in Photoexcited Azobenezene: Ultrafast Decay Resolved by sub-20-fs Pump-Probe Spectroscopy and Theoretical Simulations

Artur Nenov[1], Rocio Borrego-Varillas[2], Francesco Segatta[1], Irene Conti[1], Javier Segarra-Marti[3], Aurelio Oriana[2], Lucia Ganzer[2], Shaul Mukamel[4], Giulio Cerullo[2], Marco Garavelli[1]

[1]Dipartimento di Chimica Industriale, Università degli Studi di Bologna, Viale del Risorgimento 4, I-40136 Bologna, Italy
[2]Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, I-20133 Milano, Italy
[3]Laboratoire de Chimie, ENS de Lyon, CNRS, Université Lyon, F-69342 Lyon, France
[4]Department of Chemistry, University of California, Irvine, CA 92697-2025, USA

We use femtosecond pump-probe electronic spectroscopy in the VIS/UV range with sub-20-fs time resolution[1], combined with ab initio quantum mechanics simulations, to study the dynamics of *trans*-azobenzene isomerization. We observe two photoinduced absorption (PA) bands peaking at 475 nm and 550-700 nm respectively, that decay with a time constant τ of ~70 fs, giving rise to PA bands at 380 nm and 270 nm, which in turn decay with τ ~0.6 ps. Coherent oscillations of the PA with a period of ~170 fs are found to last for several ps. Numerical simulations combining dynamically correlated CASPT2 electronic structure computations with non-linear response theory formulated in the cumulant expansion to second order[2] resolve the nature of the detected PA and their coherent dynamics. The 475 nm and 550-700 nm bands are assigned to the bright $S_2(\pi\pi^*)$ state, while the 380 nm and 270 nm bands are fingerprints of the $S_1(n\pi^*)$ state. Mixed quantum-classical molecular dynamics simulations at CASPT2 level demonstrate that the ultrafast dynamics can be rationalized by an efficient $S_2(\pi\pi^*)\rightarrow S_1(n\pi^*)\rightarrow$GS non-adiabatic transfer involving predominantly the Franck Condon active modes NN stretching and CNN bending. Latter give rise to the oscillatory features observed in the pump-probe spectra.



[1] R. Borrego-Varillas, A. Candeo, D. Viola, M. Garavelli, S. De Silvestri, G. Cerullo and C. Manzoni, *Opt. Lett.* **38**, 3849-3852 (2014).

[2] S. Mukamel, *Principles of nonlinear optical spectroscopy*, O.U.P, New York (1995).

Atmospheric Photoisomerization Interference in the Gas-Phase Oxidation of *E,E*-2-4-Hexadienal with OH: The Ketene-Aldehyde Equilibrium

Rene Pfeifer[1], **Felipe Fantuzzi**[1], **Ricardo R. Oliveira**[1]

[1]*Instituto de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ 21941-909, Brazil.*

Aldehydes are major pollutants formed from the combustion of fossil fuels. In the atmosphere, they react mainly with hydroxyl (OH) radicals during the day and with nitrate (NO_3) radicals by night. The *E,E*-2,4-hexadienal compound is an unsaturated conjugated aldehyde, usually a by-product of the toluene photo-oxidation [1]. It can undergo through a rapid isomerization process when it is subjected to sunlight. This isomerization is a reversible process, and it leads to the formation of ketene-type compounds [2]. In this work, the mechanism of the competitive gas-phase addition of OH to the different double bonds of *E,E*-2,4-hexadienal and to the related ketene-type isomerization products was studied using Density Functional Theory (DFT) at the MO6-2X/cc-pVDZ level. The geometries of all structures were optimized without any restrictions. Vibrational frequency calculations were used to characterize the stationary points as intermediates (all frequencies are real) or as transition states (one imaginary frequency confirms the first-order saddle point configuration). The rate coefficients of each path were obtained using Transition State Theory (TST). All calculations were performed with the GAUSSIAN 09 program [3]. The results show that the reactions are exoergic, and that the OH addition to the double bond that is more distant from the aldehyde group is the most favorable from the thermodynamic point of view.

[1] Colmenar, I., Martín, P., Cabañas, B., Salgado, S. & Martínez, E. *Atmos. Environ.* **99**, 159–167 (2014).

[2] O'Connor, M. P., Wenger, J. C., Mellouki, A., Wirtz, K. & Muñoz, A. *Phys. Chem. Chem. Phys.* **8**, 5236–5246 (2006).

[3] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, *et al. Gaussian 09, Revision E.01*. Gaussian, Inc., Wallingford CT (2009).

Dissipative particle dynamics study of poly(N-isopropylamide) with carboxylic and dodecyl terminal groups in aqueous solutions

Karel Šindelka[1], **Zuzana Limpouchová**[1], **Miroslav Štěpánek**[1], **Karel Procházka**[1]

[1]*Charles Unicersity, Faculty of science, Dept. of physical and macromolecular chemistry,*
Hlavova 8, Prague, Czech Republic

We performed a parametric study of self-assembly of diblock copolymer imitating PNIPAm-C12 which was proposed as a component of various thermoresponsive drug delivery systems [1]. The focus was placed on the effect of the length of the soluble poly(N-isopropylamide) block and the charge of the carboxylic group (i.e. different pH). We also studied associative behaviour of PNIPAm-C12 in solutions containing surfactant carrying either the same or opposite charge. The simulations were performed using the computational simulation method known as the dissipative particle dynamics [2] with explicit electrostatics [3]. This highly coarse-grained method is similar to molecular dynamics and is well suited for investigation of complex systems.
We compared the simulation results with experimental measurements of light and X-ray scattering [4] and found a satisfactory agreement at the qualitative and semi-quantitative level.

[1] Z. J. Dai, T. Ngai, *J Polym. Sci. A: Polym. Chem.* **51**, 2995 (2013).

[2] R. D. Groot, P. B. Warren, *J. Chem. Phys.*, **107**, 4423 (1997).

[3] K. Procházka, K. Šindelka, X. Wang, Z. Limpouchová, M. Lísal, *Mol. Phys.*, **114**, 3077 (2016).

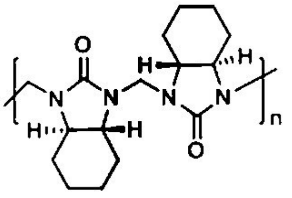
[4] J. Škvarla, J. Zedník, M. Šlouf, S. Pispas, M. Štěpánek, *Eur. Pol. J.*, **61**, 124 (2014).

Template-catalysed formation of cyclohexanohemicucurbiturils

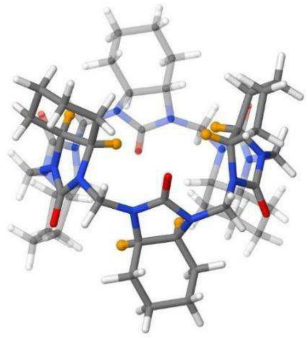
Triin Narva, Riina Aav, Toomas Tamm

[1]Department of Chemistry and Biotechnology,Tallinn University of Technology
Ehitajate tee 5, 19086 Tallinn, Estonia

Cyclohexanohemicucurbiturils (CycHC) are a family of host molecules that can bind a variety of small-sized anions within their cavity. Several cycHC's are chiral [1], which makes them stand out among the wide variety of hosts known in supramolecular chemistry. The synthesis of cycHC's involves use of a template – a small anion such as Cl^- or $HCOO^-$. The size of the cycHC formed is determined by the dimensions of the template.



cycHC



A new variety of cycHC's, composed of all-*cis* cyclohexanourea monomers, has recently been synthesized and characterized in our group. Their cavities are not closed like those of *trans* isomers, but tube-like, able to accommodate larger guests.

In this work equilibria between, and formation of, various stereoisomers of all-*cis*-cycHC were studied computationally using DFT at BP86/def-TZVP level. Role of the chloride template anion in the oligomerization reaction was found to be more important than previously reported. While earlier study of macrocyclisation mechanism of chiral cycHCs [1] had found a reaction barrier of 64 kJ/mol in the carbon-nitrogen bond formation step, in the presence of a chloride ion template the reaction step was found to proceed without any barrier.

This finding better explains the ease of chain propagation and depropagation in the interconversion of various cycHC isomers.

This work has been supported by Estonian Research Council grants PUT692 and PUT1683.

[1] E. Prigorchenko, M. Öeren, S. Kaabel, M. Fomitšenko, I. Reile, I. Järving, T. Tamm, F. Topic, K. Rissanen, R. Aav, *Chem. Comm* **51**, 10921 (2015).

Variational Transition State Theory Study of Radical Reactions

Hui Zhang,[1,2] Lu Gao,[1] and Xuefei Xu[1,*]

[1]Center for Combustion Energy, Tsinghua University, Beijing 100084, China

[2]State Key Laboratory of Chemical Resource Engineering, Institute of Materia Medica, College of Science, Beijing University of Chemical Technology, Beijing, 100029, China

Abstract: Radical reactions play important role in combustion, atmospheric chemistry, and interstellar chemistry. We take the two radical reactions as examples, H plus benzene and OH plus methanol, to introduce our recent work on variational transition state theory (VTST) study of radical reactions. Based on an accurate potential energy surface, we calculate accurate rate constants in a broad temperature range by including tunneling with small-curvature tunneling (SCT) approximation, including multistructural and torsional anharmonicity with multistructural and torsional (MS-T) method, and including anharmonicity of high-frequency mode of transition state structure by using a system-specific scaling factor of frequencies. For the pressure-dependent reactions, we use system-specific quantum RRK theory calibrated by variational transition state theory to estimate the falloff effect. The results show good agreement with the experimental observation.

References:
[1] J. L. Bao, J. Zheng, D. G. Truhlar, *J. Am. Chem. Soc.* 138, 2690–2704 (2016).
[2] J. Zheng, R. Meana-Pañeda, D. G. Truhlar, *J. Am. Chem. Soc.* 136, 5150–5160 (2014).

Different QM/MM approaches to study enzymatic reactions: ppGalNAcT2 glycosyltransferase

Pavel Janoš[1,2], **Tomáš Trnka**[1,2], **Stanislav Kozmon**[1,3], **Igor Tvaroška**[1,3], **Jaroslav Koča**[1,2]

[1]*Central European Institute of Technology (CEITEC), Masaryk University, 62500 Brno, Czech Republic*
[2]*Faculty of Science-National Centre for Biomolecular Research, Masaryk University, 62500 Brno, Czech Republic*
[3]*Institute of Chemistry, Slovak Academy of Sciences, 845 38 Bratislava, Slovak Republic*

Glycosyltransferases are enzymes that catalyze the formation of glycosidic bonds. Polypeptide UDP-GalNAc transferase 2 (ppGalNAcT2) is a metal dependent retaining glycosyltransferase. It catalyzes the transfer of GalNAc moiety from UDP-GalNAc to the hydroxyl group of either threonine or serine residue on the target protein. We use the ppGalNAcT2 as a case study to compare different QM/MM methodologies that can provide reaction paths, transition state information and either free energy or potential energy of an enzymatic reaction. [1]

The methods used include QM/MM Ab Initio MD at the DFT level using CPMD coupled with either metadynamics (MTD) or String Method (STM). The STM is used to derive the minimum free energy reaction path. The geometrical features of the free energy path and the energy profile are compared with minimum potential energy path obtained at much lower computational cost using Nudged Elastic Band (NEB) method. The MTD provides the free energy surface of the reaction. This surface represents a rough overview of the reaction and can confirm the physical relevance of optimized paths or potentially provide an initial guess for path optimization methods. As a validation of the suitability of DFT for the study of glycosyltransferase enzymatic reactions, we compared several widely used functionals with high-level DLPNO-CCSD(T)/CBS data using the potential energy profile from NEB.

[1] P. Janoš, T. Trnka, S. Kozmon, I. Tvaroška, J. Koča,. JCTC 12, 6062-6076 (2016)

On-the-fly *ab initio* semiclassical evaluation of absorption spectra of polyatomic molecules beyond the Condon approximation

Aurélien Patoz[1], **Tomislav Begušić**[1], **Jiří Vaníček**[1]

[1] *Laboratory of Theoretical Physical Chemistry, Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland*

The time-dependent approach to spectroscopy [1] allows, in contrast to the much more common time-independent approaches, evaluating electronic spectra very easily without using the Born-Oppenheimer or global harmonic approximations. Whereas the exact molecular quantum dynamics requires a global potential energy surface, and thus scales exponentially with the number of degrees of freedom, an alternative, on-the-fly semiclassical dynamics overcomes this problem and at the same time preserves the accuracy of simulated spectra of a wide range of chemical systems [2,3]. Recently, an even simpler, single-trajectory on-the-fly *ab initio* method based on Heller's thawed Gaussian approximation [4,5] (OTF-AI-TGA) was implemented as a means to simulate electronic absorption, emission, and photoelectron spectra within the Condon approximation [6,7].

Here we present an extension of this method by employing the Herzberg-Teller approximation, which, in contrast to the Condon approximation, allows a linear dependence of the transition dipole moment on nuclear coordinates. Not only does this approach make it possible to simulate symmetry-forbidden transitions, it also provides the means to quantitatively and rigorously evaluate the contribution of the Herzberg-Teller term to the spectra. Furthermore, the on-the-fly scheme does not require invoking a global harmonic approximation, and hence describes the most important anharmonicity effects. This extended version of the OTF-AI-TGA is applied to evaluate the absorption spectra of benzene and phenyl radical. Calculated spectra reproduce the experimental data and are much more accurate than the standard global harmonic approaches. Our results indicate that in the phenyl radical, including anharmonicity effects is more important than including the Herzberg-Teller contribution, while in benzene, the Herzberg-Teller vibronic contribution is essential, since the transition is electronically forbidden and the Condon approximation yields a zero spectrum.

[1] Eric J. Heller, *Acc. Chem. Res.*, **14** (12), 368 (1981).
[2] J. Tatchen and E. Pollak, *J. Chem. Phys.,* **130**(4), 041103 (2009).
[3] M. Ceotto et al., *J. Chem. Phys.,* **130** (23), 234113 (2009).
[4] Eric J. Heller, *J. Chem. Phys.,* **62** (4), 1544 (1975).
[5] Soo-Y. Lee and Eric J. Heller, *J. Chem. Phys.* **76**, 3035 (1982).
[6] M. Wehrle, M. Šulc, and J. Vaníček, *J. Chem. Phys.* **140**, 244114 (2014).
[7] M. Wehrle, S. Oberli, and J. Vaníček, *J. Phys. Chem. A* **119**, 5685 (2015).

AlgoGen : a program to perform Molecular Docking with Full Quantum Refinement (DFQR)

H. Khartabil[1,3], **G. Merieux**[1], **J-C. Boisson**[2], **E. Hénon**[1]

[1]*ICMR UMR CNRS 7312, URCA, Moulin de la Housse, Reims, France*
[2]*CReSTIC EA 3804, URCA, Moulin de la Housse, Reims, France*
[3]*Campus Universitaire des Ardennes, 4 bd Jean Delautre, Charleville-Mézières, France*

Molecular docking is a widely used technique to search for new drugs in medicinal and pharmaceutical fields. It can describe the best orientation of a ligand interacting with a biological macromolecule such as protein and enzyme. To do so, a scoring function is needed in order to determine the strength of the protein-ligand association, and to rank ligands. Standard scoring functions do not appropriately consider the electron polarization and charge-transfer. In order to overcome this drawback, our new approach is based on using docking along with quantum chemistry. In this regard, we have developed AlgoGen [1], which is a software application that combines the benefits of exploratory docking using empirical Vina scoring function [2], and Full Quantum Relaxation Refinement of the protein-ligand system (Fig. 1).

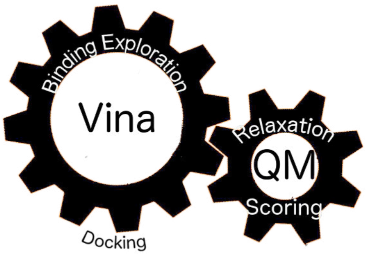


Fig. 1 Docking with Full Quantum Refinement

Recently, we have enhanced AlgoGen by developing jBox, a user-friendly Graphical Interface for ligand and protein pre-processing. Efficient detection of ligand-metal coordination by AlgoGen well be presented.

Acknowledgements to Pr R. Plantier and Dr M. Muzard (ICMR, University of Reims Champagne-Ardenne).

[1] C. Barberot, J-C. Boisson, S. Gerard, H. Khartabil, E. Thiriot, G. Monard,E. Hénon, *Comput. Theor. Chem.* **1028,** 7 (2014).

[2] O. Trott, A. J. Olson, *J. Comput. Chem.* **31**, 455 (2010).

Efficient Eigensolvers for Linear Response Time-Dependent Density Functional Theory

Eugene Vecharynski[1], Jiri Brabec[1,2], Meiyue Shao[1], Niranjan Govind[3], Chao Yang[1]

[1]*Lawrence Berkeley National Laboratory, Computational Research Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720*

[2]*J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, CZ-18223 Prague 8, Czech Republic*

[3]*Pacific Northwest National Laboratory, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352*

We present two efficient iterative algorithms for solving the linear response eigenvalue problem arising from the time dependent density functional theory. Although the matrix to be diagonalized is nonsymmetric, it has a special structure that can be exploited to save both memory and floating point operations. In particular, the nonsymmetric eigenvalue problem can be transformed into an eigenvalue problem that involves the product of two matrices M and K. We show that, because MK is self-adjoint with respect to the inner product induced by the matrix K, this product eigenvalue problem can be solved efficiently by a modified Davidson algorithm and a modified locally optimal block preconditioned conjugate gradient (LOBPCG) algorithm that make use of the K-inner product. The solution of the product eigenvalue problem yields one component of the eigenvector associated with the original eigenvalue problem. It is shown that the other component of the eigenvector can be easily recovered in an inexpensive postprocessing procedure. As a result, the algorithms we present here are more efficient than existing methods that try to approximate both components of the eigenvectors simultaneously. In particular, our numerical experiments demonstrate that the new algorithms presented here consistently outperform the existing state-of-the-art Davidson type solvers by a factor of two in both solution time and storage.

Compressed Representations of Dispersion Interactions and Long-Range Electronic Correlation

Jérôme F. Gonthier[1], **Pauline J. Ollitrault**[1], **Martin Head-Gordon**[1]

[1]*Kenneth S. Pitzer Center for Theoretical Chemistry, Department of Chemistry, University of California, Berkeley, California 94720, USA*

Dispersion interactions arise purely from long-range electronic correlation. Thus, in spite of being the weakest intermolecular force, they are present in all non-covalent dimers and are quantitatively significant in many cases, playing a significant role in complex extended assemblies such as proteins and DNA.

Detailed studies and understanding of electron correlation lead to very efficient and accurate representations using for example explicitly correlated or local methods. Low-rank accurate approximations of the full pair correlation space are now commonly available for short-range electron correlation.[1] Here, we investigate the existence and accuracy of a compressed representation for long-range electron correlation. In particular, we extract dispersion amplitudes from the CCSD doubles amplitudes in a localized orbital basis. Application of Singular Value Decomposition to the corresponding unfolded tensor[2] yields a set of two-particle geminal functions that we further analyze in terms of their occupied and virtual components.

Our investigation reveals that long-range correlation possesses compressed representations much more compact than those of short-range correlation. We identify the dominant geminal functions and reveal which set of virtual orbitals underlies them, a set that is thus particularly suited to describe dispersion. We validate the robustness of our observations in various small and medium-sized systems, and explore pathways to obtain *a priori* virtual orbitals tailored for dispersion interactions.

In addition to qualitative and quantitative insights into the compressed representation of long-range correlation, this study offers a way to obtain a well-defined dispersion energy in the basis set limit, which is invaluable to energy decomposition schemes relying on Hilbert-space partitions.[3]

[1] C. Riplinger, F. Neese, *J. Chem. Phys.* **138**, 034106 (2013).

[2] G. J. O. Beran, M. Head-Gordon, *J. Chem. Phys.* **121**, 78 (2004).

[3] J. Thirman, M. Head-Gordon, *J. Chem. Phys.* **143**, 084124 (2015).

State-of-the-art solvation free energy modelling – add more physics and do without fudge factors

Lars Sandberg[1]

[1]*Science for Life Laboratory, Drug Discovery and Development Platform & Department of Organic Chemistry, Stockholm University, Box 1031, 17121 Solna, Sweden*

The solvation free energy is essential to model with good accuracy in many areas of biology, chemistry and physics. Here we will calculate the change in free energy of a solute molecule transferred from gas phase to water solvent, the solvation free energy. The free energy is obtained from using a relevant system Hamiltonian in combination with statistical mechanics, and it is important to sample phase space sufficiently well. One helpful approach is to describe the solvent in the continuum limit, i.e. by an implicit solvent model. The focus can now be to represent and sample the solute molecule more thoroughly. The objectives for the implicit solvent model implemented here are

1. Include all physical effects liable to molecular solvation
2. Applicable to molecules found in biological and organic chemistry
3. Model parameters of solvent and solute:
   - Introduce as few model parameters as possible
   - Introduce no/few adjustable parameters fitted to experimental hydration free energy data
   - Parameters are fully transferable with explicit solvent free energy calculations
4. Calculated free energies of solvation are
   - better or comparable to the accuracy of the golden standard of explicit solvent free energy calculations
   - made with chemical accuracy, commonly defined as thermochemical predictions within 4.2 kJ/mol (1 kcal/mol)

We have calculated solvation properties in water for a set of several hundreds of organic molecules and compared with available experimental data. The predicted solvation enthalpies, entropies, and free energies show a good accuracy (mean error < 4 kJ/mol) and precision (standard deviation of mean errors between 1-3 kJ/mol) for most functional groups. However, a few functional groups that form strong hydrogen bonds (electron-donor-acceptor complex) with the first solvation shell waters will result in an additional stabilising charge-delocalisation energy. This physical effect is not part of any classical implicit (nor classical explicit) solvent model and that is why systematic errors occur. If we solvate the solute-water complex and include the polarisation stress relief from first principle, the need for corrections are shown to be much reduced.

Thermodynamic modelling of mesophase pitch for the development of high-performance carbon fibers

Caio César Ferreira Florindo[1], **Adalberto Bono Maurizio Sacchi Bassi**[1]

[1]*Department of Physical Chemistry/Institute of Chemistry/ University of Campinas, José de Castro Street – University City, Campinas, Brazil*

In order to obtain high-performance carbon fibers (HPCFs) with excellent mechanical, thermal and electrical properties, it is important to control the spinning process, since molecular shape and orientation of the mesophase pitch is determined, almost exclusively, at this process [1]. In this study, one proposes a mesoscopic continuum mathematical model for mesophase pitch-based carbon fibers, in order to describe how the mesophase regions orientation distributions influence the behavior of the pitch in homogenous flows. By using the continuity condition for the orientation distribution function (ODF) of the mesophase pitch, one can obtains a new homogenous non-linear evolution equation for ODF. This work shows only two-dimensional solutions for two types of flow: (1) simple shear flow and (2) planar elongational flow. Solutions for three-dimensional flows are also obtained, but the findings will not be displayed here. In the two-dimensional approximation, all mesophase regions are parallel to the shear plane. Thus, the angle between the shear direction and the mesophase region orientation completely specifies its orientation state. In general, the ODF shows higher and narrower probability density peaks at higher shear and elongation rates. Meanwhile, the orientation angles of the mesophase regions at low shear and elongation rates are higher than for high shear and elongation rates. The solutions for the mesophase regions show that the system behaves like shear thinning, that is, its viscosity decreases as the shear rate increases. The numerical solutions for the new homogeneous non-linear equation proposed in this work show orientation angle values strictly close to those experimentally obtained by Hamada *et al.* [2]. All calculations were performed by the Mathematica software (version 11.0).

Acknowledgments: FAPESP (Grant 2016/08563-2).

References:

[1] D. Edie, M. Dunham, *Carbon* **27,** 5 (1989).
[2] T. Hamada, M. Furuyama, Y. Sajiki, T. Tomioka, M. Endo, *J. Mater. Res.* **5,** 06 (1990).

Hydrogenation of phenyl substituted unsaturated functional groups by d^5 and d^6 metal substituted PNP complexes

Zhihong Wei, Kathrin Junge, Matthias Beller, Haijun Jiao*

Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Straße 29a, Rostock, Germany

Abstract: Catalytic hydrogenations of unsaturated functional groups are very important in organic synthesis and play key roles in the production of numerous bulk products and intermediates in the chemical and pharmaceutical industry. One of the promising examples is the aliphatic pincer chelating PN^HP ligand [$PN^HP = (i\text{Pr}_2PCH_2CH_2)_2NH$)] in conjugation with transition metals for various types of bifunctional heterolytic H_2 transformation on the basis of the effective metal-ligand cooperation. In our previous work, we explored the hydrogenation of CH_3-C≡N, Ph-CO_2CH_3 and Ph-CHO by using the d^8-M^{II} PNP pincer complexes (M = Fe, Ru, Os).[1] Herein, the structures and stability of the d^5 and d^6 metal substituted PNP pincer amido $M^5(NO)_2(PNP)/M^6(NO)(CO)(PNP)$ and amino $HM^5(NO)_2(PN^HP)/HM^6(NO)(CO)(PN^HP)$ complexes [M^5 = V, Nb and Ta, M^6 = Cr, Mo and W] complexes as well as their hydrogenation mechanisms for phenyl substituted unsaturated functional groups have been explored and compared at the B3PW91 level of density functional theory. Under H_2 environment, the computed structure and stability of the Mo and W complexes are in agreement with the experimental results.[2-4] For the designed Cr- as well as V-, Nb- and Ta-PNP complexes, the conjugated complexes can form equilibrium and fulfills the criteria of metal-ligand cooperated bifunctional hydrogenation catalysts. For the hydrogenation of Ph-C≡N, Ph-CH=NH, Ph-CH=NH-Ph, Ph-CH=N-CH_2Ph, Ph-C≡CH, Ph-CH=CH_2, Ph-CHO and Ph-CO-CH_3, the reaction prefers either a two-step or one-step mechanism for the hydridic M-H and protonic N-H transfer. The computed barrier in the increasing order of PhCHO < Ph-C≡N < Ph-C≡CH < Ph-CH=NH < Ph-$COCH_3$ ≈ Ph-CH=CH_2 < Ph-CH=N-Ph < Ph-CH=N-CH_2-Ph. These results clearly demonstrate that the designed d^5 metal substituted PNP pincer-type complexes can be promising new catalysts for the hydrogenation reactions. The d^6 metals of Mo complexes have higher catalytic activity than that of W and the designed Cr complex. The d^5 metal of Nb is more active than V and Ta as well as the d^6 metal of Mo. All of these provide the basis for experimental proofs.

[1] H. Jiao, K. Junge, E. Alberico and M. Beller, *J. Comput. Chem.* ***37***, 168 (2016).

[2] Z. Wei, K. Junge, M. Beller and H. Jiao, *Catal. Sci. & Technol.* ***7***, 2298(2017).

[3] S. Chakraborty, O. Blacque and H. Berke, *Dalton Trans.* ***44***, 6560(2015).

[4] S. Chakraborty and H. Berke, *ACS Catal.* ***4***, 2191(2014).

Adsorption and activation of water on cuboctahedral Rh and Pt nanoparticles

Andrey S. Bazhenov[1]

[1]Nanoscience Centre, Department of Chemistry, University of Jyväskylä,
P.O. Box 35, FI-40014 Jyväskylä, Finland

Transition metal catalysts find nowadays their application in major industrial processes to obtain sustainable chemicals and renewable fuels. Activation of water has been suggested to play a key role in the water-gas shift and multiple reforming processes, being in some cases acknowledged as the rate-determining step. Since the industrial catalysts operate at the nanoscale, atomic-level understanding of the water activation on relevant transition metals could provide useful information for rational design of catalysts with higher activity and selectivity.

We present a density functional theory study of the water activation on selected noble metals, where the metals are represented by M_{55} and M_{147} (M = Rh, Pt) cuboctahedral nanoparticles accompanied by the extended (100), (111) and (211) surfaces, mimicking facets and edges of the nanoparticles. We systematically evaluate adsorption and activation of a single water molecule on each relevant surface site of each structural model.

Our findings [1] indicate that both Rh and Pt are nearly equally active towards the water activation, which is reflected in a difference of <0.10 eV in adsorption and transition state energies between the two metals. Moreover, in the case of the nanoparticle models, we observe strong linear dependences of adsorption and transition state energies on the centres of the d-band projected onto the corresponding surface sites and on the generalized coordination numbers, which quantify the surface site coordination accounting for their first coordination spheres. These trends do not withhold for the extended surface models, hinting their insufficiency in describing the electronic and structural properties of the nanoparticles in the chosen size regime. The difference between Rh and Pt is observed in the stability of the dissociated water, which is higher in the case of Rh. These results are qualitatively in line with the experimental evidence of lower thermodynamic stability of Pt oxides.

[1] A. S. Bazhenov, L. Lefferts, K. Honkala, *J. Phys. Chem. C* **121**, 4324 (2017).

Symmetric dissociation and excited states with Selected Configuration Interaction with Truncation Energy Error

César X. Almora-Díaz[1], Alejandro Ramírez-Solís[1], Carlos F. Bunge[2]

[1]*Department of Physics, Centro de Investigación en Ciencias, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001 Chamilpa 62209 Cuernavaca, Morelos, México*
[2]*Department of Teoretical Physics, Instituto de Física, Universidad Nacional Autónoma de México, Apdo. Postal 20-364, México 01000, México*

A priori Selected Configuration Interaction with Truncation Error [1,3] for molecular systems and CI by parts [4] are used to approximate the total nonrelativistic electronic ground state energies of water, C_2 and N_2 at equilibrium geometry and at geometries where bond lengths are elongated until dissociation. On N_2 we use a double zeta basis set, in H_2O we use up to triple zeta quality basis sets, and with C_2 we use up to quadruple zeta basis sets. In each case we compare our all electron results of CISDTQ, CISDTQQnSx (CI-6X) and CI up to octuple excitations (CI-8X) with available results of Coupled Cluster, DMRG and other high-level electronic structure methods. In all cases CI-8X results matched converged DMRG results to within 100 microHartree. CI-6X results present Non Paralellity Errors (NPE) smaller than 1 kcal/mol. Energy values obtained within a model space (S01) up to 10 times smaller than total selected configuration space which differ up to 4 milliHartree to the total CI energy keep NPEs within the so called chemical accuracy. Finally, we compare results (within selected S01 spaces) of excited states on carbon dimer with DMRG calculations using a cc-pvdz basis set, we found that NPEs are smaller than 100 microHartree.

[1] C.F. Bunge, *J. Chem. Phys.* **125**, 014107 (2006).

[2] C.X. Almora-Díaz, *J. Chem. Phys.* **140**, 184302 (2014).

[3] C.X. Almora-Díaz, H.I.Rivera-Arrieta, C.F. Bunge *Adv. Quant. Chem.* **72**, 129 (2016).

[4] C.F. Bunge and R. Carbo-Dorca, *J. Chem. Phys.***125**, 014108 (2006).

An interpolation approach for the choice of polarization functions when using Gaussian basis sets

Fernando Ratuchne, [1] **Ana Cristina Mora,**[2] **Ricardo Celeste,**[1] **Albérico B. F. da Silva**[2]

[1]*Universidade Estadual de Centro-Oeste, Departamento de Química, Campus Cedeteg,*
CEP 85040 - 080, Guarapuava - Paraná, Brasil
[2]*Departamento de Química e Física Molecular, Instituto de Química de São Carlos,*
Universidade de São Paulo, C. P. 780, 13560 - 970, São Carlos - SP, Brasil

In the generation of basis sets, usually the primitive set is constructed for the free atom in its ground state and the description of the outer part of the electron density distribution is generally poor [1], so the addition of higher angular momentum functions (polarization functions) in the body of the primitive set of exponents improves the performance of a basis set in the molecular environment [2][3]. In this work, we have used a methodology based on the interpolation of Gaussian basis sets exponents to be used for the choice of polarization functions with any Gaussian basis set. The Gaussian primitive functions were generated here by using the polynomial Generator Coordinate Hartree-Fock (PGCHF) method [4] for Ga through Kr and the general contraction method was used for the construction of contracted Gaussian basis sets of 6Z quality in the valence. Polarization functions were added to the contracted bases by explicit optimization and also by interpolation of the exponents. The performance of the contracted basis sets, augmented with polarization functions obtained by interpolation, was tested in CISD and B3LYP calculations for the total energy of the systems Se, Se_2 and Se_6 and the results were compared with the total energy values obtained from explicit optimized exponents. The results obtained with the PGCHF Gaussian basis sets augmented with interpolated polarization functions are in good agreement with the ones augmented with explicit optimized polarization functions (exponents). The interpolation strategy can be useful to generate polarization functions for any Gaussian basis set in different series of atoms of the periodic table.

[1] T. H. Dunning, *J. Chem. Phys.* **90**, 1007 (1989).
[2] F. Jensen, J. *Chem. Phys*. **115**, 9113 (2001).
[3] F. Jensen, J. *Chem. Phys.* **138**, 014107 (2013).
[4] R. C. Barbosa and A. B. F. da Silva, *Mol. Phys.* **101**, 1073 (2003).

Theoretical pK_a calculations of difficult cases for thermodynamic cycles: amino acids and peptides.

Rodrigo Casasnovas[1], **Sebastià Sastre**[1], **Francisco Muñoz**[1], **Juan Frau**[1,2]

[1]*Departament de Química, Institut Universitari d'Investigació en Ciències de la Salut (IUNICS), Universitat de les Illes Balears, Palma de Mallorca 07122, Spain*

[2]*Instituto de Investigación Sanitaria de Palma (IdISPA), 07010, Palma, Spain*

Accurate prediction of pK_a values is a current challenge in computational chemistry. The traditional approach employs thermodynamic cycles (TC) combining gas-phase energies calculated with high ab initio methods, and solvation energies calculated with continuum solvent models [1-5]. TCs are difficult to apply to amino acids and peptides because the most stable protonation states and conformations differ between gas phase and aqueous solution. Our group has applied an alternative to TCs consisting of an isodesmic reaction (IR) proton exchange reaction in solution. We have successfully applied the IR to the prediction of pK_a values of common organic molecules [6], carbon acids [7-9] and metal complexes [9, 10]. Here we apply the IR to the pK_a calculation of amino acids and peptides obtaining mean absolute errors of 0.5-1.0 pK_a units for pK_{a1} (α-carboxyl) pK_{a2} (α-amino) and pK_{a3} (sidechain groups) of a broad set of amino acids and peptides [11].

[1] R. Casasnovas, J. Ortega-Castro, J. Frau, J. Donoso, F. Muñoz, *Int. J. Quantum Chem.* **114**, 1350 (2014).
[2] P. G. Seybold, G. C. Shields, *WIREs Comput. Mol. Sci.* **5**, 290 (2015).
[3] J. Ho, M. L. Coote, *WIREs Comput. Mol. Sci.* **1**, 649 (2011).
[4] J. Ho, M. L. Coote, *Theor. Chem. Acc.* **125**, 3 (2010).
[5] Ho, J. Phys. Chem. Chem. Phys. **17**, 2859 (2015).
[6] S. Sastre, R. Casasnovas, F. Muñoz, J. Frau *Theor. Chem. Acc.* **132**, 1310 (2013).
[7] R. Casasnovas, D. Fernandez, J. Ortega-Castro, J. Frau, J. Donoso, F. Muñoz, *Theor. Chem. Acc.*, **130**, 1 (2011).
[8] R. Casasnovas, M. Adrover, J. Ortega-Castro, J. Frau, J. Donoso, F. Muñoz *J. Phys. Chem. B*, **116**, 10665 (2012).
[9] R. Casasnovas, J. Ortega-Castro, J. Frau, J. Donoso, F. Muñoz, *J. Phys. Chem. B*, **117**, 2339 (2013).
[10] R. Casasnovas, J. Ortega-Castro, J. Donoso, J. Frau, F. Muñoz, *Phys. Chem. Chem. Phys.* **15**, 16303 (2013).
[11] S. Sastre, R. Casasnovas, F. Muñoz, J. Frau, *Phys. Chem. Chem. Phys.* **18**, 11202 (2016).

Automatic differentiation in quantum chemistry: Application in fully variational Hartree-Fock

Teresa Tamayo-Mendoza[1,*], **Christoph Kreisbeck**[1], **Alán Aspuru-Guzik**[1]

[1]*Department of Chemistry and Chemical Biology, Harvard University, University,*
12 Oxford St, Cambridge, MA 02138
[*]*ttamayomendoza@g.harvard.edu*

Automatic differentiation (AD) is a tool that allows us to calculate derivatives of implemented functions with respect to all of their parameters up to machine precision, without having to add in any other explicit functions[1]. Since it is easy to use and accurate, AD has great potential in quantum chemistry where accurate derivatives are required to compute molecular properties and optimizations[2]. Because, even though some of these derivatives have well established explicit equations, implementing them on electronic structure methods or response functions can be both time-consuming and non-trivial. First steps have already been taken toward including AD in quantum chemistry algorithms to circumvent these issues[3].

In this poster, we show how automatic differentiation can be used to compute arbitrary gradients throughout a complete quantum chemistry method with respect to any input parameter. We describe an implementation of a fully autodifferentiable Hartree-Fock (HF) algorithm. We have selected HF for two reasons: (i) it is the starting point of many electronic correlation methods, and (ii) it features mathematical functions, including eigenvectors and special functions, which are also present in more accurate methods. Finally, we present results from embedding these gradient calculations within an optimization procedure to assemble a fully variational HF method. Using the floating Gaussian framework[4], this implementation minimizes the SCF-energy with respect to all parameters of the Gaussian basis functions and molecular geometries.

[1] A. Griewank, A. Walter, Evaluating *Derivatives, Principles and Techniques of Algorithmic Differentiation,* second edition, SIAM Philadelphia, (2008).

[2] C. H. Bischof, and M. Bücker, (Ed.: J. Grotendorst), *NIC Series*, **3**, 315 (2000).

[3] U. Ekström, L. Visscher, R. Bast, A. Thorvaldsen, and K. Ruud, *J. Chem. Theory Comput.*, **6**, 1971 (2010).

[4] T. Helgaker, and J. Almlöf, *J. Chem Phys.* **89**, 4889 (1988).

Why does MP2 outperform MP3 and how can we improve perturbation theory?

Reinhold F. Fink[1]

[1] *Institute of Physical and Theoretical Chemistry, University of Tuebingen,*
Auf der Morgenstelle 18, 72076 Tuebingen, Germany

We show analytically and numerically that the performance of second and third order Møller-Plesset perturbation theory (MP2 and MP3, respectively) can be rationalized and that the obtained insight opens an avenue for improved perturbation theories. An analysis of the wave functions obtained from configuration interaction (CI), coupled-cluster (CC) theory, and perturbation theories points to systematic and relatively large deviations of the first order MP wave function from exact full CI or accurate CC counterparts [1]. It is shown that MP2 profits from a systematic error cancellation due to, respectively, an underestimation and overestimation of singlet- and triplet-coupled double excitations to electron correlation. The underlying reasons for this error are explained and it is shown that it is reduced by spin-component-scaled (SCS) MP2 [2, 3].

We demonstrate that a similar error cancellation as in MP2 does not appear in MP3 due to the variational character of third order perturbation theory. Finally, it is demonstrated that retaining the excitation-degree (RE) perturbation theory [4, 5] provides much better wavefunctions than MP2 and that these errors can be further reduced by combining the unperturbed Hamiltonians of MP and RE.

[1] R. F. Fink, *J. Chem. Phys.* **145**, 184101 (2016).

[2] S. Grimme, *J. Chem. Phys.* **118,** 9095, (2003).

[3] S. Grimme, L. Goerigk, and R. F. Fink, *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2,** 886, (2012).

[4] R. F. Fink, *Chem. Phys. Lett.* **428,** 461 (2006).

[5] R. F. Fink, *Chem. Phys.* **356,** 39, (2009).

Binary mixtures of ionic liquids with a common anion: a molecular dynamics study

Iuliia V. Voroshylova[1,2], **Elisabete S. C. Ferreira**[1,2], **André Melo**[2], **Carlos M. Pereira**[1], **M. Natália D.S. Cordeiro**[2]

[1]LAQV@REQUIMTE/[2]CIQUP, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal

Ionic liquids (ILs) are promising materials with a number of possible applications, ranging from catalytic and reaction media to plausible electrolytes for batteries and supercapacitors. Nevertheless, ILs present some known drawbacks, such as relatively high viscosity and low conductivity. Recently, it has been proposed a way of overcoming these drawbacks by mixing different ILs, which allows a fine-tuning of their physicochemical properties [1]. Experimental studies show that the most pronounced effect on physical and chemical properties, first of all, on capacitance, occurs in ILs mixtures with small additions of IL with a different anion [2, 3].

In this study we carried out molecular dynamics (MD) simulations to understand at the molecular level the causes for some mixtures of ILs having quasi-ideal behaviour, while other mixtures showing quite large deviations from ideality. Towards this goal, we have simulated three ILs mixtures with a common cation, *i.e.*: [BMIM][FAP]/[BMIM][PF_6], [BMIM][PF_6]/[BMIM][TFSI] and [BMIM][FAP]/[BMIM][TFSI] (Fig. 1), in a wide concentration range, reproducing the experimentally studied ones [3]. The simulations of these three pure ILs were also carried out for comparison purposes. The excess molar volume of the mixtures is estimated and discussed. The MD results were further analysed in terms of radial distribution functions (centre-of-mass and atom-atom), running coordination numbers and hydrogen-bonds-like interactions.

Acknowledgements. This work received financial support from Fundação para a Ciência e Tecnologia (FCT, Lisbon, Portugal) through postdoctoral research grants with the reference SFRH/BPD/97918/2013 and SFRH/BPD/90343/2012.

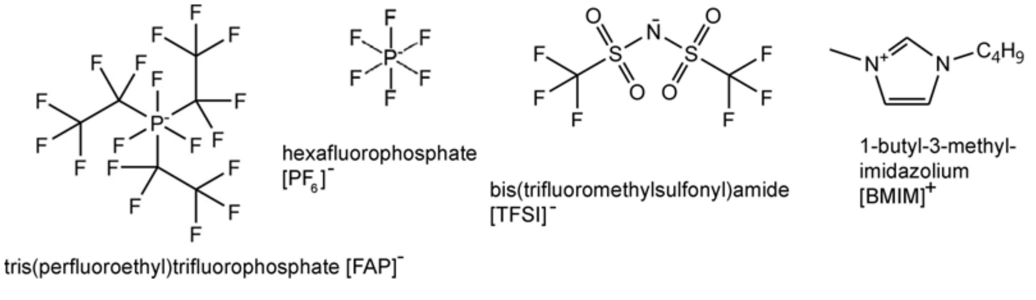


Fig. 1. Structural formulas of the ions of the studied ionic liquids.

[1] S. Cha S. and D. Kim, *Phys. Chem. Chem. Phys.*, **17**, 29786 (2015).

[2] R. Costa, C. M. Pereira and A. F. Silva, *Electrochem. Comm.*, **57**, 10 (2015).

[3] R. Costa, I. V. Voroshylova, M. N. D. S. Cordeiro, C. M. Pereira and A. F. Silva, *Electrochem. Acta*, in press (2017)

Nonlinear optical properties from TDDFT: trials and tribulations

Shane Parker[1], **Filipp Furche**[1]

[1]*Department of Chemistry, University of California Irvine, 1102 Natural Sciences II Irvine, CA, USA*

Nonlinear response theory plays a central role in theoretical materials chemistry and applications of nonlinear response theory within time-dependent density functional theory (TDDFT) are increasingly important, from the calculation of nonlinear optical properties used to characterize complex materials to the excited-state properties and couplings needed to simulate non-adiabatic molecular dynamics. I will present an efficient implementation of the TDDFT quadratic response function, including the computation of excited state absorption spectra of perylene diimide dimers, two-photon absorption spectra of twisted conjugated porphyrins, and hyperpolarizability of octupolar calixarenes. Distressingly, recent descriptions of unphysical divergences in excited-state properties[1] and the inconsistent behaviors of multiphoton processes[2] near single-photon absorption resonances have called into question the general applicability of existing nonlinear response theories. Finally, using the aforementioned systems as examples, I will sketch the successes and failures of existing nonlinear response methods and discuss possible routes for resolving the deficiencies in nonlinear response theories.

References

[1] S. M. Parker, S. Roy, F. Furche, *J. Chem. Phys.* **2016**, *145*, 134105.

[2] Z. Hu, J. Autschbach, L. Jensen, *J. Chem. Theory Comput.* **2016**, *12*, 1294–1304.

Challenges and procedures towards automated flow chemistry

Loïc M. Roch,[1] and Alán Aspuru-Guzik[1]

[1]*Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, MA, USA*

Over the past decade new technologies and machines have profoundly changed the way we work, addressing constraints encountered in research lab, such as budget and waste minimization.[1] Pioneered by the pharmaceutical industry, the incorporation of high-throughput screening to continuous flow chemistry emerged as a valuable tool for a more rational search process of the *Application Space* (*A.S.*) towards an efficient and automated synthesis of new promising organic candidates.[2-4]

However, given the multidimensionality of the search space to idealize and maximize specific features of the system under study, *e.g.*, yield of the reaction, electrochemical properties, photophysical properties, etc., a combinatory approach to that vast *A.S.* is not viable. As such, artificial intelligence appears as a method of choice for a faster characterization of the *A.S.* Consequently, bridging the gap between automated procedures and machine learning algorithms becomes a necessity to guide and optimize flow processes.

Herein, we present the challenges and procedures towards automated flow chemistry.

[1] S. V. Ley, D. E. Fitzpatrick, R. J. Ingham, and R. M. Myers, *Angew. Chem. Int. Ed.*, **54**, 3449 (2015).
[2] B. J. Reizman and K. F. Jensen , *Acc. Chem. Res.*, **49**, 1786, (2016).
[3] C. A. Nicolaou, I. A. Watson, H. Hu and J. Wang, *J. Chem. Inf. Model.*, , **56**, 1253 (2016).
[4] A. G. Godfrey, T. Masquelin and H. Hemmerle, *Drug Discov. Today*, **18**, 795 (2013).

Relativistic effects on NMR spectroscopic parameters of atoms belonging to Hydrogen-bonds

Teresita Santa Cruz and Gustavo A. Aucar

Physics Department, Natural and Exact Science Faculty, Northeastern University of Argentina and Institute of Modeling and Innovation on Technology, IMIT CONICET-UNNE, Corrientes, Argentina

Relativistic effects on NMR spectroscopic parameters were usually considered on molecular systems where hydrogen bonds, HB, were not part of it [1,2]. What we present here is an study on which are the main patterns of such effects on two HB containing systems: malonaldehyde and Schiff basis, where the oxygen atom was replaced by selenium. We analyzed the magnitude and the origin of such parameters in the process of proton transmission.

One of the main relativistic effects on light atoms is due to the proximity of a heavy-atom, an effect named heavy-atom effect on light atoms (HALA) [3,4]. This is mainly of Spin-orbit (SO) type for magnetic shieldings, and until now it was only well-defined for covalent bonds. We show here that relativistic effects on both NMR spectroscopic parameters are transmitted through HB.

For shieldings, when the hydrogen atom that belongs to the HB is close to the heavy atom, SO effects are larger than Spin-free, SF, effects. The opposite happens when that hydrogen is close to the light atom.
When the proton is transferred from a light donor to a heavy acceptor there is an increase of the relativistic effect and also a change of the sign of this effect.

A similar pattern is observed for J-couplings among Se and H, being the SF contribution the largest one in the whole process of hydrogen transference.

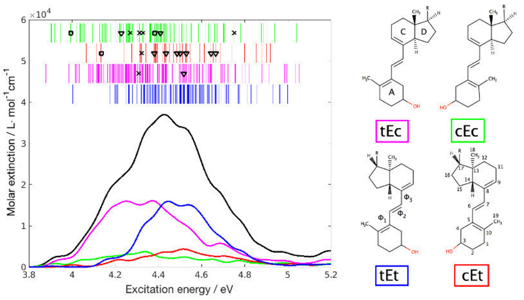
[1] G. A. Aucar, R. H. Romero, A. F. Maldonado, Int. Rev. on Phys. Chem. **29**, 1(2010).
[2] P. Pyykkö, Chem. Rev. **112**, 371 (2012).
[3] P. Pyykkö, A. Görling, and N. Rösch, Mol. Phys. **61**, 195 (1987).
[4] M. Kaupp, O. L. Malkina, V. G. Malkin, and P. Pyykkö, Chem. Eur. J. **4**, 118 (1998).

Mechanisms of surface O removal by H_2 and CO activation on Fe and Co surfaces

Shaoli Liu and Haijun Jiao

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, Shanxi 030001, China;
Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Strasse 29a, 18059 Rostock, Germany (haijun.jiao@catalysis.de)

Water chemistry on solid surfaces is of central importance to a broad range of scientific and technological processes, such as corrosion, electrochemistry, nanoparticle self-assembly, environmental chemistry, lubricants and heterogeneous catalysis. However, molecular mechanisms of water interaction with solid-state surfaces are poorly understood. An atomic level investigation into water-metal interaction is necessary for understanding the mechanisms of many heterogeneous catalytic reactions. On the basis of DFT and atomistic thermodynamics we studied H2O dissociative adsorption on Fe(110), Fe(100) and Fe(111) surfaces; and different mechanisms as well as surface OH and O have been found. For the water-gas shift reaction on these surfaces no BEP relationship can be found. In addition, surface O removal by H_2 and CO the activation on several iron cobalt surfaces has been investigated; and the mechanisms depend on Co crystal phases. These results provide the basis for understanding the experimental observation.



p

Figure 1: Wavelength and conformational dependency of tachysterol photochemistry [3].

The quantum biology of vitamin D – Insights from non-adiabatic dynamics

Enrico Tapavicza[1], **Travis Thompson**[1], **Cecilia Cisneros**[1], **Adam Smith**[1], **Noel Baluyot**[1]

[1]*Department of Chemistry and Biochemistry, California State University, Long Beach, 1250 Bellflower Blvd, Long beach, USA*

The main vitamin D source for humans is its generation by the sun's ultraviolet (UV) light. Oral administration of large vitamin D quantities can lead to an overdose, which affects negatively many regulation cycles in our body. In contrast, vitamin D overproduction due to extended sun exposure has never been observed [1]. A complex network of vitamin D photo isomers that are connected by reversible chemical and photochemical reactions in our skin prevents vitamin D overproduction. The self-regulation mechanism is still under debate [1]. An important feature is the characteristic wavelength dependent photochemistry: long-wavelength UV light induces different photo reactions than short-wavelength UV light. As a consequence, the distribution of photo isomers depends on day time and season. To understand the vitamin D photoequilibrium, we apply non-adiabatic molecular dynamics simulations [2] to study the photo dynamics of several vitamin D related reactions. Our study [3] confirms a recent hypothesis [4] that vitamin D can be formed from tachysterol at long-wavelength UV light.

[1] MacLaughlin, J.; Anderson, R.; Holick, M. *Science* **1982**, *216*, 1001–1003; van Dijk, A.; den Outer, P.; van Kranen, H.; Slaper, H. *Photochem. Photobiol. Sci.* **2016**, *15*, 896–909.

[2] Tapavicza, E.; Meyer, A. M.; Furche, F. *Phys. Chem. Chem. Phys.* **2011**, *13*, 20986.

[3] Cisneros, C.,Thompson, T.,Baluyot, N.,Smith, A.C., Tapavicza, E. *Phys. Chem. Chem. Phys.* **2017**, *19*, 5763.

[4] Andreo, K. Generation of previtamin D3 from tachysterol3: A novel approach for producing vitamin D3 in the winter. Ph.D. thesis, Boston university, **2015**.

Dual structure-based approach towards the design of inhibitors of the Dengue virus envelope protein

Emilse S. Leal[1,£], M. Gabriela Aucar[2,3,£], Leopoldo G. Gebhard[4], María J. Pascual[5], Andrea V. Gamarnik[4], Claudio N. Cavasotto[2,*], Mariela Bollini[1,*]

[1]Laboratory of Medicinal Chemistry, Centro de Investigaciones en Bionanociencias (CIBION)-CONICET, Godoy Cruz 2390, Ciudad de Buenos Aires, Argentina
[2]Laboratory of Computational Chemistry and Drug Design, Biomedicine Research Institute of Buenos Aires - CONICET - Partner Institute of the Max Planck Society, Godoy Cruz 2390, Ciudad de Buenos Aires, Argentina
[3]Physics Department, Natural and Exact Science Faculty, Northeastern University of Argentina and Institute of Modelling and Innovation on Technology (IMIT)-CONICET, Avenida Libertad 5460, Corrientes, Argentina
[4]Fundación Instituto Leloir-CONICET, Av. Patricias Argentinas 435, Ciudad de Buenos Aires, Argentina
[5]Instituto de Investigaciones Biotecnológicas, Universidad Nacional de San Martín, CONICET, Av. 25 de Mayo y Francia, San Martín, Prov. de Buenos Aires, Argentina
[£]Equally contributed to this work; [*]To whom correspondence should be addressed

Dengue is a mosquito-borne viral disease that has become a major public health concern worldwide in recent years. At present, dengue is endemic in many popular tourist destinations in Latin America, Southeast Asia and the Pacific islands.[1] However, no clinically approved antiviral therapy is available. The first dengue vaccine has been recently approved and licensed in six countries, but it was reported to be 60% effective and not to generate immunity against all serotypes reported. To satisfy this unmet medical need for an antiviral therapy, both industry and academia have taken multiple approaches to develope anti dengue virus agents. Entry of the dengue virus into a host cell is mediated by its major envelope protein, *E*. The crystal structure of the *E* protein reveals a hydrophobic pocket occupied by the detergent n-octyl-β-D-glucoside (β-OG) lying at a hinge region between domains I and II. [2] Therefore, the E protein is an attractive target for the development of antiviral agents. We used *in silico* structure-based virtual screening and *de novo* design approaches to identify small-molecules that likely bind to the β-OG binding site. Twenty-three structurally different compounds were selected from docking-based virtual screening and ten compounds emerging from *de novo* design were synthesized. The antiviral activity of the compounds was evaluated using an assay based on a luciferase-expressing dengue reporter virus. Six compounds showed antiviral activity in the 3-10 μM range and displayed a good therapeutic index. Based on their antiviral potency and selectivity, these compounds will be subject of a more detailed and elaborate virological study to gain insights into the precise molecular mechanism of action.

[1] http://www.who.int/mediacentre/factsheets/fs117/es/.
[2] Modis, Y.; Ogata, S.; Clements, D.; Harrison, S. C. *Proc. Natl. Acad. Sci. U. S. A.* **2003**, *100*, 6986–6991.

Benchmark noncovalent interaction energies: balancing databases and improving dispersion damping functions

Konrad Patkowski[1]

[1]*Department of Chemistry and Biochemistry, Auburn University, 179 Chemistry Building, Auburn, AL 36849, USA*

Databases of benchmark intermolecular interaction energies have become an indispensable tool for both the assessment of existing approaches (DFT, wave function, or (semi)empirical) and the development of new approximations (parameterized density functionals, spin component scaling, ...). The "gold standard" CCSD(T) approach is the method of choice for generating accurate benchmark data, and the best strategies for obtaining basis set-converged values have been thoroughly investigated. However, the predictive power of benchmark databases depends just as much on the accuracy of individual results as on the selection of complexes and configurations making up the entire dataset. The recent development of "third-generation" benchmark databases highlights the need for including diverse interaction types (as classified by symmetry-adapted perturbation theory), diverse intermolecular separations, and diverse angular orientations (both favorable and unfavorable). In contrast, most of the existing benchmark databases are biased towards van der Waals minima and longer distances as well as towards optimal angular orientations. Trying to improve the diversity and balance of different separations, orientations, and interaction types, we arrive at a new database [1] composed of 1526 structures in the training set and 6773 more in the validation set. As the first application of this database, we revisit the problem of determining damping parameters for Grimme's "DFT plus dispersion" (DFT-D3) variants, as these 2-3 functional-dependent coefficients were originally fitted to a highly limited set of benchmark data. Sticking to 3 damping parameters and preserving (or slightly extending) the original forms of -D3 damping functions, we were able to reduce the average DFT-D3 errors by about a quarter and to substantially alleviate (but not eliminate) the inaccuracies in the mildly repulsive region of the potential energy surfaces. However, the new database presents a particularly attractive venue for a further improvement of dispersion damping functions, going beyond the established functional forms. As a first step in this direction, we explore linear combinations of error functions as approximations to an arbitrary increasing function of interatomic distance as well as map out the optimal damping function by piecewise interpolation.

[1] D. G. A. Smith, L. A. Burns, K. Patkowski, and C. D. Sherrill, *J. Phys. Chem. Lett.* **7**, 2197 (2016).

Explaining the NMR spectrum of the active site of photoactive yellow protein

Phillip Taenzler[1], **Keyarash Sadeghian**[1] , **Christian Ochsenfeld**[1]

[1]*Department of Chemistry, University of Munich (LMU) Butenandtstrasse 7,*
D-81377 Munich, Germany

We report our theoretical findings on the NMR properties of the hydrogen bond network around the active site of photoactive yellow protein (PYP), a bacterial photoreceptor to short-wavelength light. A previously published neutron diffraction structure of PYP [1] featured an unusually short hydrogen bond between PYP's chromophore, *p*-coumaric acid, and the nearby glutamate-46, in which the proton was found at the midpoint between the donor and acceptor groups. This discovery led to both theoretical and experimental investigations into the properties of the hydrogen bond network, with particular emphasis on its NMR properties. However, theoretical and experimental results achieved little concordance. Therefore, we report our discovery of a rapid conformational exchange mechanism in the active site of PYP, which controls the NMR shifts of the participating hydrogen bonds. It is only by considering this dynamical behavior of the active site that the experimentally measured NMR shifts [2] of the hydrogen bond network can be explained [3].

[1] S. Yamaguchi *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **106**, 440 (2009).

[2] P. A. Sigala, M. A. Tsuchida, D. Herschlag, *Proc. Natl. Acad. Sci. U.S.A.* **106**, 9232 (2009)

[3] P. J. Taenzler, K. Sadeghian, C. Ochsenfeld, *J. Chem. Theory. Comput.* **12**, 5170 (2016)

Charge Transfer of a prokaryotic (6-4) Photolyase PhrB

Daniel Holub,[1] Tomáš Kubař,[1] Marcus Elstner,[1] Natacha Gillet[1]

[1]*Department for Theoretical Chemical Biology, Institute for Physical Chemistry, Karlsruhe Institute for Technology, Kaiserstr. 12, 76131, Karlsruhe, Germany*

Photolyases are light sensitive enzymes and their main task is the binding and repair of damaged DNA. This function involves several electron transfer (ET) steps, which activate a non-covalent bond FAD cofactor and carry an electron to the damage in the DNA. Quantum dynamics simulations of ET use a QM/MM approach in which the traveling charge and some selected sites e.g. amino acids are calculated with a QM-method (DFTB) and coupled to the rest of the system being propagated with MM methods.

Reaction times for several ET steps in a photolyase, PhrB of *Agrobacterium fabrum,* were calculated and compared to other proteins of this family. The same simulations were performed for mutations of PhrB to indicate the correlation between specific amino acids and the ET.

The product of these ET processes are systems with separated charges which force the protein and the environment to adopt. This leads to several processes e.g. proton transfer reactions or structural changes in the protein which will also be described and compared to experimental studies.

Quantum Vibrational Spectroscopy of Biomolecules using *ab initio* Classical Separable Potentials

Barak Hirshberg[1], **R. Benny Gerber**[1,2]

[1]*Institute of Chemistry and the Fritz Haber Center for Molecular Dynamics, the Hebrew University, Jerusalem, 9190401, Israel*
[2]*Department of Chemistry, University of California, Irvine, CA 92967, USA*

Describing the quantum dynamics of molecules that contain more than 5-6 atoms remains one of the most difficult challenges of theoretical chemistry. While treating the motion of the atoms classically is a very good approximation for heavier atoms and higher temperatures, vibrational spectroscopy is an example in which a quantum dynamical description is often essential. In addition, it is one of the strictest tests for the quality of the potential energy surface (PES). In order to calculate the vibrational spectrum of large molecules quantum mechanically, we recently developed the *ab initio* CSP (AICSP) method[1,2].

The method extends the CSP method[3] to use *ab initio* PES for the calculation of quantum anharmonic spectra. It is a separable method, which assumes each mode evolves in time under the influence of an effective potential obtained from classical *ab initio* molecular dynamics simulations. These potentials implicitly couple each mode to all other normal modes of vibration. We test AICSP using MP2 and ωB97X-D potentials for the vibrational spectroscopy of H-X stretching modes of amino acids (proline, alanine and glycine) as well as the guanine-cytosine base-pair, with very good agreement with experimental results. The tests suggest that the method can be applied successfully to larger biomolecules, such as peptides or small proteins. In addition, the method can be used to calculate vibrational lineshapes and linewidths as well as time-dependent spectroscopy.

[1] B. Hirshberg, L. Sagiv, and R. B. Gerber J. Chem. Theory Comput. 13 (2017) 982–991.

[2] B. Hirshberg and R.B. Gerber Advances in Quantum Chemistry, Academic Press, Volume 75, 2017, 1–26, ISSN 0065-3276, http://doi.org/10.1016/bs.aiq.2017.01.002.

[3] P. Jungwirth and R.B. Gerber The Journal of Chemical Physics (1995) 102, 6046.

Studying the nature of hydride transfer and its role in the enzymatic catalysis.

R. García-Meseguer[1], D. Laage[2], J. T. Hynes[2] and I. Tuñón[1]

[1] *Departamento de Química Física, Universidad de Valencia, 46100 Burjassot, Spain.*

[2] *Departament de Chimie, École Normale Supérieure, 75005 Paris, France.*

Abstract

Hydrogen transfer reactions are chemical processes of undeniable importance in chemistry and biology. These reactions involve the transfer of a light particle associated to charge transfer between the reacting fragments. Thus, these processes may simultaneously involve quantum tunneling and a strong coupling between the chemical system and the environment. The simulation of these reactions is challenging due to the importance of both nuclear and electronic quantum effects, as well as the effects that the environmental degrees of freedom can have in the reaction.

Formate Dehydrogenase (FDH) is an enzyme that catalyzes the oxidation of formate to carbon dioxide with the NAD+ cofactor. The chemical step is the hydride transfer from formate to the cofactor. This study is based in the implementation of a new environmental coordinate for QM/MM simulations defined as the relaxed energy gap between the states resulting from the hydride transfer between the donor and acceptor atoms.

This coordinate allows the quantization of the motion not only for the transferred hydride but also of the secondary hydrogen atom bonded to the acceptor atom, which moves simultaneously with the primary hydrogen. The transition state defined according to this coordinate shows a broad distribution of donor-acceptor distances where the hydride transfer can take place in different regimes: over the barrier and through the barrier.[1] Rate constant and Kinetic Isotope Effects Have been evaluated taking into account these different regimes using an adequate expression for the transition between states. These results were compared with experimental results and with theoretical results obtained using the standard aproximation.

[1] D. Borgis, J. T. Hynes *J. Phys. Chem.* **1996**, *100*, 1118-1128.

Insights into the Photochromism of a Red/Green Cyanobacteriochrome

Christian Wiebeler, Aditya G. Rao, Igor Schapiro

Fritz Haber Center for Molecular Dynamics Research, Institute of Chemistry, The Hebrew University of Jerusalem, Israel

Cyanobacteriochromes (CBCRs) are promising candidates for the use as photoswitches in biotechnological applications, owing to their photochromism, compactness and spectral diversity. In case of Slr1393, one isomer absorbs red light (P_R) and the other one green (P_G) (Fig. 1 B). The two forms can be interconverted into each other by light illumination. Slr1393 binds phycocyanobilin (PCB) as chromophore and the crystal structures of both forms have been obtained recently. Comparing PCB from both structures shows that one double bond isomerization occurs during the photoconversion (Fig. 1 A). In this contribution, results of quantum chemical and hybrid QM/MM calculations of the P_R and P_G forms of Slr1393 will be presented.
In order to understand the photophysical properties, quantum chemical calculations for PCB were performed. This is extended by wave function analysis and QM/MM investigations of the protein to obtain further insights on the molecular level. In addition, the vibronic spectrum for PCB in the P_R form is presented explaining the fine structure of the measured absorption.
Finally, first results regarding the photochemistry of the truncated PCB chromophore in gas phase will be shown. The study follows an approach recently used [1] and is based on Tully's Fewest Switches Surface Hopping. It demonstrates that the explicit treatment of the protein environment is needed to understand the photochemistry of Slr1393.

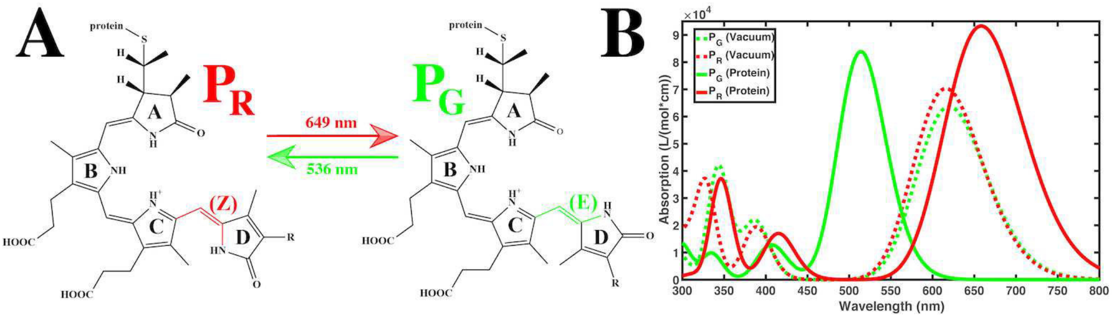


Figure 1: (A) Reaction scheme of PCB photoisomerization, the wavelengths refer to the experimental absorption maxima; (B) Calculated absorption for the P_R (red) and P_G (green) forms of PCB determined for vacuum (dotted) and protein geometry (solid).

[1] C. Wiebeler *et al.*, *Phys. Chem. Chem. Phys.* **16**, 14531 (2014).

Global optimization, analysis and simulation – the recent developments within the CAST program

Daniel Bellinger[1], Dustin Kaiser[1], Susanne Sauer[1], Bastian Michels[1], Michael Prem[1], Julian Erdmannsdörfer[1], Sara Wirsing[1] and Bernd Engels[1]

[1] Institut für Phys. und Theor. Chemie, Universität Würzburg, Emil-Fischer-Straße. 42, 97074 Würzburg, Germany

The CAST (**C**onformational **A**nalysis and **S**earch **T**ool)[1] contains efficient global optimization routines based on a combination of basin hopping and Tabu Search[2-3], and reaction path search approaches which combine the Nudged Elastic Band (NEB)[4] with the PathOpt[5-6] approach. It also allows MD and MC simulations, e.g. to perform free energy perturbation calculations (FEP). By its modular conception, the implemented algorithms can be easily applied employing different energy-calculating methods ranging from different force fields up to fast DFT calculations with Terachem.

The program was recently extended by the following new features: An exciton modelling approach, a new available energy interface (Gaussian09), a modified FEP routine, Principal Component Analysis (PCA)[7] and new possibilities for reaction pathway (RP) determination. The modified FEP method tries to decrease the computational effort by partitioning the system into active and inactive regions. To analyze and characterize MD or MC simulations we implemented a PCA based approach. For RP optimizations CAST now offers several additional NEB methods. In the case of exciton modelling the approach which was developed by Brückner et al.[8-9] is integrated within CAST.

[1] C. Grebner, J. Becker, D. Weber, D. Bellinger, M. Tafipolski, C. Brückner, B. Engels, *J. Comput. Chem.* **35**, 1801 (2014).

[2] C. Grebner, J. Becker, S. Stepanenko, B. Engels, *J. Comput. Chem.* **32**, 2245 (2011).

[3] C. Grebner, J. Kästner, W. Thiel, B. Engels, *J. Chem. Theo. Comp.* **9**, 814 (2013).

[4] G. Henkelman, B. P. Uberuaga, H. Jónsson, *J. Chem. Phys.* **113**, 9901 (2000).

[5] C. Grebner, L. P. Pason, B. Engels, *J. Comp. Chem.* **34**, 1810 (2013).

[6] D. Weber, D. Bellinger, B. Engels, *Methods in Enzymology* **578**, 145 (2016).

[7] A. Altis, P. H. Nguyen, R. Hegger, G. Stock, *J. Chem. Phys.* **126**, 244111 (2007)

[8] C. Brückner, F. Würthner, K. Meerholz, B. Engels, *J. Phys. Chem. C* **121**, 4 (2017).

[9] C. Brückner, F. Würthner, K. Meerholz, B. Engels, *J. Phys. Chem. C* **121**, 26 (2017)

Dispersion-Corrected DFT Study of Enantiospecific Adsorption of Amino Acids on Hydroxylated Quartz Surfaces

Alastair Price[1], **and Erin R. Johnson**[1]

[1]*Department of Chemistry, Dalhousie University, 6274 Coburg Road, Halifax, Canada*

The chirality of amino acids is an important issue facing modern science with a further need to understand how controlled growth of enantiopure crystals can be achieved experimentally. [1] Hydroxylated quartz surfaces have been shown to preferentially bind specific enantiomers of amino acids, making it suitable for enantiospecific separations. [2,3] We extend the current understanding of the interaction of amino acids with these surfaces by using dispersion-corrected DFT methods, e.g., B86bPBE-XDM.[4]. In addition, we contrast the use of planewave approaches and low cost methods to perform these calculations. This work can be used as a stepping stone to provide further insight into how the amino acid crystal interacts with this surface.

[1] A. J. Gellman and D. S. Sholl, *AIChE* **55**, 2484 (2009).

[2] J. W. Han and D. S. Sholl, *Langmuir* **25**, 10737 (2009).

[3] J. W. Han and D. S. Sholl, *Phys. Chem. Chem. Phys.* **12** 8024 (2010).

[4] A. Otero-de-la-Roza, and E. R. Johnson, *J. Chem. Phys.* **136**, 174109 (2012).

Minimum Energy Path Calculations Accelerated with Gaussian Process Regression

Vilhjálmur Ásgeirsson[1], **Freyja B. Dagbjartsdóttir**[1] , **Olli-Pekka Koistinen**[1,2,3], **Aki Vehtari**[2,3], **Hannes Jónsson**[1,3]

[1]*Science Institute and Faculty of Physical Sciences, University of Iceland, Dunhagi 3, Reykjavík, Iceland*
[2]*Department of Computer Science, Helsinki Institute for Information Technology, Aalto University, Espoo, Finland*
[3]*Department of Applied Physics, Aalto University, Finland*

The minimum energy path (MEP) connecting two local minima on a potential energy surface (PES) represents a transition path of maximal statistical weight, and the rise in energy along the path provides an estimate of the activation energy for the transition. The nudged elastic band (NEB) method[1] is a commonly used method for finding MEPs. There, paths are represented by a discrete set of system images connected by springs to control the spacing of the images. Starting with some initial path, the perpendicular component of the gradient and the parallel component of fictitious spring force are then collectively zeroed for all the intermediate images to converge on the nearest MEP. In tandem, a climbing image can be used to obtain rigorous convergence on the maximum along the path, a first order saddle point on the PES. NEB is routinely employed in combination with electronic structure methods, where a single calculation typically involves on the order of a hundred energy and gradient calculations per image to reach convergence. The calculations, therefore, require large computational resources. We have accelerated NEB calculations with Gaussian process regression (GPR)[2, 3]. An approximate energy surface (AES) is constructed locally near the path and refined iteratively by training the model with previous energy and gradient evaluations. The NEB calculations are performed on the AES and the images relaxed to new positions in each GPR iteration. Additional energy and gradient calculations are then carried out and fed to the GPR training set until convergence to the true MEP is reached. GPR is found to reduce the number of energy and gradient calculations in NEB calculations by an order of magnitude in well documented benchmark problems.[3]

[1] G. Henkelman, B. P. Uberuaga, H. Jónsson, *J. Chem. Phys.* **13**, 9901 (2000).

[2] O-P. Koistinen, E. Maras, A. Vehtari, H. Jónsson, *Nanosystems: Phys. Chem. Math.* **7**, 925 (2016).

[3] O-P. Koistinen, F. B. Dagbjartsdóttir, V. Ásgeirsson, A. Vehtari, H. Jónsson, *J. Chem. Phys.* (submitted, 2017).

Theoretical investigation into the enzymatic excision mechanism in AP endonuclease (Ape1)

Hossein Batebi, Petra Imhof.

Department Of Physics, Freie Universität Berlin, Arnimallee 14, Berlin, Germany

There is a plethora of studies looking at DNA repair systems, base-excision repair, nucleotide-excision repair, mismatch repair and double-strand break repair. In this project, we seek greater insights into base excision repair system. We investigate the mechanism by which human AP endonuclease cleaves the DNA backbone at abasic sites, the products of base excision by DNA glycosylases. AP endonuclease requiers a metal cofactor to be functional. However, the number of metal ions necessary for catalysis nor their precise role is known. In order to elucidate the enzymatic mechanism of AP endonuclease, we have performed reaction path calculations for a number of different mechanisms. In addition, molecular dynamics simulations have been successfully applied to study the role of AP-endonuclease (Ape1) active site residues in stabilization of the enzyme-DNA substrate complex.

Steering Orbital Optimization out of Local Minima and Saddle Points Toward Lower Energy.

Alain C. Vaucher[1], **Markus Reiher**[1]

[1]*ETH Zürich, Laboratorium für Physikalische Chemie, Vladimir-Prelog-Weg 2, CH-8093 Zürich, Switzerland*

In Hartree–Fock and Kohn–Sham density functional theory formalisms, the electronic density and the electronic energy of some molecular system are obtained in an iterative procedure that solves the Roothaan–Hall equations. It is often ignored that these equations can have multiple self-consistent solutions corresponding to different electronic energies. Whereas some of these solutions can be saddle points in the variational space of an electronic wave function approximation, they can also correspond to different local minima, of which only the one with the lowest energy is of interest. Converging to unwanted (i.e. high-energy) solutions delivers incorrect molecular properties, and, accordingly, a misleading description of chemical reactivity. In particular, consecutive calculations of closely related molecular structures, as in ab inito molecular dynamics or in interactive explorations of chemical reactivity [2, 3, 4, 5], are also affected by this problem. While stability analysis [6, 7] can detect saddle points by analyzing the local character of solutions, it cannot predict whether a solution is the global minimum or only a local minimum. Also, other methods such as electron smearing [8] can be very useful to improve convergence, but fail to reliably direct incorrect solutions to the one with the lowest energy. In order to detect and avoid convergence to incorrect electronic densities, we introduce a scheme relying on a randomized perturbation of the converged molecular orbitals, which is intended to push orbital convergence to other electronic densities (of potentially lower electronic energy) [9].

[1] R. P. Feynman, *Phys. Rev.* **56**, 340 (1939).

[2] K. H. Marti, M. Reiher, *J. Comput. Chem.* **30**, 2010–2020 (2009).

[3] M. P. Haag, M. Reiher, *Int. J. Quantum Chem.* **113**, 8–20 (2013).

[4] M. P. Haag, M. Reiher, *Faraday Discuss.* **169**, 89–118 (2014).

[5] M. P. Haag, A. C. Vaucher, M. Bosson, S. Redon, M. Reiher, *ChemPhysChem* **15**, 3301–3319 (2014).

[6] R. Seeger, J. A. Pople, *J. Chem. Phys.* **66**, 3045–3050 (1977).

[7] R. Bauernschmitt, R. Ahlrichs, *J. Chem. Phys.* **104**, 9047–9052 (1996).

[8] V. A. Basiuk, *Int. J. Quantum Chem.* **111**, 4197–4205 (2011).

[9] A. C. Vaucher, M. Reiher, *J. Chem. Theory Comput.* **13**, 1219–1228 (2017).

Soft Matter Morphologies with Atomistic Resolution from Coarse-Grain Solvent Evaporation Simulations

Riccardo Alessandri[1, 2], **Jaakko J. Uusitalo**[1, 2], **Alex H. de Vries**[1, 2], **Remco W. A. Havenith**[1, 3, 4], **Siewert J. Marrink**[1, 2]

[1] *Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*
[2] *Groningen Biomolecular Sciences and Biotechnology Institute, University of Groningen, Nijenborgh 7, 9747 AG Groningen, The Netherlands*
[3] *Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*
[4] *Ghent Quantum Chemistry Group, Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 (S3), B-9000 Gent, Belgium*

Control over the morphology of the active layer of bulk heterojunction (BHJ) organic solar cells is paramount to achieve high efficiency devices. However, no method currently available can predict morphologies for a novel donor:acceptor blend. An approach which allows to reach relevant length scales, retain chemical specificity, mimic experimental fabrication conditions, and which is suited for high-throughput schemes has been proven challenging to find. Here [1], we propose a multiscale method to generate atom-resolved morphologies of BHJs which conforms to these requirements. Coarse-grain (CG) molecular dynamics simulations are employed to simulate the large-scale morphological organization during solution-processing (Figure). The use of CG models which retain chemical specificity translates into a direct path to the rational design of donor and acceptor compounds which differ only slightly in chemical nature. Finally, the direct retrieval of fully atomistic detail is possible through backmapping (Figure, close up), opening the way for improved quantum mechanical calculations addressing the charge separation mechanism. The method is illustrated for the poly(3-hexyl-thiophene) (P3HT):phenyl-C61-butyric acid methyl ester (PCBM) mixture, and found to predict morphologies in agreement with experimental data. The effect of drying rate, P3HT molecular weight and thermal annealing are investigated extensively, resulting in trends mimicking experimental findings. The proposed methodology can help reduce the parameter space which has to be explored before obtaining optimal morphologies not only for BHJ solar cells but for any other solution-processed soft matter device.

[1] R. Alessandri, J. J. Uusitalo, A. H. de Vries, Remco W. A. Havenith, Siewert J. Marrink, *J. Am. Chem. Soc.* **139**, 3697 (2017).

Highly accurate dipole transition probabilities in molecules from finite-field relativistic multireference coupled cluster calculations.

Ephraim Eliav[1], Timur A. Isaev[2], Artur Kudrin[3], Alexander A. Medvedev[3], Leonid V. Skripnikov[2], Andrey V. Stolyarov[3], and Andrei Zaitsevskii[2,3]

[1]*School of chemistry, Tel-Aviv University, 69978 Tel-Aviv, Israel*

[2]*Department of Innovations, NRC KI – PNPI, 188300 Gatchina, Russia*

[3]*Chemistry Department, Moscow State University, 119991 Moscow, Russia*

Relativistic multireference coupled cluster (CC) methods are recognized as a robust and accurate tool for evaluating electronic transition energies in molecules containing heavy atoms. However, CC methods do not provide an explicit representation of many-electron wavefunctions, so that the direct estimate of the off-diagonal electric dipole matrix elements is not straightforward. The procedures employed to compute these entities through constructing transition density matrices are quite cumbersome and their implementation depends on the particular form of multireference CC theory. An attractive and universal alternative approach consists of evaluating transition dipoles by the finite-field technique [1], exploiting the approximate off-diagonal Hellmann-Feynman-like relations for effective operators and effective Hamiltonian eigenstates. This approach is based on the response of model space parts of many-electron wavefunctions to an external electric field. Nevertheless, the resulting transition moments incorporate implicitly the bulk of the contributions from the remainder (outer-space) part of these wavefunctions.

We report here an application of the finite-field technique in the frames of relativistic Fock-space coupled cluster methods to atoms, heavy alkali dimers, group II element halides and hydroxides, as well as to exciplexes formed by heavy alkali metal and rare gas atoms. The dependence of the resulting transition dipoles and lifetimes on the model space size is estimated and the stability of the finite-difference approximations for the derivatives with respect to the applied electric field strength is analyzed. The impact of effective spin-orbit interactions on radiative properties of the studied molecular systems is highlighted. The frontier implementation of computed transition probabilities for optimizing the laser synthesis of ultracold molecules and alkali metal - rare gas laser media is discussed.

The finite-field technique was implemented on the top of the DIRAC15 code [2].

[1] A. Zaitsevskii, A. P. Pychtchev, *Eur. Phys. J. D* **4**, 303 (1998).

[2] R. Bast, T. Saue, L. Visscher, H. J. Aa. Jensen, et al., DIRAC, a relativistic *ab initio* electronic structure program, release DIRAC15 (2015).

Trying to unravel the mechanisms of cytotoxicity for the $[Mo(\eta^3\text{-}C_3H_5)Br(CO)_2(phen)]$ complex: Intercalation vs. Groove Binding

Adrià Gil[1*], **Sawssen Elleuchi**[1,2], **Khaled Jarraya**[2], **Maria José Calhorda**[1*]

[1]*Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande 1749-016 Lisboa, Portugal*

[2]*Laboratory of Inorganic Chemistry UR11RS73, Faculty of Sciences of Sfax, 3000, Sfax, Tunisia*

Abstract: The interaction of the $[Mo(\eta^3\text{-}C_3H_5)Br(CO)_2(phen)]$ metal complex [1] with DNA has been studied at computational level by docking, recently developed semiempirical methods including dispersion and QM/MM methods. The $[Mo(\eta^3\text{-}C_3H_5)Br(CO)_2(phen)]$ metal complex exists as two main isomers in solution. Indeed, in one isomer phenanthroline (phen) is coordinated in the equatorial plane (Eq), whereas in the other one N of the phen is coordinated in an equatorial position and the other one in an axial position (Ax). Although the Eq structure is more stable, there is not a great difference between the energy of the isomers and we studied both systems, Eq and Ax, interacting with DNA trying to explain the experimentally found cytotoxicity.[1] We also took into account two different modes of interaction with DNA, that is, groove binding and intercalation, since such competition has been recently described in the bibliography for metal complexes with flat ligands interacting with DNA.[2-4] PM6-DH2 semiempirical method including dispersion and QM/MM methods by using M11L/6-31+G(d,p):AMBER were calibrated with the intercalated 1n37 structure of PDB and were observed to perform very well. On the other hand, for interaction of $[Mo(\eta^3\text{-}C_3H_5)Br(CO)_2(phen)]$ metal complex with the $(AGACGTCT)_2$ DNA octamer, it is observed that the $[Mo(\eta^3\text{-}C_3H_5)Br(CO)_2(phen)]$ metal complex prefers the intercalation rather than the groove binding for both isomers Eq and Ax. Moreover, also in both cases, intercalation via minor groove is more favored than through the major groove. However, it must be said that for the Ax isomer, although the most stable structure corresponds to an intercalated system through the minor groove, we found more structures intercalating via major groove in our analysis with the 100 most representative structures of the docking conformational search.

[1] D. Bandarra, M. Lopes, T. Lopes, J. Almeida, M. S. Saraiva, M. Vasconcellos-Dias, C. D. Nunes, V. Félix, P. Brandão, P. D. Vaz, M. Meireles, M. J. Calhorda, *J. Inorg. Biochem.* **104**, 1171 (2010).

[2] A. Mukherjee, R. Lavery, B. Bagchi, J. T. Hynes, *J. Am. Chem. Soc.* **130**, 9747 (2008).

[3] W. D. Sasikala and A. Mukherjee, *Phys. Chem. Chem. Phys.* **15**, 6446 (2013).

[4] D. Franco, A. V. Vargiu, A. Magistrato, *Inorg. Chem.* **53**, 7999 (2014).

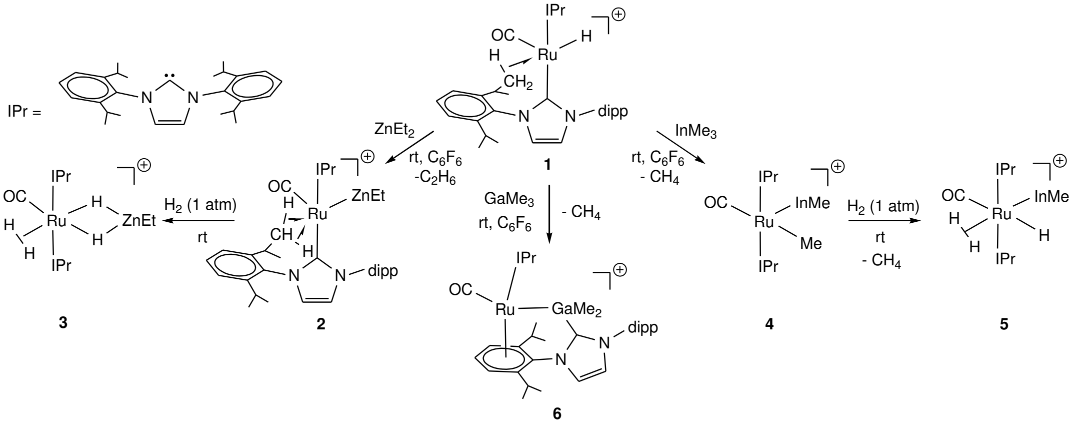
DFT Study of Heterobimetallic Complexes Derived from the e-deficient Ru-H Complex, $[Ru(IPr)_2(CO)H]^+$

Nasir A. Rajabi[1], Ian M. Riddlestone[2], John P. Lowe[2], Mary F. Mahon[2], Stuart A. Macgregor[1], Michael K. Whittlesey[2]

[1]*Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK*

[2]*Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, U.K*

Heterobimetallic complexes featuring transition metal (TM) and main group (MG) metals show great potential in the activation of small molecules.[1] Experimentally the cationic ruthenium hydride species **1** is a useful precursor to such species through reaction with MG-alkyls. For example, with $ZnEt_2$ elimination of ethane produces {Ru–Zn} species **2**.[1b] With $InMe_3$ methane is lost, but transfer of a second Me group to Ru also occurs to form {Ru-In} species **3**. With $GaMe_3$ methane is also lost, but in this case the IPr ligand transfers from Ru to Ga to give **6**. Both **2** and **6** then undergo H_2 activation reactions to produce **3** and **5**, respectively.



DFT calculations have been used to elucidate the formation mechanism of these Ru-MG heterobimetallic complexes. Our calculations show that formation of **2** and **4** involves one alkyl transfer from the MG centre to the Ru and an alkane reductive elimination step on the Ru centre to give the Ru^0-Zn^{II} and Ru^0-In^{III} species, respectively. Additionally, for the Ru^0-In^{III} species, the reductive elimination step induces a second alkyl transfer from the In centre to Ru to produce **4**. In comparison to **2** and **4**, formation of **6** occurs with initial IPr ligand transfer from Ru to Ga followed by Me transfer from the Ga to Ru. Reductive elimination of methane then forms a Ru^0-Ga^{III} intermediate from which one of the dipp rings of the IPr ligand to the Ga centre gives an η^6 interaction with Ru to produce the half-sandwich Ru complex **6**. H_2 activation across the Ru-Zn bond in **2** occurs homolytically and transfers two hydrides into the bridging position to give **3**. In contrast to **3**, H_2 activation in **4** proceeds with a sigma-bond metathesis step and forms **5** and methane.

[1] a) A. Maity, T. S. Teets, *Chem. Rev.*, **116**, 8873 (2016). b) I. M. Riddlestone, N. A. Rajabi, J. P. Lowe, M. F. Mahon, S. A. Macgregor, M. K. Whittlesey, *J. Am. Chem. Soc.*, **138**, 11081 (2016).

Central Fields from Jensen's Form

Jan Linderberg

Institute of Chemistry, Aarhus University, Langelandsgade 140, Aarhus C, Denmark

Jensen [1] formulated an energy functional for the Fermi-Thomas atom that included the Dirac exchange. A numerical procedure emanating from the finite element approach [2] is developed in order to search approximate solutions to central fields in spherical geometry.

It holds that the energy functional

$$J(q) = \int_0^\infty dr \left[\left(\frac{\mu}{e} - \frac{eZ_n}{r} \right) q + \frac{q\kappa_K}{e} \left(\sqrt[3]{\frac{q}{4\pi e r^2}} \right)^2 - \frac{q\kappa_A}{e} \sqrt[3]{\frac{q}{4\pi e r^2}} + \frac{e^2}{2} \left(\frac{dZ_e}{dr} \right)^2 \right]$$

is stationary for a consistently determined radial charge density $q = q(r)$ in a central field determined by an external, (nuclear), potential of the form $eZ_n(r)/r$. Coefficients κ_K and κ_A define the kinetic and exchange (*Austausch)* energy densities while the last term is the electron density self-interaction, $q = q(r) = -er[d^2 Z_e(r)/dr^2]$.

A modest implementation of the finite element method represents the derivative dZ_e/dr as a piecewise linear function

$$\frac{dZ_e}{dr} = \left(\frac{r_j - r}{r_j - r_{j-1}} \right) \frac{\zeta_{j-1}}{h} + \left(\frac{r - r_{j-1}}{r_j - r_{j-1}} \right) \frac{\zeta_j}{h}; \quad r_{j-1} \le r \le r_j.$$

All integrals are then accessible analytically and the functional becomes a function of the amplitudes:

$$J(q) \to J(\zeta_0, \zeta_1, \zeta_2, \dots \zeta_N).$$

Optimization of the function leads to third degree algebraic equations that provide a marching procedure on the grid of points $\{r_j \mid j = 0, 1, 2, \dots N\}$. Initial and final values warrant attention.

[1] H. Jensen, *Z. Physik.* **89**, 713 (1934), *ibid.* **93,** 232, 1935.

[2] P. G. Ciarlet, *The Finite Element Method for Elliptic Problems* (North-Holland, Amsterdam, 1980)

A Theoretical Study of CO Dissociation and C-C Bond Formation Mechanism on Fe(710)

Teng Li[1,2,3], **Haijun Jiao**[1,4]

[1]State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, China
[2]National Energy Center for Coal to Liquids, Synfuels China Co., Ltd., Huairou District, Beijing, 101400, China
[3]University of Chinese Academy of Sciences, No. 19A Yuquan Road, Beijing, 100049, P. R. China
[4]Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein Strasse 29a, 18059 Rostock, Germany

Abstract: Pure metals are often used as the simple model to investigate the mechanisms of Fischer-Tropsch Synthesis both experimentally and theoretically. However, the perfect surfaces of Fe(110), Co(0001) and Ru(0001) are inactive for CO dissociation [1] and prefers methanol formation on Co(0001) [2]. It is necessary to take the open or stepped surfaces into consideration. Spin-polarized DFT has been used to study CO dissociation by direct or H-assisted path, CHx (x = 1, 2) self-coupling and CO insertion on Fe(710). Our computational results show that CO prefers the fourfold site above the stepped site [3] and is more likely to break C-O bond directly rather than H-assisted activation. On Fe(710), CH_4 formation is neither kinetically nor thermodynamically favored. Among CHx hydrogenation ($CH+H \rightarrow CH_2$, $CH_2+H \rightarrow CH_3$) with self-coupling ($CH+CH \rightarrow C_2H_2$, $CH_2+CH_2 \rightarrow CH_2CH_2$) and CO insertion ($CH+CO \rightarrow HCCO$, $CH_2+CO \rightarrow H_2CCO$), HC and CO coupling is most likely. Finally, CO prefers direct dissociation and insertion into surface CH group for C-C formation on Fe(710).

[1] M. R. Elahifard, M. P. Jigato, J. W. Niemantsverdriet. ChemPhysChem. 13, 89 (2012).

[2] S. Liu, Y. Li, J. Wang, H. Jiao. Catal. Sci. Technol. 6, 8336 (2016).

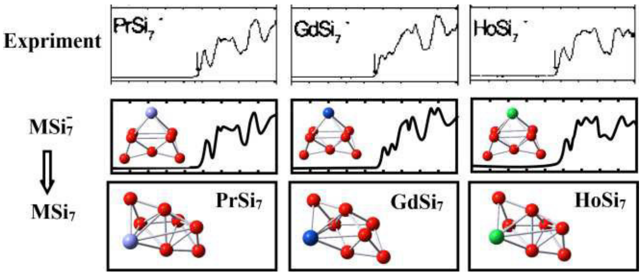
[3] D. C. Sorescu. J. Phys. Chem. C. 112, 10472 (2008).

Structural Assignment, Electronic and Magnetic Properties of $Si_7M^{0/-}$ with M = Pr, Gd, Ho

Tran Dieu Hang, Huynh Minh Hung and Minh Tho Nguyen[1]
Department of Chemistry, University of Leuven, B-3001 Leuven, Belgium

Abstract:

The ground state geometries of the neutral and anionic lanthanide-metal-doped silicon clusters $Si_7M^{0/-}$ with M = Pr, Gd, Ho were determined by quantum chemical computations and a detailed comparison with previous experimental photoelectron spectra. The hybrid B3LYP functional is found to be suitable for predicting the ground electronic states of lanthanide-metal-doped silicon clusters and reproducing their photoelectron spectra. All the most stable isomers are substitutive derivatives of the bicapped octahedron shape of pure $Si_8^{0/-}$ clusters. The bicapped octahedron Si_7M is generated by substituting one silicon atom on the D4h planar of octahedron by one M atom. Replacement of a Si atom on the C2 axis of another bicapped octahedron a lanthanide metal atom, where two capping Si atoms are situated in front of opposite triangular face on a side of the central square, gives rise to the anionic Si_7M^-. The limited participation of f-electrons of the lanthanide metal atoms on the valence electronic structure and thereby on the bonding of $Si_7M^{0/-}$ induces high magnetic moments of the doped clusters. As a consequence, not only $Si_7M^{0/-}$ but also $Si_nLn^{0/-}$ clusters are expected to be suitable building blocks for assembling silicon-based cluster materials with high magnetism.



[1] Hang, T. D.; Hung, H. M.; Nguyen, M. T, *Phys. Chem. Chem. Phys.* **2016**, *18* (31054).

Modelling Photoinduced Events and Non-Linear Spectroscopy in Complex Multichromophoric Systems

Francesco Segatta[1,2,*], L. Cupellini[3], S. Jurinovich[3], S. Taioli[1], M. Garavelli[2] and B. Mennucci[3]

[1]European Center for Theoretical Studies in Nuclear Physics and Related Areas (ECT-FBK), 38123 Trento, Italy*
[2]Dipartimento di Chimica Industriale "Toso Montanari", University of Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy
[3]Dipartimento di Chimica e Chimica Industriale, University of Pisa, via G. Moruzzi 13, 56124 Pisa, Italy
**francesco.segatta2@unibo.it*

Light-Harvesting (LH) Pigment-Protein Complexes in plants and photosynthetic bacteria, constitute the fundamental units through which sunlight is collected. The high complexity of such systems, where multiple interacting chromophores are embedded in a fluctuating protein matrix, makes it extremely difficult to study their response to external excitations. In this respect, non-linear electronic spectroscopies, such as the Two-Dimensional Electronic Spectroscopy (2DES), represent one of the most powerful techniques available [1]: high density of information is obtained, but to accurately disentangle all the measured signals and reach a detailed and reliable map of the energy transfer (ET) routes, it is mandatory to integrate the experimental measurements with theoretical models [2].

Here we introduce a fully Quantum-Chemistry based protocol to simulate and interpret linear and non-linear spectroscopy (2DES) of complex multichromophoric architectures of known structure. The proposed scheme relies on a QM/MM multi-scale approach [3], able to link single chromophore units with the entire molecular aggregate via a so called Frenkel Exciton Hamiltonian. This includes molecular vibrations and environmental fluctuations, eventually delivering the system's manifold of states and their relaxation pathways with very high accuracy. Application to the LH2 test case, employed here as a challenging playground, gives an unprecedented insight into the interpretation of the spectral signatures of the measured 2DES signals.

[1] T. Brixner, J. Stenger, H. M. Vaswani, M. Cho, R. E. Blankenship, G. R. Fleming, *Nature* **434**, 625 (2005).

[2] F. Segatta, L. Cupellini, S. Jurinovich, S. Mukamel, M. Dapor, S. Taioli, M. Garavelli, and B. Mennucci, *J. Am. Chem. Soc.* **139**, 7558 (2017).

[3] C. Curutchet, B. Mennucci, *Chemical Reviews* **117**, 294 (2016).

Localization errors and controllable sparsity in the coupled-cluster wave function for time-dependent response theory

R. Glenn, Andrew M. James, T. Daniel Crawford

Department of Chemistry, Virginia Tech, Blacksburg, Virginia, U.S.A.

A time-dependent framework for calculating the response of a large molecular system to an external field is motivated by the fact that the frequency-domain approach requires an efficient large-scale eigenvalue solver. Recent calculations show that the time-dependent framework provides more accurate spectra for higher energies and molecules with a large density of states [1,2]. Reduced scaling approaches to frequency-domain coupled-cluster response theory have shown localization errors and controllable sparsity in the wave function [3]. Here, we compare a time-dependent vs. frequency-dependent framework for the calculation of the linear response and examine the resulting localization errors and sparsity in the ground state wave function. Three different reduced-scaling coupled-cluster methods based upon projected atomic orbitals (PAOs), pair natural orbitals (PNOs), and orbital specific virtuals (OSVs) are employed to calculate the linear response in the time-domain. As a benchmark, we choose pseudo-linear structures such as fluoroalkane chains as well as three-dimensional structures where the localization errors are known to behave significantly differently [3].

[1] J. J. Goings and X. Li, *J. Chem. Phys.* **44**, 234102 (2016).

[2] D. R. Nascimento and A. E. DePrince, *J. Chem. Theory Comput.* **12**, 5834 (2016).

[3] H. R. McAlexander and T. D. Crawford, *J. Chem. Theory Comput.* **12**, 209 (2016).

Investigating π-acid-base interactions of supramolecular cyclic trinuclear coinage metal complexes

Fabian Bohle[1], **Stefan Grimme**[1], **Raiko Hahn**[2], **Birgit Esser**[2]

[1]*Mulliken Center for Theoretical Chemistry, Institut für Physikalische und Theoretische Chemie, Universität Bonn, Beringstraße 4, D-53115 Bonn, Germany*
[2]*Institut für Organische Chemie, Albert-Ludwigs-Universität Freiburg, Albertstr. 21, D-79104 Freiburg, Germany*

The detection of small, electron deficient, aromatic compounds is a task directly connected with π-acid-base interactions. To gain deeper understanding of these noncovalent interactions, the association free energies of electron rich cyclic trinuclear gold(I) complexes that are stacked with electron deficient systems are calculated and compared to experiment. In our quantum chemistry standard protocol [1] for calculating association free energies, ΔG_a is obtained as the sum of the electronic association energy ΔE, thermostatistical corrections to free energy (in gas phase) ΔG^T_{RRHO} and the solvation free energy $\Delta\delta G^T_{solv}$. All Geometries were preoptimized with the newly developed tight binding method GFN-xTB [2] and further refined with the global hybrid functional PBEh-3c [3]. Accurate single-point energies were obtained at the PW6B95-$D3^{ATM}$/def2-QZVP level. Thermostatistical corrections were evaluated at the same level of geometry optimization and solvation free energies were obtained with the implicit solvent model COSMO-RS.

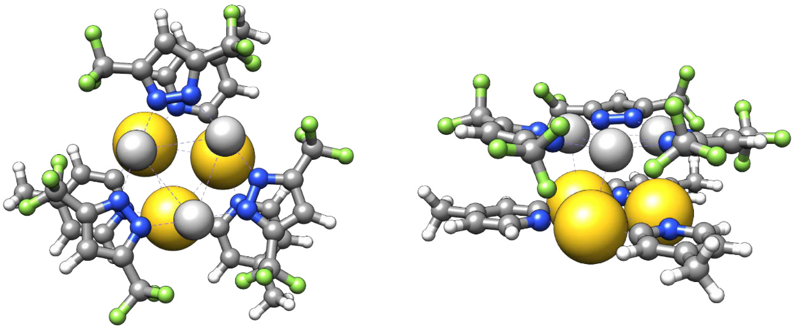


Figure 1: Complex of a pyridinate gold(I)-complex (π-base) stacked with a pyrazolate silver(I)-complex (π-acid), depicting top- and side-view.

[1] S. Grimme, *Chem. Eur. J.* **18**, 9955-9964 (2012).

[2] S. Grimme, C. Bannwarth, P. Shushkov, *J. Chem. Theory Comput.* **13**, 1989–2009 (2017).

[3] S. Grimme, J. G. Brandenburg, C. Bannwarth, A. Hansen, *J. Chem. Phys.* **143**, 054107 (2015).

Explicitly correlated electronic structure methods: progress towards increasing efficiency

Travis H. Thompson[1], **Christian Ochsenfeld**[1]

[1]*Department of Chemistry, University of Munich (LMU), Butenandtstr. 7,*
D-81377 Munich, Germany

Explicitly correlated methods aim to treat the shortcomings of wave function approximations built as Fock space expansions by introducing terms that depend explicitly on interelectronic distances. Such two-electron terms are able to describe short-range correlation much more efficiently than expansions using only one-electron orbitals, leading to relaxed basis set requirements. On the other hand, they lead to more complicated molecular integrals that have only rather recently been made computationaly feasible. We review some proven explicitly correlated methods already in widespread use and discuss their advantages compared to traditional methods. We also discuss some techniques recently developed for conquering the challenges that arise in explicitly correlated theories and describe our path towards further increases in efficiency.

Understanding Chemical Bonding in Terms of Electronic Correlations

G. Barcza[1], **Sz. Szalay**[1], **Ö. Legeza**[1], **T. Szilvási**[2], **L. Veis**[3], **E. Fertitta**[4], **B. Paulus**[4]

[1] *"Lendület" Research Group, Wigner Research Centre for Physics, Budapest, Hungary*
[2] *Department of Chemical and Biological Engineering, University of Wisconsin-Madison, US*
[3] *J. Heyrovsky Institute of Physical Chemistry, Prague, Czech Republic*
[4] *Institut für Chemie und Biochemie, Freie Universität Berlin, Germany*

Quantum information theory (QIT) emerged in physics as standard technique to investigate effective models of interacting quantum systems. The success of the method arises the question what we can learn from QIT applying it to molecules which are inherently quantum systems as well [1]. By the rigorous analysis of the central quantities of standard QIT, which describes bonding purely in terms of two-orbital correlations, we identify covalent bond, donor-acceptor dative bond, multiple bond, charge-shift bond indicating unified picture of fundamental chemical models from ab initio [2].
In order to give a better description of more complicated multiple bonds and aromaticity, we introduce the genuine multiorbital correlation theory, consisting of a framework for handling the structure of multiorbital correlations, a toolbox of true multiorbital correlation measures, and the formulation of the multiorbital correlation clustering, together with an algorithm for obtaining that. These make it possible to quantify the correctness of the associated ”naive” bonding picture. As proof of concept, we apply the theory for the investigation of the bond structures of several molecules. We show that the non-existence of well-defined multiorbital correlation clustering provides a reason for debated bonding picture of the dicarbon [3].

[1] E Fertitta, B Paulus, G Barcza, Ö Legeza *Phys. Rev. B* **90** (24), 245129 (2014)

[2] T. Szilvási, G. Barcza, Ö. Legeza *submitted to Scientific Reports* arXiv:1509.04241

[3] S. Szalay, G. Barcza, T. Szilvási, L. Veis. Ö. Legeza, *Scientific Reports* **7**, 2237 (2017).

Proton Coupled Electron Transfer and Competing Mechanisms in Free Radical Reactions in Aqueous Solutions

Ivana Nikšić-Franjić,[1] Iva Džeba,[2] Marija Bonifačić,[1] Aleksandar Sabljić,[1] Ivan Ljubić[1]

[1]Department of Physical Chemistry, Ruđer Bošković Institute, Zagreb, Croatia
[2]Department of Materials Chemistry, Ruđer Bošković Institute, Zagreb, Croatia

Reactions of dehalogenation of haloorganic substrates induced by small α-hydroxyalkyl and α-aminoalkyl alkyl free radicals in aqueous solutions are found to exhibit a rich variety of closely competing mechanisms, notably proton-coupled electron transfer (PCET), hydrogen atom transfer (HAT), free radical substitutions, abstractions and additions, etc. We present combined experimental and theoretical studies of the mechanisms and kinetics of reactions between several such free radicals derived from ethanol, 2-propanol, ethylamine, N-ethylmethylamine, and anionic glycine, with various halogenated organics, such as alkyl-halides, haloacetates, 5-bromouracil, and iodoacetamide. The reactions are conducted in non-buffered and buffered (bicarbonate and phosphate buffer systems) aqueous solutions, in which the free radicals are generated by the process of γ- or pulse radiolysis. We test the predictions of a range of density functionals against the experimental product yields and reaction rate constants. The water solvent is modeled as the polarizable continuum (PCM) with the addition of one explicit water molecule at the most. These reaction systems, while being much simpler than the usual context of PCET (e.g. catalysis, biochemistry), prove to be especially suited for studying this fundamentally important mechanism because the unambiguous fingerprint of the PCET is a radical chain reaction which considerably enhances the dehalogenation yields. Also, the contribution due to the PCET can be handily controlled because it crucially depends on the proton accepting affinity of the buffer anion. Since the main thermodynamic pull for the PCET is the formation of the corresponding carbonyl or imine double bond, the choice of the alcohol (amine) precursor provides yet another means of the reaction control. The extra water molecule is seen to introduce new relevant reaction channels, such as the water assisted PCET. The kinetics of these fast reactions is difficult to model accurately because the dominant channels are typically characterized by the negative apparent activation energies. The best results for the reaction barriers and rate constants are provided by the double hybrid density functionals.

[1] P. Neta, J. Grodkowski, A. B. Ross, *J. Phys. Chem. Ref. Data* **25**, 709 (1996).
[2] I. Ljubić, B. Matasović, M. Bonifačić, *Phys. Chem. Chem. Phys.* **15**, 18001 (2013).
[3] I. Ljubić, A. Sabljić, M. Bonifačić, *J. Phys. Chem. B* **120**, 11810 (2016).

Modelling Pt^{II}(Ligand) – Amyloid-β Interactions: Prediction of Ligand Effects

Matthew Turner[1], **Robert J. Deeth**[2], **James A. Platts**[1]

[1]*School of Chemistry, Cardiff University, Park Place, Cardiff, UK*
[2]*Department of Chemistry, University of Warwick, Gibbet Hill, Coventry, UK*

Alzheimer's disease (AD) is a neurodegenerative condition associated with progressive cognitive decline in patients. The causes and development of AD are poorly understood, but one hallmark of AD is the presence of amyloid plaques. The early stages of the Aβ aggregation process have therefore become a target for the development of AD-therapeutics [1]. The N-terminal domain of Aβ contains His-rich high-affinity metal binding sites, responsible for physiological coordination of Cu^{II}/Zn. One route to AD-therapeutics involves disrupting coordination by using compounds that occupy these binding sites, hindering the Aβ aggregation process. Recently, Barnham *et al.* showed that Pt^{II}(phenanthroline) complexes inhibit Aβ aggregation and limit its neurotoxicity *in vitro* [2].

In this work, Ligand Field Molecular Mechanics (LFMM), DFT and semi empirical methods are applied to a series of Pt^{II}-Ligand systems binding to the N-terminal domain of the Aβ peptide. Molecular dynamics (LFMM/AMBER) is used to explore the conformational freedom of the peptide fragment, and identifies favourable Pt^{II}-binding modes and peptide conformations. Pt^{II} coordination depends on the nature of the ligand, providing evidence that binding mode may be controlled by ligand design. Structural analysis of the sampled Pt^{II}-Aβ conformations shows that platinum coordination disrupts existing secondary structure in Aβ and promotes formation of ligand-specific turn-type secondary structure. [3][4]

References:

[1] D. Valensin, C. Gabbiani, L. Messori, *Coord. Chem. Rev.,* **256**, 2357, (2012).

[2] K.J. Barnham, V.B. Kenche, G.D. Ciccotosto, D.P. Smith, D.J. Tew, X. Lu, K.Perez, G.A. Cranston, T.J. Johanssen, I. Volitakis, A.I. Bush, C.L. Masters, A.R. White, J.P. Smith, R.A. Cherny, R. Cappai, *Proc. Natl. Acad. Sci. U.S.A.,* **105**, 6813, (2008).

[3] M. Turner, J.A. Platts and R.J. Deeth, *J. Chem. Theory Comput.,* **12**, 1385, (2016).

[4] M. Turner, R.J. Deeth and J.A. Platts, *J. Inorg. Biochem.,* **173**, 44, (2017).

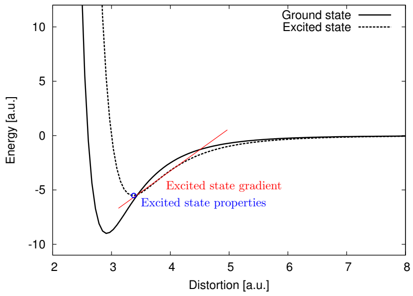
Double residues of response functions in density matrix-based response theory

Daniel H. Friese[1], **Kenneth Ruud**[2]

[1]*Institut für Theoretische und Computerchemie, Heinrich-Heine-Universität Düsseldorf,*
Universitätsstraße 1, 40225 Düsseldorf, Germany
[2]*Centre for Theoretical and Comutational Chemistry, University of Tromsø, Hansine Hansens*
veg 18, 9037 Tromsø, Norway

The calculation of excited state molecular properties such as gradients, dipole gradients and Hessians is a challenge for quantum chemistry due to the complexity of the fundamental expressions which increases dramatically with the property order. In recent years, the framework of density matrix-based response theory has proven to offer a very efficient tool for the calculation of higher-order molecular properties as it can be formulated in an open-ended recursive algorithm[1] which reduces programming effort for higher-order properties to a negligible level. For both response functions (ground state molecular properties)[2] and single residues (transition properties between the ground and excited states)[3, 4] this technique has allowed to study e.g. multidimensional vibrational spectroscopy, multiphoton absorption and multiphoton circular dichroism.

We will now present a first extension of this framework to double residues which will allow for calculations of both excited state molecular properties and transition moments between excited states. This approach requires some changes in the fundamental theory. The first of these will be presented for first- and second-order excited state properties.



[1] M. Ringholm, D. Jonsson, K. Ruud, *J. Comput. Chem.* **35**, 622 (2014).

[2] Y. Cornaton, M. Ringholm, O. Louant, K. Ruud, *Phys. Chem. Chem. Phys* **18**, 4201 (2016).

[3] D. H. Friese, M. Beerepoot, M. Ringholm, K. Ruud, *J. Chem. Theo. Comput.* **11**, 1129 (2015).

[4] D. H. Friese, M. Ringholm, B. Gao, K. Ruud, *J. Comp. Chem.* **11**, 1184 (2015).

Hydrogenation of Carbon Dioxide over Magnesium and Copper Alkoxide-Functionalized Metal-Organic Framework

Daniela Guzmán-Angel[1], **Soledad Gutiérrez-Oliva**[1], **Alejandro Toro-Labbé**[1]

[1] *Laboratorio de Química Teórica Computacional (QTC), Facultad de Química, Pontificia Universidad Católica de Chile, Av. Vicuña Mackenna 4860, Macul, Santiago, Chile*

In recent years, many approaches have been proposed and developed to reduce emissions [1, 2], immobilization of CO_2 via hydrogenation to form formic acid (HCOOH) has been revealed as one of the most promising strategies [3–5]. In addition, catalytic hydrogenation provides a variety of useful compounds for fine chemistry and industrial applications [6].

In this work, we have studied the reaction mechanism of hydrogenation of carbon dioxide catalyzed by magnesium and copper alkoxide-functionalized metal-organic framework (Mg-MOF-5 and Cu-MOF-5). The aim of this study is to compare the mechanism involved between the reaction with and without catalyst, and between both alkoxide, to understand how these influence the reaction. Both reactions, with and without catalyst, proceed via stepwise mechanism; however, a more detailed analysis of the electronic activity during the reaction shows that they are different. Transition states and energy barriers are discussed in terms of the reaction force analysis (RFA) and Marcus equation. Equilibrium and rate constants are determined and their physical nature is unveiled.

All the systems are characterized computationally using Density Functional Theory (DFT) with the methodology M06-L and the basis set 6-31G(d,p) for H, C and O, while the Mg and Zn atoms were described with the LANL2ZD pseudopotentials basis set. All calculations were performed with Gaussian 09 [7].

Acknowledgments: This work was supported by FONDECYT through project 1141098 and CONICYT-PCHA/Doctorado Nacional/2016-21161202 fellowship.

[1] D. Aaron and C. Tsouris, *Sep. Sci. Technol.*, **40**(1-3), 321 (2005).

[2] H. Q. Yang, Z. H. Xu, M. H. Fran, R. Gupta, R. B. Slimane, A. E. Bland and I. Wright, *J. Environ. Sci. (China)*, **20**(1),14 (2008).

[3] G. Féerey, *Chem. Soc. Rev.*, **37**, 191 (2008).

[4] T. Maihom, S. Wannakao, B. Boekfa and J. Limtrakul, *J. Phys. Chem. C*, **117**, 17650 (2013).

[5] C. Federsel, R. Jackstell and M. Beller, *Angew. Chem., Int. Ed.*, **49**, 6254 (2010).

[6] W. Wang, S. Wang, X. Ma and J. Gong, *Chem. Soc. Rev.*, **40**, 3703 (2011).

[7] M. J. Frisch et al., *Gaussian 09*, Rev B01, Gaussian, Inc., Wallingford CT (2010).

Efficient Implementation of the Approximate Exchange Kernel Method

Guo P. Chen, Matthew M. Agee, Filipp Furche

Department of Chemistry, University of California, Irvine, 1102 Natural Sciences II, Irvine, USA

The approximate exchange kernel (AXK) method is the leading correction to the random-phase approximation (RPA) for the ground-state correlation energy functional within RPA-renormalized many-body perturbation theory [1, 2]. However, the relatively high computational cost of AXK has hampered its widespread application in the past. In practice, it is important to strike a balance between favorable computational scaling with system size N and a small prefactor. Here we present two AXK algorithms with asymptotic scaling of $O(N^4 \ln N)$ and $O(N^5 \ln N)$, respectively. Both algorithms take advantage of the resolution-of-the-identity (RI) approximation and imaginary frequency integration. For systems with up to approximately 100–200 atoms, applications to alkene chains illustrate that the $O(N^5 \ln N)$ algorithm is more efficient than the integral-direct $O(N^4 \ln N)$ algorithm. The new RI-AXK implementation in TURBOMOLE enables correlation energy calculations for molecules with well over 100 atoms on a single cluster node.

[1] J. E. Bates, F. Furche, *J. Chem. Phys.* **139**, 171103 (2013).

[2] G. P. Chen, V. K. Voora, M. M. Agee, S. G. Balasubramani, F. Furche, *Annu. Rev. Phys. Chem.* **68**, 421 (2017).

Many-Fermion Tunneling Through a Barrier

Elke Fasshauer[1], **Axel Lode**[2]

[1]*Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen, Denmark*

[2]*Department of Physics, University of Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland*

The tunneling of one electron through a potential is analytically solvable and a quantum mechanics textbook example. But what happens, if not only one electron is involved, but several electrons are trapped? To answer this basic question, the quantum dynamics of two electrons were studied using the Multi-Configurational Time-Dependent Hartree for Fermions (MCTDHF) method [1] implemented in the MCTDH-X program package [2]. This method allows for a numerically exact description.

We show that the fermions tunnel through the barrier individually, while they escape over the barrier collectively [3].

[1] O. E. Alon, A. I. Streltsov, L. S. Cederbaum, *J. Chem. Phys.* **127**, 154103 (2007).

[2] A. U. J. Lode, M. C. Tsatsos, E. Fasshauer, The Multiconfigurational Time- Dependent Hartree for Indistinguishable Particles X package (2015), http://ultracold.org.

[3] E. Fasshauer, A. U. J. Lode, *J. Phys. Rev. A* **93**, 033635 (2016).

Quantitative analysis of axial chirality in biaryl and related compounds

Inbal Tuvi-Arad

Department of Natural Sciences, The Open University of Israel, Raanana 4353701, *Israel*

Axial chirality of biaryl compounds is an important phenomenon in chemistry, particularly in the context of biological activity and catalysis. Here we apply the method of continuous symmetry and chirality measures to quantify the level of distortion of each structure and estimate the abundance of this type of chirality. For this purpose the coordinates of thousands of derivatives of biaryl compounds as well as other compounds with hindered rotation were extracted from the Cambridge crystallographic database and their distortion levels were evaluated. In addition, symmetry maps, (e.g., Figure 1 for biphenyl) were used to identify structural distortion paths. DFT calculations in the gas phase were performed in order to explore the relation between energy and chirality. Almost all molecules in our study are chiral to some degree. Additional analysis of biaryl ligands extracted from the protein data bank shows that the degree of chirality in such compounds can reach high levels, similarly, and sometimes even higher than related compounds with chiral centers. Implications of the interplay between structural flexibility and chirality are discussed.

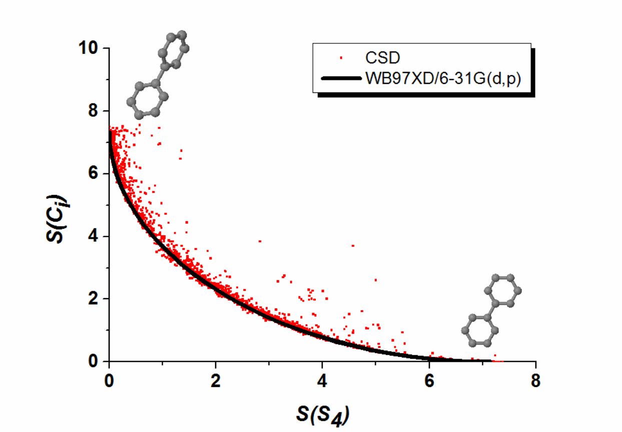


Figure 1. Symmetry map based on 2345 organic derivatives of biphenyl. $S(C_i)$ represents the distance of each structure from the planar conformer. $S(S_4)$ represents the distance of each structure from the perpendicular conformer. Red dots - Cambridge crystallographic data. Black line - distortion along the minimum energy path in the gas phase.

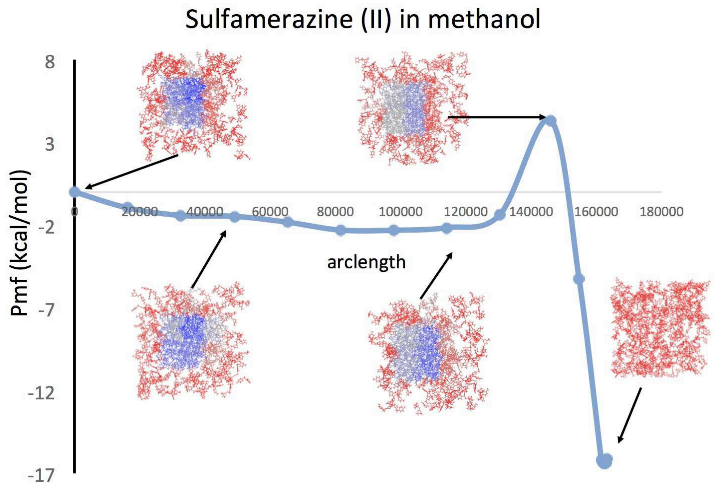
Understanding the Crystallization Tendency of Sulfadiazine and Sulfamerazine in Different Solvents

Chenxiang Liu[1]**, Erik E. Santiso**[1] **and Geoffrey P. F. Wood**[2]

[1]*Department of Chemical & Biomolecular Engineering, North Carolina State University, Raleigh, NC, USA.*

[2]*Pfizer Global Research and Development, Eastern Point Road, Groton, CT, 06340, USA*

Crystallization from solution is fundamental to the pharmaceutical industry where most products consist of molecular crystals. The arrangement of molecules in the crystal lattice determines a number of key quality attributes such as solubility, bioavailability and manufacturability and so greatly influences processing and formulation of solid pharmaceutical products. However, under traditional drug discovery paradigms consideration of the molecular crystal typically comes after the chemical entity has been fixed. At times, this results in a large amount of resources being expended on candidate drug molecules with poor solid-state properties. Computational methods focused on determining the likelihood that a new chemical entity can be successfully crystallized have the potential for alleviating this burden. To this end, we seek to understand the crystallization tendency of two model drug molecules: sulfamerzine and sulfadianze. We employ the string method in collective variables[1] along with Santiso-style crystal order parameters[2]. Using this methodology we calculate minimum free energy pathways of the nucleation process in three different solvents. Calculated barriers are compared with experiments that measure the nucleation induction times at various supersaturations. We describe the important similarities and differences between the two different systems and their interactions with the three solvent systems.



---

[1] L. Maragliano, A. Fischer, E. Vanden-Eijnden, G. Ciccotti, *J. Chem. Phys.*, **125**, 024106 (2006).

[2] E. E. Santiso, et al. *J. Chem. Phys.*​**134**, 064109 (2011).

Generalized coupled-cluster approaches for quantum simulation of strongly correlated system.

Jhonathan Romero[1], **Hannah Sim**[1], **Libor Veis**[2], **Gian Giacomo Guerreschi**[3], **Alán Aspuru-Guzik**[1]

[1]Department of Chemistry and Chemical Biology. Harvard University. 12 Oxford Street, Cambridge MA, 02138
[2]Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Dolejškova 3, 18223 Prague 8, Czech Republic
[3]Intel Labs, Santa Clara, California 95054, United States

Quantum computers are becoming large enough to perform tasks beyond the capabilities of the biggest quantum supercomputers. The first generation of quantum machines are expected to have between 50 to 100 qubits and being able to execute thousands of quantum operations, however, they will lack error-correction. To exploit these “pre-threshold” machines as quantum simulators for chemistry, we need algorithms that are relatively robust to machine noise and can be run using fewer gates. One example of such algorithms is the variational quantum eigensolver (VQE) [1,2]. In this approach, quantum states are prepared based on a given ansatz followed by the measurement of the energy on the quantum computer. The information of the energy is then used to optimize the variational parameters associated to the ansatz using a classical optimization routine. Traditionally, single-reference unitary coupled cluster [1-4] has been used as the canonical ansatz for chemistry simulations. In this work, I present an extension of the unitarity coupled cluster approach to multireference cases. Our method is based on the preparation of an entangled initial state, obtained using classical density matrix renormalization group (DMRG) approaches, followed by the application of a generalized unitary coupled cluster implementation (GUCCI), where all the possible excitation operators are considered. We present numerical simulations of the quantum algorithm for the Hubbard model and a variety of strongly correlated molecular systems.

[1] A. Peruzzo, J.R. McClean, P. Shadbolt, M-H. Yung, X-Q. Zhou, P.J. Love, A. Aspuru-Guzik, and J.L. O'brien, "A variational eigenvalue solver on a quantum processor," *Nat. Commun.* **5**, 4213 (2014).

[2] J. R. McClean, J. Romero, R. Babbush, and A. Aspuru-Guzik, *New. J. Phys.* **18,** 023023 (2016).

[3] M-H. Yung,, J. Casanova, A. Mezzacapo, J. McClean, L. Lamata, A. Aspuru-Guzik, and E. Solano. *Sci. Rep.* **4**, 3589 (2014).

[4] J. Romero, R. Babbush, J.R. McClean, C. Hempel, P. Love, and A. Aspuru-Guzik, arXiv:1701.02691 (2017).

A consistent molecular model to predict the behavior of early tetravalent actinides.

E. Acher[1], D. Guillaumont[1], M. Masella[2], V. Vallet[3], F. Réal[3]

[1]CEA / Nuclear Energy Division / Research Department on Mining and Fuel Recycling / SPDS / LILA,BP 17171 F-30207, Bagnols sur Cèze, France
[2]CEA / DRF/JOLIOT/SB2SM/LBSR, Centre CEA de Saclay, 91191, Gif sur Yvette, France
[3]Univ. Lille, CNRS / UMR 8523 / PhLAM - Physique des Lasers Atomes et Molecules, F-59000 Lille, France

The aim of the present study is to investigate and revisit the behavior of early tetravalent actinides, from thorium to plutonium in aqueous solution by the use of classical mechanics simulations; the latter element having not been studied by this modeling approach so far. While spectroscopy provides a good insight into the interatomic distances, the hydration structure, exchange dynamics and coordination numbers remain quite inaccurate [1]. Our objective is to probe the local structure and explore the trends along the early actinide series in the bulk conditions with molecular dynamics (MD) simulations that allows us to monitor the dynamics of a hydrated actinide in bulk conditions on a long-time scale (> 10 ns). However, the reliability of the MD results entirely depends on the quality of the force-field (FF), i.e., the description of the interaction between the solute and the solvent (An/water molecule interaction), and also on the description of the solvent properties. We propose an innovative FF model that accounts, not only for the standard electrostatic and repulsion interactions, but also for polarization and charge-transfer terms, many-body effects, and explicit hydrogen bonds in the water/water interactions.

Pursuing the efforts initiated by Réal *et al.* to simulate the Th(IV) and Cm(III) in aqueous solution [2,3,4], we present here a consistent FF model adjusted to state-of-the-art *ab initio* calculations, i.e., without using any experimental input, for the early tetravalent actinides series (Th, Pa, U, Np, Pu), and the associated results coming from bulk simulations. The average actinide/water distances almost perfectly agree with the reported EXAFS/HEXS values and our MD simulations predict that all early actinides hold 10 water molecules in their first hydration sphere. These results represent a first step towards a better description of these elements in solution or at interface.

[1] K. E. Knope, L. Soderholm, *Chem. Rev.* **113**, 944 (2013).

[2] F. Réal, V. Vallet, J. P. Flament, M. Masella, *Chem. Phys.* **16**, 139 (2013).

[3] F. Réal, M. Trumm, V. Vallet, B. Schimmelpfennig, M. Masella, J. -P. Flament, *J. Phys. Chem. B* **114**, 15913 (2010).

[4] F. Réal, M. Trumm, B. Schimmelpfennig, M. Masella, V. Vallet, *J. Comput. Chem.* **34**, 707 (2013).

The PNO-MP2 Gradient and its Application to Molecular Geometry Optimizations

Marius S. Frank[1], **Gunnar Schmitz**[2] , **Christof Hättig**[1]

[1]*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Universitätsstrasse 150, Bochum, Germany*
[2]*Department of Chemistry, Aarhus University, Aarhus C, Denmark*

Pair Natural Orbitals (PNOs) offer a systematic way to exploit the sparsity in the dynamical electron correlation by a truncation of the virtual space using a single user-defined threshold T_{PNO}. The very compact representation of the virtual space spanned by PNOs (provided a localized occupied space) enables the development of reduced scaling local counterparts to well-established canonical methods.

Due to the fact that the error of the PNO approxmation in energies has already been intensively investigated, the next natural step is to determine the performance of PNOs on the determination of equilibrium geometries and molecular properties.

Here, an implementation of the PNO-MP2 gradient is presented, in which the PNOs are iteratively constructed from orbital specific virtuals (OSVs) to reduce the computational demands of the PNO construction.

The gradient is applied to geometry optimizations of a wide variety of molecules and clusters. The accuracy of PNO-MP2 in the description of bond lengths and bond angles is then investigated by carrying out a statictical analysis of the errors with respect to canonical RI-MP2.

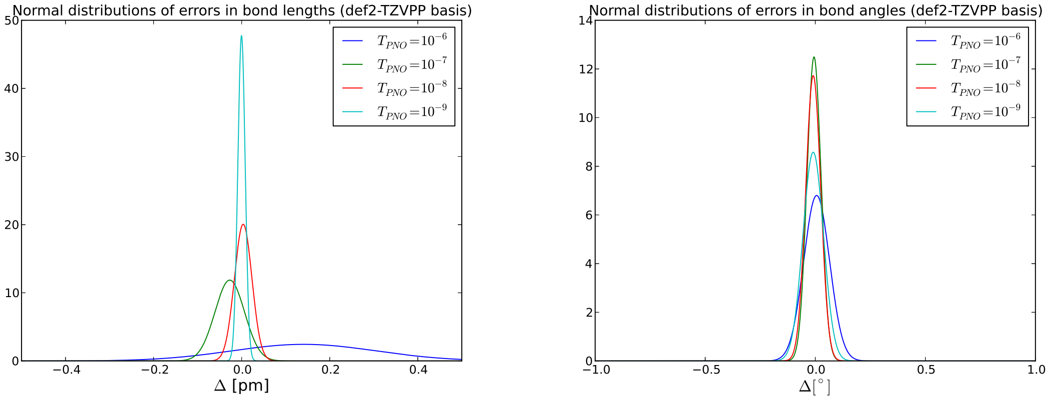


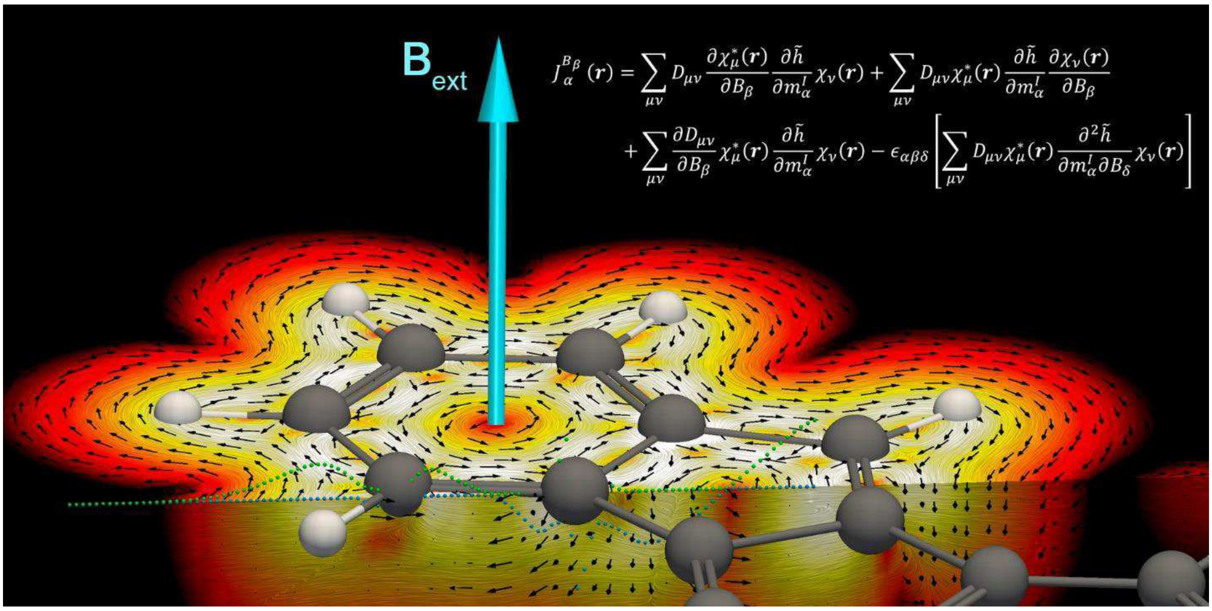
Figure 1: Normal distributions of errors in bond lengths and bond angles in Baker's test set for geometry optimizations.

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

Maria Dimitrova[1], **Heike Fliegl** [2], **Dage Sundholm**[1]

[1]Department of Chemistry, University of Helsinki, A. I. Virtasen aukio 1, 00014 Helsinki, Finland
[2] Centre for Theoretical and Computational Chemistry (CTCC), Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, 0315 Oslo, Norway.

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



$$J_\alpha^{B_\beta}(\boldsymbol{r}) = \sum_{\mu\nu} D_{\mu\nu} \frac{\partial \chi_\mu^*(\boldsymbol{r})}{\partial B_\beta} \frac{\partial \tilde{h}}{\partial m_\alpha^I} \chi_\nu(\boldsymbol{r}) + \sum_{\mu\nu} D_{\mu\nu} \chi_\mu^*(\boldsymbol{r}) \frac{\partial \tilde{h}}{\partial m_\alpha^I} \frac{\partial \chi_\nu(\boldsymbol{r})}{\partial B_\beta}$$
$$+ \sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial B_\beta} \chi_\mu^*(\boldsymbol{r}) \frac{\partial \tilde{h}}{\partial m_\alpha^I} \chi_\nu(\boldsymbol{r}) - \epsilon_{\alpha\beta\delta} \left[\sum_{\mu\nu} D_{\mu\nu} \chi_\mu^*(\boldsymbol{r}) \frac{\partial^2 \tilde{h}}{\partial m_\alpha^I \partial B_\delta} \chi_\nu(\boldsymbol{r}) \right]$$

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

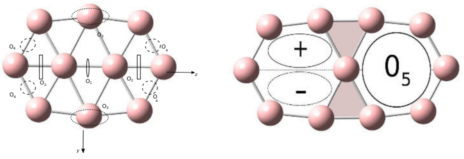
[1] D. Sundholm, H. Fliegl and R. J. Berger, *WIREs Comput. Mol Sci.* **639** (2016).
[2] M. Dimitrova, H. Fliegl, D. Sundholm, *PCCP* (2017) (manuscript).

Valence bonds in elognated boron clusters

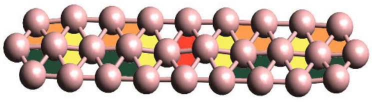
Athanasios G. Arvanitidis[1], **Kie Zen Lim**[1, 2], **Remco W.A. Havenith**[2, 3], **Arnout Ceulemans**[1]

[1]*Quantum Chemistry and Physical Chemistry Section Celestijnenlaan 200f - box 2404 3001 Leuven, Theoretical Chemistry*
[2]*Zernike Institute for Advanced Materials and Stratingh Institute for Chemistry, University of Groningen, 9747 AG Groningen, The Netherlands*
[3]*Ghent Quantum Chemistry Group, Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 (S3), B-9000 Gent, Belgium*

Boron is the new carbon. As opposed to carbon, it adopts multi-center bonding patterns, thus challenging the traditional valence bond approaches. Especially planar and bowl shaped boron clusters are well documented in the literature[1]. This poster presents the comparison between valence bonds in hydrocarbons and a well-defined family of the so-called elongated boron clusters of type B_{7+3n}^{q-}. The origin of the series is the B_7^- anion, which is extended repeatedly by B_3 units along a given direction up to B_{28}^-. Electron counting rules for σ and π bonding are introduced and the multi-center inner-bonding motif is explored and explained[3]. Using AdNDP[2], the inner electronic structure of these clusters is examined, rationalizing the tendency of boron to adopt delocalized 4c-2e bonds. Resonance is recognized as the key element to explain the bonding of the inner framework. To prove our hypothesis of 4c-2e bonds, the group-theoretical induction method is used. It describes the symmetries of the molecular orbitals as a binary code, which is found to be fully consistent with the ab initio results. The combination of the induction method and the 4c-2e scheme provides a clear valence bond scheme for these elongated clusters.



Orbits 0_1 to 0_5



B_{28}^{2-} cluster with C_{2h} symmetry

[1] Alina P. Sergeeva, Ivan A. Popov, Zachary A. Piazza, Wei-Li Li, Constantin Romanescu, Lai-Sheng Wang and Alexander I. Boldyrev, *Acc.Chem.Res*, **4**, 1349-1358 (2014)

[2] Dmitry Yu. Zubarev and Alexander I. Boldyrev, *Phys. Chem. Chem. Phys* ,**34**, 5207-5217 (2008)

[3] Athanasios G. Arvanitidis, Truong B. Tai, Minh Tho Nguyen and Arnout Ceulemans, *Phys.Chem.Chem.Phys.*, **34**, 18311-18318 (2014)

Complexation of some divalent cations with morin: a spectroscopic and theoretical study

Aurélien Moncomble, Diksha Jani Thaviligadu, Jean-Paul Cornard

Univ. Lille, CNRS, UMR 8516 - LASIR - Laboratoire de Spectrochimie Infrarouge et Raman, F-59000 Lille, France
aurelien.moncomble@univ-lille1.fr

Flavonoids are compounds that are involved in the secondary metabolism of several higher vegetables. Then their presence in the environment is very common and their interaction with others species such as cations is likely.

In previous studies, we have developed a methodology that deeply associates the electronic spectra measurements and quantum chemistry computations to determine the preferential fixation site of the cation [1,2]. In this study, we focused on the reactivity of morin, a well studied flavonoid, with zinc (II). This system had been previously studied but no consensus was obtained on the binding site. Then we applied our methodology to this system to determine more precisely the stoichiometry of the actual complex, its binding site along with the coordination sphere.

Density functional theory (DFT) based optimizations of conceivable structures, followed by time dependent computations of the electronic transitions, lead to UV-visible spectra that were compared with the experimental ones, obtained from chemometrics treatment of the experimental data.

An important aspect of these computations was the precise description of the solvent. Indeed, the solvent molecules present in the coordination sphere of the cation also act as ligands, so the description of the complex solvation needs a hybrid model associating microsolvation around the cation with an implicit model at larger distance

This methodology associating experiments and computations shed light on the morin-zinc (II) system and determined the nature of the actual complex formed in theses conditions. Following these results, the same methodology was applied to the study to manganese (II) complexation and these results will be presented.

[1] J. P. Cornard, L. Dangleterre, C. Lapouge, *J. Phys. Chem. A* **109**, 10044 (2005).
[2] A. Moncomble, J. P. Cornard, *RSC Adv.* **4**, 29050 (2014).

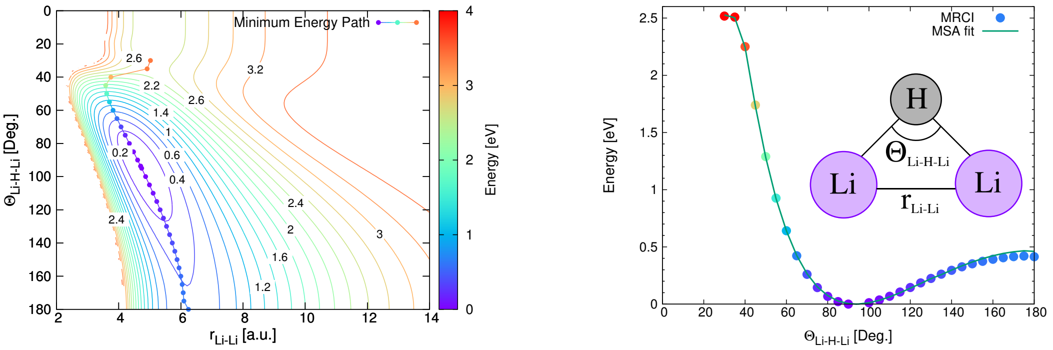
Li_2H vibrational energy levels from a new global ab initio potential energy surface

Michiko Ahn-Furudate[1,2], **Denis Hagebaum-Reignier**[1], **Gwang-Hi Jeung**[1]

[1] *Institut des Sciences Moléculaires de Marseille, Department of Chemistry, Aix-Marseille University, Marseilles, France*
[2] *Deptartment of Mechatronics Engineering, Chungnam National University, Daejeon, Republic of Korea*

In this work, we built a new global potential energy surface (PES) for the ground electronic state of Li_2H, based on ≈ 20000 *ab initio* points at the MRCI level of theory including the core-core and core-valence correlation (See Figure 1 (a) and (b)). These data were fitted using the MSA code [1], based on permutationally invariant fitting bases. The features of our surface compare very well with those of recent global PESs [2]. Accurate vibrational energy levels were then computed using the MULTIMODE software [3], which relies on a hierarchical $n-$mode representation of the potential.

We show that the bent Li_2H molecule in its ground electronic state can support up to 25 vibrational levels below the barrier to linearity (Figure1 (b)). These results could help identify spectroscopic lines in an unsolved visible spectrum [4].



(a) (b)

Figure 1: (a) Potential energy surface and (b) barrier to linearity of the $\tilde{X}A_1$ state of Li_2H

[1] Z. Xie and J. M. Bowman. *Journal of Chemical Theory and Computation*, **6**, 26 (2010)

[2] Y.-Z. Song, Y.-Q. Li, S.-B. Gao and Q.-T. Meng. *The European Physical Journal D*, **68** (2014). M. Yuan, W. Li and M. Chen. *International Journal of Quantum Chemistry*, **117**, e25380 (2017)

[3] J. M. Bowman, S. Carter and X. Huang. *International Reviews in Physical Chemistry*, **22**, 533 (2003)

[4] J. B. Crooks, K. R. Way, S.-C. Yang, C.-Y. R. Wu and W. C. Stwalley. *The Journal of Chemical Physics*, **69**, 490 (1978)

The Catalytic Mechanism of GatA: A Molecular Dynamics and QM/MM Study

Paul Meister[1], **James W. Gauld**[1],

[1]*Department of Chemistry and Biochemistry, University of Windsor, 401 Sunset Avenue, Windsor, Ontario, Canada*

Aminoacyl-tRNA synthetases (aaRSs) are an ancient family of proteins tasked with charging their cognate $tRNA^{aa}$ with the correct amino acid. Most organisms utilize at least 20 different aaRSs, one for each proteinogenic amino acid. Notably, in some bacteria and archaea, $Asn\text{-}tRNA^{Asn}$ or $Gln\text{-}tRNA^{Gln}$ aminoacylation occurs via initial attachment of an Asp and Glu to $tRNA^{Asn/Gln}$, respectively. To maintain translational fidelity, the incorrect amino acid is typically edited through an array of editing mechanisms. However, in the case of non-discriminating (ND)-aaRSs this does not occur. Instead, Asp and Glu are converted to the correct ones through amidation by glutamine amidotransferase, GatCAB, a heterotrimeric protein. In the GatA active site, an ammonia-containing donor is deaminated to supply the GatB active site with a nitrogen source for use in coverting Asp/Glu to Asn/Gln, respectively. The mechanism by which this occurs is not entirely understood. The deamination reaction is achieved through an unusual Ser-*cis*Ser-Lys catalytic triad, a feature common to amidase signature enzymes. We have used molecular dynamics (MD) and quantum mechanical/molecular mechanics (QM/MM) methods to computationally study the mechanism of ammonia cleavage from two potential ammonia donors, Asn and Gln, in *Aquifex aeolicus* GatA (PDB ID: 3H0R[1]). QM/MM studies were performed at the ONIOM(B3LYP-D3/6-311+G(2df,p):Amber//B3LYP-D3/6-31G(d,p):Amber) level of theory. The results of these studies provide deeper insights into the catalytic mechanism for similar amidase signature enzymes, and provide a foundation for the development of novel therapeutics.

[1] J. Wu, W. Bu, K. Sheppard, M. Kitabatake, S. T. Kwon, D. Söll, J. L. Smity, *J. Mol. Bio.* **391**, 703 (2009).

The 340-cavity in neuraminidase provides new opportunities for influenza drug development

Nanyu Han[1], **Yuguang Mu**[2], **Zunxi Huang**[1]

[1]*School of Life Sciences, Yunnan Normal University, Kunming, China*
[2]*School of Biological Sciences, Nanyang Technological University, Singapore*

Abstract: Influenza neuraminidase (NA) is a pivotal target for viral infection control. However, the accumulating of mutations compromise the efficacy of NA inhibitors. Thus, it is critical to design new drugs targeted to different motifs of NA. Recently, a new motif called 340-cavity was discovered in NA subtypes close to the calcium binding site. The presence of calcium is known to influence NA activity and thermostability. Therefore, the 340-cavity is a putative ligand-binding site for affecting the normal function of NA. In this study, we performed molecular dynamics simulations of different NA subtypes to explore the mechanism of 340-loop formation. Ligand-binding site prediction and fragment library screening were also carried out to provide evidence for the 340-cavity as a druggable pocket. We found that residues G342 and P/R344 in the 340-loop determine the size of the 340-cavity, and the calcium ion plays an important role in maintaining the conformation of the 340-loop through contacts with G345 and Q347. In addition, the 340-cavity is predicted to be a ligand-binding site by metaPocket, and a sequence analysis method is proposed to predict the existence of the 340-cavity. Our study shows that the 340-cavity is not an occasional or atypical domain in NA subtypes, and it has potential to function as a new hotspot for influenza drug binding.

[1] N. Han, Y. Mu, *et al. Biochem. Biophys. Res. Commun.* **470(1)**: 130-136 (2016).

A Reliability Parameter for Frozen-Density Embedding Calculations

Alexander Zech[1], **Niccolo Ricardi**[1], **Stefan Prager**[2], **Andreas Dreuw**[2], **Tomasz A. Wesolowski**[1]

[1]*Department of Physical Chemistry, University of Geneva, Quai Ernest-Ansermet 30, 1205 Geneva, Switzerland*
[2]*Interdisciplinary Center for Scientific Computing, University of Heidelberg, Im Neuenheimer Feld 205, 69120 Heidelberg, Germany*

In the presence of an environment, excitation energies, properties and sometimes even reactivity of the target molecule may change drastically. Thus, including environmental effects into quantum chemical calculations either by implicit or explicit models is necessary for an adequate description of these systems. Frozen-Density Embedding Theory (FDET)[1, 2] provides a formal framework in which the whole system is described by means of two independent quantities: the embedded wavefunction (interacting or not) and the density associated with the environment. The FDET approach can conveniently be combined with pertubative wavefunction methods, e.g. the Algebraic Diagrammatic Construction (ADC) scheme for the polarization propagator[3] giving rise to FDE-ADC[4]. The current implementation of FDE-ADC uses the Linearized FDET formalism[5], which in comparison to FDET, is significantly less expensive computationally and more importantly leads to self-consistency between the energy and embedding potential preserving simultaneously the orthogonality of the embedded wave functions for each electronic state. We present a system-independent reliability parameter for FDE-ADC calculations which is computed at the beginning of each embedding calculation.

30 molecular model systems were studied using supermolecular FDE-ADC(2) and compared against their ADC(2) reference of the full system. The molecular test systems were chosen to investigate molecule - environment interactions of varying strength from dispersion interaction up to multiple hydrogen bonds. The mean absolute error of the excitation energies for each system shows linear correlation with the reliability parameter calculated with the densities $\rho_A^{ref}(\mathbf{r})$ and $\rho_B(\mathbf{r})$ used to construct the embedding potential. The initial results show that the reliability parameter is a promising tool to estimate the accuary of the embedding calculation from the start and to identify problematic results.

[1] T. A. Wesolowski, A. Warshel, *J. Phys. Chem.* **97**, 8050 (1993).

[2] T. A. Wesolowski, *Phys. Rev. A* **77**, 012504 (2008).

[3] J. Schirmer, *Phys. Rev. A* **26**, 2395 (1982).

[4] S. Prager, A. Zech, F. Aquilante, A. Dreuw, T. A. Wesolowski, *J. Chem. Phys.* **144**, 204103 (2016).

[5] A. Zech, F. Aquilante, T. A. Wesolowski, *J. Chem. Phys.* **143**, 164106 (2015).

Computer modelling of FRET-based protein nanosensors

Joshua A Mitchell[1], Jason H. Whitfield[1], Will H. Zhang[1], Colin Jackson[1], Megan L. O'Mara[1]

[1] *The Australian National University, Acton, ACT, Australia*

Ratiometric fluorescent nanosensors can be engineered by combining fluorescent probes with a solute binding protein, and taking advantage of the conformational change associated with binding to alter the distance between fluorophores. The resulting change in Förster Resonance Energy Transfer (FRET) can yield a ratiometric sensor. While proteins that exhibit a conformational change upon substrate binding are available for a huge number of sensor targets, simply fusing fluorescent proteins to such a protein is often insufficient to develop a useful sensor. Unfortunately, the reasons behind this difficulty are enigmatic, and the large size and flexibility of the fusion proteins traditionally used as sensors have resisted computational modelling. We describe a combined computational and experimental technique that allows us to rapidly engineer sensors for diverse analytes with excellent sensitivity and requiring little-to-no experimental optimisation, and discuss our next steps in modelling these proteins.

Tensor-decomposed vibrational coupled-cluster theory

Niels Kristian Madsen[1], **Ian H. Godtliebsen**[1], **Ove Christiansen**[1]

[1]*Department of Chemistry, Aarhus University, Langelandsgade 140, Aarhus, Denmark*

Vibrational coupled-cluster (VCC) theory is a highly accurate method for obtaining vibrational spectra and properties of small to medium-sized molecules. Calculating the vibrational energy and wave function requires the solution of a set of non-linear equations. We have implemented an array of different non-linear equation solvers ranging from simple, diagonal quasi-Newton schemes to a full Newton-Raphson method and we find that the *conjugate residual with optimal trial vectors* (CROP) algorithm has the shortest time-to-solution as well as a small memory requirement [1]. The computational bottelneck of any VCC calculation is the calculation of the error vector from a set of trial amplitudes. For high-order VCC methods this shows steep polynomial scaling w.r.t. the size of the moleule and the number of one-mode basis functions. Both the computational cost and the memory requirements of the VCC solver can be reduced by decomposing the VCC amplitudes and error vectors to the CANDECOMP/PARAFAC (CP) tensor format. Using the CP format allows us to automatically adapt the size of the parameter space as well as the computational effort to the strength of the physical interactions in the molecule while maintaining the same accuracy as the standard VCC method. We have implemented our VCC algorithms and equation solvers such that the VCC equations can be solved without constructing any tensors in full dimension. The tensors are automatically recompressed during the summation of the many terms in the VCC equations and the accuracy is adapted in a dynamic way to the step size of the equation solver in order to save computational effort while maintaining the fast convergence rate of the CROP algorithm. Our test calculations show that the CP-VCC method allows for significant reductions of both computational cost and memory consumption compared to standard VCC calculations which paves the way for applying high-order VCC methods to larger molecules.

[1] N. K. Madsen, I. H. Godtliebsen, O. Christiansen, *J. Chem. Phys.* **146**, 134110 (2017).

Inhibition Mechanisms of Cathepsin B

-A Theoretical Study-

A. Heilos[1], A. Geiß[1], B. Engels [1], P. Schmid[1], W. Waigel[1]

[1]Department of Physical and Theoretical Chemistry, University of Würzburg, Emil-Fischer-Str. 42, Würzburg, Germany

As a lysosomal cysteine protease Cathepsin B belongs to the so called housekeeping proteins. Hence, its natural substrates are peptide bonds of amino acid chains. Most ligands for proteases interact with their target non-covalently. Consequently the lower reactivity of such drugs prevent unintended side-reaction with DNA or other proteins. However, they have the drawback that their free energy of binding do generally not exceed 15 kcal/mol. Covalently binding inhibitors on the other hand provide higher binding affinities and therefore more efficient inhibition. We investigated carbamate-based ligands as potential covalent inhibitors. In order to avoid side reactions it is important to completely understand the inhibition mechanism of an enzyme. We calculated and compared possible reaction mechanisms using QM and QM/MM methods. Here, the focus lies on a mechanism where the active-site Cys29-anion acts as a base in the first step of the reaction instead of as a nucleophile.[1] The calculations show that water seems to play an important role in proton transfer-processes.

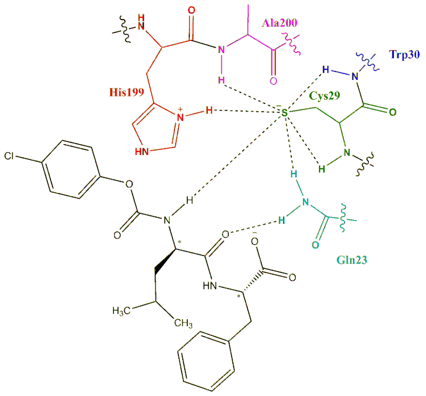


Fig1: Active site of CathB with carbamate-based inhibitor.

[1] Gütschow and Co-word, *Chem.Med.Chem.* **8**, 1330 (2014).

Methane Activation by Titanium Neopentylidene Complexes: Modification of the ligands

Dragan B. Ninković,[1] Salvador Moncho,[1] Predrag V. Petrović,[1] Snežana D. Zarić,[1,2] Michael B. Hall,[3] and Edward N. Brothers,[1]

[1]Science Program, Texas A&M University at Qatar, Texas A&M Engineering Building, Education City, Doha, Qatar.

[2] Department of Chemistry, University of Belgrade, 1000 Belgrade, Serbia.

[3] Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, USA.

The conversion of natural gas to useful chemical compounds is challenging due to the carbon-hydrogen (C-H) bond being fairly inert and solution to this problem is still elusive. The titanium neopentylidene complex (PNP)Ti=CH^{t}Bu(CH$_2$^{t}Bu) (PNP = N[2-P^{i}Pr$_2$-4-methylphenyl]$^{2-}$) reported by Mindiola and coworkers is capable of activating both benzene [1] and methane [2] C-H bonds under mild conditions. They have studied the mechanism of the reaction using B3LYP method that do not included dispersion. We have revised the mechanism in our previous work [3] using ωB97XD functional to include influence of the dispersion and also to get better agreement with the experimental data. It was shown that dispersion correction is crucial to the accuracy of modeling this reaction and we found a new conformer that is both more stable and kinetically more reactive [3].

In this study we have investigated the effect of modifying the PNP and CH^{t}Bu ligands on C-H bond activation. Additionally we have investigated tautomerization reaction of the C-H activation product to form a terminal methylidene, this reaction competes with the hydrogen abstraction reaction. Results have showed that replacing the ^{i}Pr groups in the PNP ligand with ^{t}Bu groups, both C-H activation and tautomerization reactions become more energetically favorable than in the unmodified complex, with tautomerization favored over H abstraction. Modification of the PNP ligand where N atom is replaced with P results in lower barrier for the tautomerization reaction and tautomerization product is only slightly less stable than product of C-H activation. Most of the ligand modifications do not change the barriers significantly indicating a significant resilience of this titanium complex, which could be used to enhance the practical aspects of the complex without a significant loss of its activity.

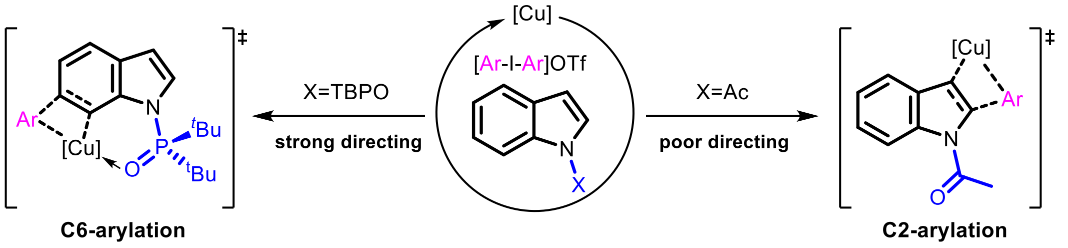
[1] B. Bailey, H. Fan, J. C. Huffman, M-H Baik, D. J. Mindiola, *J. Am.Chem. Soc.* **129**, 8781 (2007).
[2] J. A. Flores, V. N. Cavaliere, D. Buck, B. Pinter, G. Chen, M. G. Crestani, M-H. Baik, D. J. Mindiola, *Chem. Sci.* **2**, 1457 (2011).
[3]D. B. Ninković, S. Moncho, P. V. Petrović, S. D. Zarić, M. B. Hall, E. N. Brothers, *J. Coord. Chem.* **69**, 1759 (2016).

Computational Investigations for Cu-Catalyzed Site-Selective Arylation of Indoles: The Directing Group Effects

Ting Wang, Xinhao Zhang* and Yun-Dong Wu*

Lab of Computational Chemistry and Drug Design, Laboratory of Chemical Genomics, Peking University Shenzhen Graduate School, Shenzhen 518055, China.

Mechanistic study of the copper-catalyzed site-selective C-H arylation of indoles with diaryliodonium[1], [2] salts has been performed by density functional theory (DFT) in order to understand the origin of regioselectivity and the directing group effects. According to our studies, the reaction most likely undergoes a Heck-like four-membered-ring mechanism, which involves an aryl-Cu(III) complex.[3] In the presence of strong directing group N-P(O)^{t}Bu$_2$ (TBPO), Cu center is located at C7 or C2-site, while the steric hindrance makes C7-postion prefer over C2-postion. Thus, it leads to C6-arylation product through the Heck-like four-membered-ring transition state. However, N-Ac is a poor directing group, so the electronic effect becomes dominant for selectivity. Since C3 is most electron-rich, Cu(III) center would like to coordinate with C3 carbon, and then the aryl group bonded to copper is installed to the C2-postion. The computational findings are in good agreement with experimental observations and could account for the effects of directing groups.



[1] R. J. Phipps, N. P. Grimster, M. J. Gaunt, *J. Am. Chem. Soc.* **130**, 8172 (2008).
[2] B. Chen, X.-L. Hou, Y.-X. Li, Y. -D. Wu, *J. Am. Chem. Soc.* **133**, 7668 (2011).
[3] Y. Q. Yang, R. R. Li, Y. Zhao, Z. Z. Shi, *J. Am. Chem. Soc.* **138**, 8735 (2016).

Interplay of orbital breathing and electron correlation in corner-sharing cuprates

Nikolay Bogdanov[1], **Giovanni Li Manni**[1], **Sandeep Sharma**[1], **Olle Gunnarsson**[1], **Ali Alavi**[1,2]

[1]*Max Planck Institute for Solid State Research, Stuttgart, Germany*
[2]*University Chemical Laboratory, Cambridge, U.K*

Electronic and magnetic properties of one- and two-dimensional cuprates have been investigated for several decades but are still not fully understood. One of the unsolved problems is the origin of the large anti-ferromagnetic (AF) exchange in cuprates with corner-sharing geometry. It is known that this large AF exchange is an important ingredient for the high-temperature superconductivity and exotic phenomena like spin-charge [1] and spin-orbital separation [2]. We study the electronic structure of two corner-sharing cuprates, one-dimensional Sr_2CuO_3 with one of the largest exchange strengths and the layered La_2CuO_4, the parent compound of the high-temperature superconductors, with state-of-the-art wavefunction-based *ab initio* calculations. We find that in order to obtain reasonable agreement with the experimentally observed large magnetic exchange couplings, it is necessary to go beyond multiband models containing only Cu $3d$ and O $2p$ bands. To capture the competing orbital breathing and intra-site correlation effects, it is necessary to extend the model space with diffuse Cu $4d$ and O $3p$ orbitals. For a Cu-O-Cu unit this leads to a problem of 24 electrons in 26 orbitals that can't be solved with conventional methods. In our study we employ full configuration interaction quantum Monte Carlo (FCIQMC) [3, 4] and density matrix renormalization group (DMRG) [5] techniques. The diffuse Cu $4d$ and O $3p$ orbitals add new channels for superexchange and can be considered as a contemporary ingredient for effective Hamiltonian studies.

[1] B. J. Kim, H. Koh, E. Rotenberg, S.-J. Oh, H. Eisaki, N. Motoyama, S. Uchida, T. Tohyama, S. Maekawa, Z.-X. Shen, and C. Kim, *Nat. Phys.* **2**, 397 (2006).

[2] J. Schlappa, K. Wohlfeld, K. J. Zhou, M. Mourigal, M. W. Haverkort, V. N. Strocov, L. Hozoi, C. Monney, S. Nishimoto, S. Singh, A. Revcolevschi, J.-S. Caux, L. Patthey, H. M. Ronnow, J. van den Brink, and T. Schmitt *Nature* **485**, 82 (2012).

[3] G. H. Booth, A. J. W. Thom, and A. Alavi, *J. Chem. Phys.* **131**, 054106 (2009).

[4] G. Li Manni, S. D. Smart, and A. Alavi *J. Chem. Theory Comput.* **12**, 1245 (2016).

[5] G. K.-L. Chan and S. Sharma, *Ann. Rev. Phys. Chem.* **62**, 465 (2011).

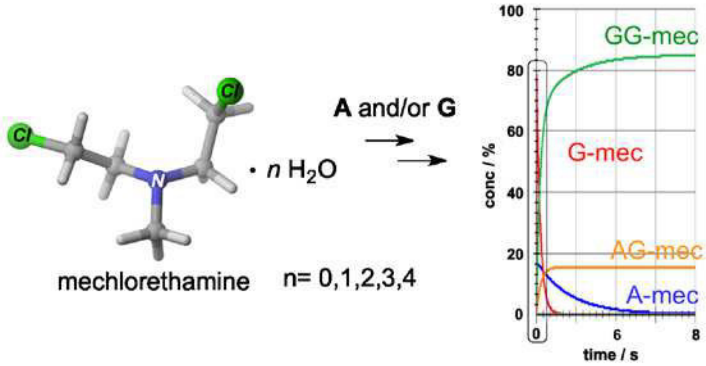
Mono- and Di- Alkylation processes of DNA-bases by Anticancer Drug Mechlorethamine

Olatz Larrañaga[1], **Abel de Cózar***[,1,2], **and Fernando P. Cossío***[,1]

[1]Department of Organic Chemistry I, Faculty of Chemistry, UPV/EHU and Donostia International Physics Center (DIPC) and Centro de Innovación en Química Avanzada (ORFEO-CINQA), P.K. 1072, 20018 San Sebastián, Spain.
[2]IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Spain.

Nitrogen mustard is the general name of bis(2-chloroethyl)amine derivatives such as mechloroethamine, chlorambucyl and mephalan and they were developed during Second World War. Although these DNA alkylating agents were synthesized to use them as chemical warfare agents, their activity was also tested in chemical trials. In particular, nitrogen mustard mechlorethamine (mec) was the first drug in being developed as an anticancer agent and nowadays it is still in use against Hodgkin's disease, chronic leukemia, breast, lung and ovarian cancer [1].

In this work, the reactivity of mec with purine bases adenine (A) or guanine (G) towards formation of mono- and dialkylated adducts has been studied using density functional theory (DFT). Our results suggest that DNA alkylation by nitrogen mustard mechlorethamine occur via aziridine intermediate instead of direct substitution. It was also found that formation of GG-mec diadduct is kinetically favored, followed by that of AG-mec.



[1] (a) A. Gilman, F. S. Philips, *Science* **103**, 409-436 (1946). (b) K. W. Khon, C. L. Spears, P. Doty, *J. Mol. Biol.* **19**, 266-288 (1966). (c) P. D. Lawley, J. H. Lethbridge, P. A. Edwards, K. V. Shooter, *J. Mol. Biol.* **39**, 181-198 (1969).

The interaction of complex biomolecules with zeolitic layers: Ab initio and molecular dynamics study

Miroslav Rubeš[1], Michal Trachta[1], and Ota Bludský[1]

[1]Insititute of organic chemistry and biochemistry, AS CR, v.v.i., Flemingovo n. 2, Prague, Czech Republic

The interaction of complex biomolecules such as proteins with inorganic supports is of growing interest in biotechnology applications.[1] The nature of involved interactions (e.g. dispersion, hydrogen-bonding) is well understood. For making reliable predictions of conformational changes at the protein/support interface, the accuracy of the underlying computational model is of the utmost importance. We have investigated the interaction of 19 amino acid side chains in the C_β-representation with the 2D-UTL lamella (IPC-1P). The periodic DFT optimizations with two different functionals (vdW-DF2 and PBE augmented with dispersion correction) have been tested and resulting structures and interaction energies have been compared against large cluster calculations at the MP2 level of theory. The results show that the error of dispersion corrected DFT (DC-DFT) methods can reach up to 30 kJ.mol-1, which significantly impacts the dynamical behaviour of adsorbed proteins. The performance of each tested DC-DFT approach also changes with the hydrophobic and hydrophilic character of the adsorption site. Particularly, the performance of DC-DFT methods differ significantly for the silanol nest sites where a strong hydrogen bonds are formed. The implications of these findings have been addressed through re-parameterization of generic force fields using accurate DC-DFT calculations yielding system-specific (non-transferable) ab initio force fields (AIFFs). The conformational behaviour has been investigated on large oligo/poly peptide models using MD simulations with AIFFs parameterized for specific Ace-*X*-NMe/α-quartz interactions (*X* stands for one of 19 amino acids). The MD simulations have enabled to evaluate the most relevant contributions to stabilizing interactions between proteins and the inorganic support.

[1] Rimola, A.; Costa, D.; Sodupe, M.; Lambert, J.; Ugliengo, P. *Chem. Rev.* **2013**, *113*, 4216–4313.

Analytic Open-Shell Local MP2 Gradients using Intrinsic Bond Orbitals

M. Dornbach[1], **H.-J. Werner**[1]

[1]*Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany*

Local electron correlation treatments enable the calculation of single point energies for molecules with hundreds of atoms. So far, low-order scaling analytical gradient methods only exist for closed-shell local second-order Møller-Plesset perturbation theory (LMP2) [1, 2], based on Pipek-Mezey (PM) localization [3] of the occupied orbitals and using domains of projected atomic orbitals (PAOs) for the external orbital space. In this work we have implemented analytical LMP2 energy gradients using PM localization as well as intrinsic bond orbitals (IBOs) [4, 5] for closed-shell and local restricted open-shell MP2 (LRMP2). The generation of IBOs is an alternative ansatz for occupied space localization. Contrary to PM, IBOs are faster to compute and are very insensitive to basis set variations. In particular, they avoid artifacts with diffuse basis sets. IBOs are obtained by projections of the occupied orbitals onto a minimal basis of atomic orbitals, yielding so-called intrinsic atomic orbitals (IAOs). The localization is then carried out in the basis of IAOs. The projections used in generating IBOs make it more challenging to derive the analytical gradient expressions and to implement the method efficiently. The open-shell formalism is also more involved than the corresponding closed-shell theory, but the computational effort is similar as in the closed-shell case. Both, an integral-direct and a density fitting implementation are available, and we will present benchmarks with these methods for closed-shell and open-shell systems.

[1] ElAzhary, A., Rauhut, G., Pulay, P., and Werner, H.-J. *J. Chem. Phys.*, **1998**, *108*, 5185.

[2] Schütz, M., Werner, H.-J., Lindh, R., and Manby, F. R. *J. Chem. Phys.*, **2004**, *121*, 737.

[3] Pipek, J. and Mezey, P. G. *J. Chem. Phys.* **1989**, *90*, 4916.

[4] Knizia, G. *J. Chem. Theory Comput.*, **2013**, *9*, 4834.

[5] Janowski, T. *J. Chem. Theory Comput.* **2014**, *10*, 3085.

The Zwitterionic Nature of the Tetrasilatetramide $Si_4\{N(SiMe_3)Dipp\}_4$ - Quantum Chemical Characterization of a Small Silicon Cluster

Christian Mück-Lichtenfeld[1], **Felicitas Lips**[2]

[1] *Organisch-Chemisches Institut and Center for Multiscale Theory and Computation, Westfälische Wilhelms-Universität, Corrensstraße 40, 48163 Münster, Germany*
[2] *Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität, Corrensstraße 28/30, 48163 Münster, Germany*

Tetrasilatetramide **1** has been synthesized and characterized spectroscopically. The observed closed shell character of **1** and the chemical bonding in the Si_4 core has been investigated with quantum chemical methods.[1] The butterfly shape of **1** can be shown to be a consequence of larger aryl groups destabilizing the chair conformation, which is preferred by the model $Si_4\{NMe_2\}_4$ (**2**). The closed shell character of **2** can be proven with CASSCF calculations.

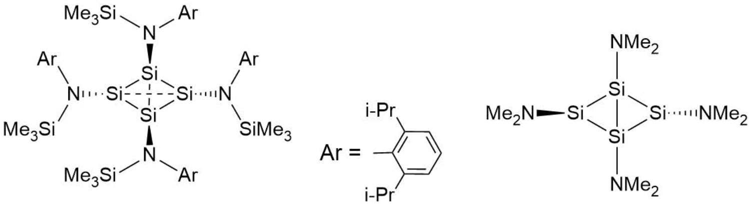


Figure 1: Tetrasilatetramides **1** and **2** (Model)

The two trivalent Si atoms in **1** have different contributions to the HOMO and LUMO (Figure 2) and notably different partial charges. This leads to zwitterionic character of the central ring and non-symmetric out-of-plane bending of the amido substituents. DFT-analysis of the potential energy and MD simulations show that the bending angles are correlated and interchange fast.

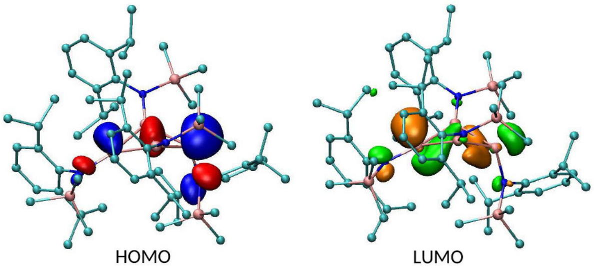


Figure 2: Frontier Orbitals of **1**

[1] J. Keuter, K. Schwedtmann, O. Janka, C. Doerenkamp, H. Eckert, C. Mück-Lichtenfeld, F. Lips, *submitted*

Empirical Charge Scheme for Transition Metals and Lanthanoids: Development and Applications

Bodo Martin[1], **Peter Comba**[1]

[1]*Inorganic Chemistry, Heidelberg University, Im Neuenheimer Feld 270, Heidelberg, Germany*

Molecular surface polarities are important descriptors for QSAR models for e.g. predicting hydrophobicities or biodistributions. While the derivation of "atomic charges" for organic compounds is well established, this is not yet the case for complexes containing transition metals or lanthanoids. Based on previous results [1-2] we present an MM-based model for geometry optimization, atomic charge parameterization via a Qeq-based approach and logD predictions for complexes containing In^{III}, Ga^{III}, La^{III}, Lu^{III} and Tb^{III}, which are of particular interest as possible radiopharmaceuticals for multimodal imaging as PET or SPECT centers.

[1] P. Comba; B. Martin; A. Sanyal, *J. Comput. Chem.* **34**, 1598 (2013).
[2] P. Comba; B. Martin; A. Sanyal; H. Stephan, *Dalton Trans.* **42**, 11066 (2013).

Explicit-Implicit Embedding Strategy to calculate Raman and Raman Optical Activity Spectra of Solvated Systems

Tommaso Giovannini[a], **Marta Olszówka**[a], **Franco Egidi**[a], **James R. Cheeseman**[b], **Giovanni Scalmani**[b], **Chiara Cappelli**[a]

[a] *Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy*
[b] *Gaussian Inc. 340 Quinnipiac St Bldg 40, Wallingford, CT 06492, USA*
tommaso.giovannini@sns.it

The increasing availability of QM strategies for the calculation of the molecular response to an external electric field has allowed the study of a great number of spectroscopic properties for isolated molecules. However, most experimental data are measured in solution. Computational strategies to include environmental effects are nowadays valuable tools used to bridge the gap between theory and experiment [1,2]. Here, we rely on a mixed explicit/implicit description of the environment based on a multiscale approach [3].

More in detail, in this work we extend the fully polarizable QM/MM/PCM model based on fluctuating charges (FQ) [4-8] (QM/FQ/PCM) to analytical third derivatives with respect to electric/magnetic field and nuclear coordinates, which are used to calculate Raman and Raman Optical Activity (ROA) spectra. In this model, the solvent molecules are explicitly described in terms of the FQs, i.e point charges that can vary in agreement with the Electronegativity Equalization Principle (EEP) [9]. A third layer is also considered and described by means of the Polarizable Continuum Model (PCM). [10]

To test our implementation, we apply the method to the Raman and ROA spectra of (R)-Methyloxirane and (S)-methyl lactate in aqueous solution [11], for which our approach has already been proven to reliably reproduce other optical properties [12,13].

[1] F. Egidi, C. Cappelli. *Elsevier Reference Module in Chemistry, Molecular Sciences and Chemical Engineering* 2015.
[2] H.M. Senn, W. Thiel. *Angew. Chem. Int. Ed.* **48**, 1198-1229 (2009).
[3] A. Warshel, M. Levitt. *J. Mol. Biol.* **103**, 227-249 (1976).
[4] C. Cappelli, *Int. J. Quantum Chem.* **116**, 1532–1542 (2016).
[5] Lipparini, F., Barone, V. *J. Chem. Theory Comput.* **7**, 3711 (2011).
[6] Lipparini, F., Cappelli, C., Barone, V. *J. Chem. Theory Comput.* **8**, 4153 (2012).
[7] Lipparini, F., Cappelli, C., Scalmani, G., De Mitri, N., Barone, V. *J. Chem. Theory Comput.* **8**, 4270 (2012).
[8] Lipparini, F., Cappelli, C., Barone, V. J. Chem. Phys. **138**, 234108 (2013).
[9] R.T. Sanderson. *Science* **114**, 670-672 (1951).
[10] Tomasi, J., Mennucci, B., Cammi, R. *Chem. Rev.*, **105**, 2999-3094 (2005).
[11] T. Giovannini, M. Olszówka, F. Egidi, J. R. Cheeseman, G. Scalmani, C. Cappelli *submitted.*
[12] F. Lipparini, F. Egidi, C. Cappelli, V. Barone. *J. Chem. Theory Comput.* **9**, 1880-1884 (2013).
[13] T. Giovannini, M. Olszówka, C. Cappelli, *J. Chem. Theory Comput.* **12**, 5483-5492 (2016).

An Accurate Force Field for Both Folded and Disordered States of Peptides and Proteins

Hao-Nan Wu[1], **Fan Jiang**[1], **Yun-Dong Wu**[1,2]

[1]*Laboratory of Computational Chemistry and Drug Design, Laboratory of Chemical Genomics, Peking University Shenzhen Graduate School, Shenzhen, China*
[2]*College of Chemistry and Molecular Engineering, Peking University, Beijing, China*
E-mails: wuhn@pku.edu.cn, jiangfan@pku.edu.cn, wuyd@pkusz.edu.cn

Although force fields that can well describe the folded or unfolded structures of peptides and proteins have been developed separately, the physical model that accurately describe both folded and disordered systems is still an unsolved challenge. Recently, a new water model TIP4P-D[1] has been proposed to correct the significantly underestimated radius of gyrations (R_g) of unfolded (disordered) peptides and proteins in previous simulations, but it cannot stabilize the native structures of α-helical and β-hairpin systems when used with popular force fields. Here, we found that our recently developed residue-specific force fields (RSFF1 and RSFF2)[2,3] can successfully fold these model systems with the TIP4P-D. Especially, when extra Lennard-Jones potentials between all backbone O_i and H_{i+4} atoms were added to mimic the special cooperativity in α-helix formation, the modified RSFF2+ force field with the TIP4P-D water can excellently reproduce experimental melting curves of both α-helical and β-hairpin systems at the full temperature range, and produces more expanded unfolded structures in better agreement with experiments at the same time.[4] The new RSFF2+/TIP4P-D method can also stabilize the native structures of well folded globular proteins and reproduce their NMR order parameters very well. It may pave the way for more harmonious descriptions of the systems including both folded and disordered states in solution, such as marginally stable proteins, structured proteins with disordered loops.

Reference:

[1] S. Piana, A. G. Donchev, P. Robustelli, D. E. Shaw, *J. Phys. Chem. B* **119**, 5113 (2015)
[2] F. Jiang, C.-Y. Zhou, Y.-D. Wu, *J. Phys. Chem. B* **118**, 6983 (2014)
[3] C.-Y. Zhou, F. Jiang, Y.-D. Wu, *J. Phys. Chem. B* **119**, 1035 (2015)
[4] H.-N. Wu, F. Jiang, Y.-D. Wu, *J. Phys. Chem. Lett.* in revision.

Rotational Constants and Vibrational Spectra of Acenaphthene Water Complexes.

Jens Antony[1], Stefan Grimme[1], Melanie Schnell[2]

[1]*Mulliken Center for Theoretical Chemistry, Institute of Physical and Theoretical Chemistry, University Bonn, Beringstraße 4, D-53115 Bonn, Germany*
[2]*Max-Plank-Institut für Struktur und Dynamik der Materie, Luruper Chaussee 149, D-22761 Hamburg, Germany*

The noncovalent complexes of acenaphthene and one, two or three water molecules are characterized theoretically in the course of a joint theoretical-experimental project within the DFG priority program "Control of London dispersion interactions in molecular chemistry" (SPP 1807). Microwave spectroscopy experiments were performed by the group of M.S., infrared spectra have been recorded by A. Rijs and A.K. Lemmens at the FELIX free electron laser laboratory.
Molecular parameters determined by rotational spectroscopy are computed using a previously described protocol.[1] The experimental B_0 values are back-corrected to equilibrium rotational constants (B_e) by computation of the vibrational corrections ΔB_{vib} using perturbation theory. Employing a new, well-performing spin-component scaled MP2 variant,[2] computed B_e values deviate from experimental back-corrected ones by less than one percent, thus allowing unambiguous structural assignments.
Theoretical reproduction of vibrational spectra in the far infrared region appears challenging due to strong anharmonic effects of intramolecular motions in the water cluster requiring a treatment beyond vibrational perturbation theory. Here we address this issue by performing quantum mechanical calculations of stationary states in one dimensional potentials obtained by deforming the complex out of its equilibrium structure along normal modes, an approach that has been applied to another hydrogen bonded system earlier.[3] With classical dynamics simulation in full dimensionality on the same (or eventually on a different) potential energy surface remaining anharmonic effects are approximated.[4, 5] Beyond qualitative insight into the nature of the anharmonic motions the applied procedure promises also a quantitative reproduction of the measured spectra when a sufficiently high level of electronic structure theory is used.

[1] S. Grimme, M. Steinmetz, *Phys. Chem. Chem. Phys.* **15**, 16031-16042 (2013).

[2] T. Risthaus, M. Steinmetz, S. Grimme, *J. Comput. Chem.* **35**, 1509-1516 (2014).

[3] J. Antony, G. v. Helden, G. Meijer, B. Schmidt, *J. Chem. Phys.* **123**, 014305 (2005).

[4] M. Brehm, B. Kirchner, *J. Chem. Inf. Model.* **51**, 2007-2023 (2011).

[5] M. Thomas, M. Brehm, R. Fligg, P. Vöhringer, B. Kirchner, *Phys. Chem. Chem. Phys.* **15**, 6608-6622 (2013).

A Scalable and Efficient Approach to Polarizable Force Fields in Molecular Dynamics Simulations

Jonathan P. Coles[1]

Physik-Department, Technische Universität München, James-Franck-Str. 1, 85748 Garching, Germany

Standard biophysical molecular dynamics simulations use complex, fixed-charge force field models to capture the atomic interactions of solvated proteins and other organic molecules. These force fields are typically parameterized to reproduce experimental results and are often very specific to the system being simulated. More flexible models that capture induced polarization and dynamically account for the changing electrostatic environment around proteins and DNA are increasingly recognized as a critical step towards more accurate and predictive simulations. However, such models are generally much more computationally expensive, which has limited their adoption. In this talk, I will present a sophisticated, polarizable force field model [1] that can be evaluated with an efficient $O(N)$ implementation of the Fast Multipole Method [2]. Together, the cost overhead of using a polarizable force field has been significantly reduced, allowing simulations of large molecules to be achieved. Recent work involving a highly scalable and parallel version of FMM will be presented along with an application to large biomolecules.

References

[1] F. Réal, V. Vallet, J.-P. Flament, M. Masella, *J. Chem. Phys.* **Sept. 2013**, *139*.

[2] J. P. Coles, M. Masella, *J. Chem. Phys.* **Jan. 2015**, *142*.

Properties of Molecular Magnets

Andreas Nyvang[1], **Maja Thomsen**[1], **Jacob Overgaard**[1], **Jeppe Olsen**[1], **James P. S. Walsh**[2], **Jeffrey R. Long**[3], **Phil Bunting**[3], **Michael Atanasov**[4]

[1]*Kemisk Institut, Aarhus Universitet, Langelandsgade 140, 8000 Aarhus C, Denmark*
[2]*Northwestern University, Evanston, IL 60208, USA*
[3]*Department of Chemistry, University of California, Berkeley, California 94720-1460, USA*
[4]*Max Planck Institute for Chemical Energy Conversion, 45470 Mülheim an der Ruhr, Germany*

Starting with the observation that a Mn_{12} molecule showed molecular magnetism [1], the field of single molecule magnets has developed rapidly.

For such complexes, Density Functional Theory calculations is often not sufficient, and instead multi-configurational wavefunction methods are necessary.

Recently, there has been an interest in semi-linear organometallic complexes. The idea is that by having a semi-linear complex, the oxidation state of the metal center can have a very low oxidation state, and additionally there will be near-degenerate states leading to a highly anisotropic magnetic moment due to the influence of ligands and spin-orbit coupling. In particular, pseudolinear complexes with iron in oxidation states I and II have shown promising results [2].

The poster will show examples of this for an iron(I) and an iron(II) complex, both with a structure similar to the one shown in figure 1. This will include energies of spin-orbit coupled states as well as magnetic properties, such as the **g** tensor and magnetic susceptibility using the program MOLCAS [3].

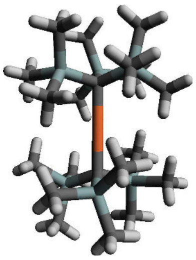


Figure 1: Pseudolinear iron(II) complex.

[1] Sessoli, R. and Gatteschi, D. and Caneschi, A. and Novak, M. A. *Nature* **365**, 141 (1993).

[2] Zazrozny, J. M. *Nat. Chem.* **5**, 577 (2013).

[3] Aquilante, F. *et al J. Comput. Chem.* **37**, 506 (2015).

Solvent Dynamics Controls the Schlenk Equilibrium of Grignard Reagents: Computational Study of CH_3MgCl in Tetrahydrofuran.

Raphael M. Peltzer,[a,b] **Odile Eisenstein,**[b,c] **Ainara Nova,***,[a,b] **Michele Cascella***,[a,b]

a Department of Chemistry, University of Oslo, Sem Sælands vei 26, 0371 Oslo, Norway

b Centre for Theoretical and Computational Chemistry (CTCC), University of Oslo, Sem Sælands vei 26, 0371 Oslo, Norway

c Institut Charles Gerhardt, UMR 5253 CNRS-Université de Montpellier, cc 1501, Place E. Bataillon, Université de Montpellier 34095 Montpellier, France.

** email to: ainara.nova@kjemi.uio.no, michele.cascella@kjemi.uio.no*

The Schlenk equilibrium [1] is a complex reaction governing the presence of multiple chemical species in solution of Grignard reagents. [2] A full characterization at the molecular level of the transformation of CH_3MgCl into $MgCl_2$ and $Mg(CH_3)_2$ in tetrahydrofuran (THF) by means of ab initio molecular dynamics simulations with enhanced-sampling metadynamics was carried out. The reaction occurs via formation of dinuclear species bridged by chlorine atoms. At room temperature, the different chemical species involved in the reaction accept multiple solvation structures, with two to four THF molecules that can coordinate the Mg atoms. The energy difference between all dinuclear solvated structures is lower than 5 kcal mol^{-1}. The solvent is shown to be a direct key player driving the Schlenk mechanism. In particular, our study illustrates how the most stable symmetrically solvated dinuclear species, $(THF)CH_3Mg(\mu\text{-}Cl)_2MgCH_3(THF)$ and $(THF)CH_3Mg(\mu\text{-}Cl)(\mu\text{-}CH_3)MgCl(THF)$, need to evolve to *less* stable asymmetrically solvated species, $(THF)CH_3Mg(\mu\text{-}Cl)_2MgCH_3(THF)_2$ and $(THF)CH_3Mg(\mu\text{-}Cl)(\mu\text{-}CH_3)MgCl(THF)_2$, in order to yield ligand exchange or product dissociation. In addition, the transferred ligands are always departing from an axial position of a pentacoordinated Mg atom. Thus, solvent dynamics is key to successive Mg–Cl and $Mg–CH_3$ bond cleavages because bond breaking occurs at the most solvated Mg atom and the formation of bonds takes place at the least solvated one. The dynamics of the solvent also contributes to keep relatively flat the free energy profile of the Schlenk equilibrium.

[1] Schlenk, W.; Schlenk, W., *Ber. dtsch. Chem. Ges. A/B* **1929,** *62*, 920-924.

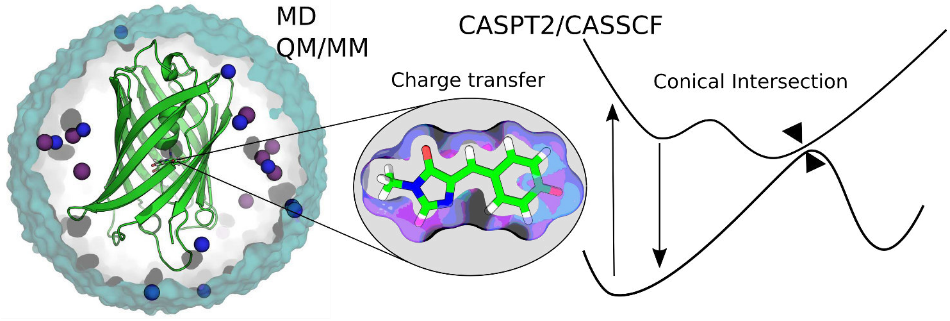
[2] V. Grignard, *C. r. d. l'Acad. des Sciences* **1900,** *130*, 1322-1324.

A rational look at fluorescent proteins through excited state reaction path calculations

Daryna Smyrnova[1], **María del Carmen Marín**[2,3], **Massimo Olivucci**[2,3], **Arnout Ceulemans**[1]

[1]*Quantum Chemistry and Physical Chemistry Division, Department of Chemistry , KU Leuven,*
Celestijnenlaan 200F, 3001 Heverlee, Belgium
[2]*Department of Biotechnology, Chemistry e Pharmacy, Universitá di Siena, via A. Moro 2,*
I-53100 Siena, Italy
[3]*Department of Chemistry, Bowling Green State University, Bowling Green, OH 43403, USA*

One reversibly-switchable fluorescent protein (RSFP) Dronpa[1] and four of its closest mutants (rsFastLime, rsKame, Padron (anionic form) and bsDronpa) spread over 40 nm in absorption maxima and only 18 nm in emission. They carry exactly the same chromophore and differ just in a few mutations thus providing an ideal set for mechanistic investigations. Using input from MD simulations and QM/MM calculations[2] we assess major reasons controlling the spectral tuning and photophysical properties on the basis of a consistent model set. On the basis of the RSFPs models, which are based on a CASPT2//CASSCF level of QM theory we reproduce an experimental absorption/emission trend with only 1.5 kcal/mol blue-shift. Then we analyse the chromphore's charge-transfer patterns during the absorption and emission, which in turn trigger a cascade of a hydrogen-bond-network rearrangements indicating preparation to isomerization. Also we show how contribution of an individual aminoacids correlates with spectral tuning of the absorption and emission. Furthermore, we identify how the conical intersection topography correlates with protein's photophysical properties. Thus we establish a detailed mechanistic explanation of a higher absorption sensitivity in comparison to emission as well as provide a consistent protocol for a high-throughput study of spectral tuning in RSFPs.



[1] Stiel et al, *Biochem. J.* **402**, 35 (2007)

[2] Smyrnova et al, *J. Phys. Chem. B* **120**, 12820 – 12825 (2016)

Controlling electron transfer through selective vibrational excitation.

Theo Keane[1], **Milan Delor**[2] , **Julia A. Weinstein**[1], **Anthony J. H. M. Meijer**[1]

[1]*Department of Chemistry, University of Sheffield, Brook Hill, Sheffield, United Kingdom*
[2]*Department of Chemistry, University of California, Berkeley, California, United States*

Electron transfer is a fundamental physical process and underpins various phenomena, including photosynthesis. Over the past decade, there has been increasing interest in the manipulation of electron transfer pathways through selective vibrational excitation, from both theoretical[1] and experimental[2] perspectives.
Recently, we have investigated a series of Pt(II) acetylide complexes in which electronic transfer can be manipulated,[3, 4] as illustrated in Figure 1.

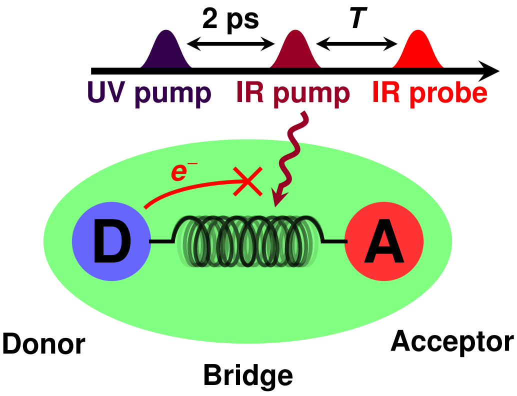


Figure 1: Illustration of the vibrational control phenomenon

In this contribution, we will outline the advances made in the efforts to understand the vibrational control phenomenon.

[1] D. Xiao, S. S. Skourtis, I. V. Rubstov, D. N. Beratan, *Nano Lett.*, **9**, 1818 (2009).

[2] Z. Lin, C. M. Lawrence, D. Xiao, V. V. Kireev, S. S. Skourtis, J. L. Sessler, D. N. Beratan, I. V. Rubstov, *J. Am. Chem. Soc.*, **131**, 18060 (2009).

[3] M. Delor, P. A. Scattergood, I. V. Sazanovich, A. W. Parker, G. M. Greetham, A. J. H. M. Meijer, M. Towrie, J. A. Weinstein, *Science*, **346**, 1492 (2014).

[4] M. Delor, T. Keane, P. A. Scattergood, I. V. Sazanovich, G. M. Greetham, M. Towrie, A. J. H. M. Meijer, J. A. Weinstein, *Nature Chem.*, **7**, 689 (2015).

Improving AMBER non-bond parameters for inorganic and alkyl oxoanions, when experimental data is not available

Sadra Kashef Ol Gheta[1], **Ana Vila Verde**[1]

[1]*Department of Theory & Bio-systems, Max Planck Institute of Colloids and Interfaces,*
Am Mühlenberg 1, 14476 Potsdam, Germany

Organic and inorganic oxoanions are abundant in biological systems and play a significant role in many physiological processes. The molecular scale behavior of these ions towards proteins and other biomolecules are not completely understood, partly due to the absence of reliable model parameters. A good parameter should be able to capture both ion-water and ion-ion interactions simultaneously, and reproduce the corresponding thermodynamics properties. However, for many ions, reliable thermodynamic data are not necessarily available in the literature, restraining us from developing proper parameters for the ions of our interest. Here, we propose an approach that combines the ab initio calculations with the empirical optimization, to develop non-bond parameters for ions in aqueous solutions. We developed parameters for the interaction of HSO4-, RSO4-, RSO3-, H2PO4-, R2PO4-, CH3COO-, SO42-, HPO42- and RPO42- with TIP3P water, as well as with Na+, NH4+ and RNH3+ (R=alkyl groups), using our approach. The approach yields an internally consistent parameter set for the ion-water and ion-ion interactions, for the ions above.

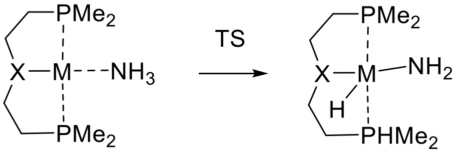
Computationally Guided Design of Transition Metal PXP Pincer Complexes for NH_3 Fixation

Julen Munarriz[1], **Victor Polo**[1]

[1]Departamento de Química Física and Instituto de Biocomputación y Física de los Sistemas Complejos (BIFI), Universidad de Zaragoza. Pl. S. Francisco S/N 50009, Zaragoza, Spain

Ammonia fixation is one of the most challenging chemical reactions as it would open new synthetic routes for hydroamination processes as well as contribute to remove ammonium-derived byproducts that are harmful for the environment. One promising way of achieving this is through N-H oxidative addition by transition metal complexes and under mild conditions. However, although some paradigmatic examples have been reported, this kind of processes are rare as the metal-amido parent species tend not to be thermodynamically favorable. [1][2]

The electronic features that govern this processes have not been fully characterized. In order to shed light, a comprehensive analysis of the factors determining energy cost and activation barrier for the oxidative addition of ammonia to the metal center (Ir and Rh) of some paradigmatic and promising PXP complexes (X = B, Si, C, O, N) is presented.



R P

M: Ir, Rh
X: B, CH, O, N, SiH

Electron localization function analysis provided an understanding of the sequence of bond formation and cleavage, allowing to understand the changes on electron pairing along reaction path. This way, it was possible to reveal that the metal oxidation from M(I) to M(III) takes place at the transition state, having an important effect in the activation energy. On the contrary, electrostatic interactions between the metal and the atom situated in *trans* position to ammonia (X) (which were revealed using Interacting Quantum Atoms, IQA, approach) were found to be crucial for the energy variation of the whole oxidative addition process. It is also remarkable to notice that the formed metal-amido product presents a significant double bond character, as shown by Natural Bond Orbital (NBO) analysis.

[1] J. Zhao, A. S. Golman, J. F. Hartwig, *Science* **307**, 1080 (2005).

[2] E. Morgan, D. F. MacLean, R. McDonald, L. Turculet, *J. Am. Chem. Soc.* **131**, 14234 (2009).

How reliable is density functional theory to describe uranium-based molecular compounds?

Daniel Reta,[1] Fabrizio Ortu,[1] Simon Randall,[1] David P. Mills,[1] Nicholas F. Chilton,[1] Richard E. P. Winpenny,[1] Louise Natrajan,[1] Bryan Edwards[2] and Nikolas Kaltsoyannis[1]

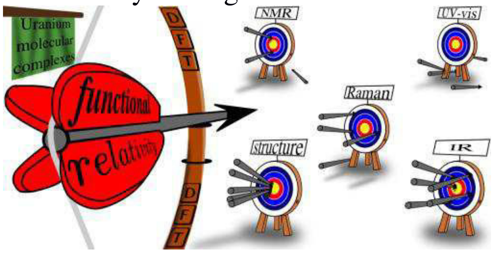
[1]School of Chemistry, The University of Manchester, Oxford Road, Manchester M13 9PL, UK

[2]Science and Technology Facilities Council, Rutherford Appleton Laboratory, Harwell Oxford, Didcot OX11 0QX, UK

Molecular uranium complexes are the most widely studied in actinide chemistry, and make a significant and growing contribution to inorganic and organometallic chemistry. However, reliable computational procedures to accurately describe the properties of such systems are not yet available. In this contribution, 18 experimentally characterized molecular uranium compounds, in oxidation states ranging from III to VI and with a variety of ligand environments, are studied computationally using density functional theory (DFT). For all investigated compounds, X-ray crystallographic, infra-red and Raman spectroscopic data are compared to the computed geometries and vibrational frequencies; for a selection of closed-shell U(VI) compounds, NMR parameters and UV-Vis spectra are compared to ^{1}H and ^{13}C NMR chemical shifts, spin-spin couplings and electronic absorption spectra, to establish which computational approach yields the closest agreement with experiment.

For each of the mentioned experimental observables, the impact of the chosen functional is addressed by investigating different representative functionals belonging to the main families in DFT, i.e., generalized gradient approximation (GGA), *meta*-GGA, hybrid and range-corrected approaches. The description of relativistic effects on the uranium centers was performed via a relativistic pseudopotential and associated valence basis set, or with an all-electron basis set with the ZORA Hamiltonian. The effect of the nature and type of the employed basis set, together with the inclusion of dispersion corrections was also investigated.

Our results clearly identify which theoretical and computational procedure is best suited for the description of a given experimental observable, and permits us to rationalize the situations in which DFT performs erratically in a systematic manner. We believe that suggestions derived from our study on how to computationally describe uranium-based molecular compounds will prove valuable for the community of actinide chemists, and in my presentation I will set out the key findings and recommendations from our work.



Prediction of DFT-derived point-charges using a Machine Learning Model

P. Bleiziffer[1], **S. Riniker**[1]

[1]*Laboratory of Physical Chemistry, ETH Zurich, Vladimir-Prelog-Weg 2, 8093 Zurich, Switzerland*

The parametrisation of classical bimolecular force fields, that are applied to systems like proteins, DNA, lipids and sugars is relatively straight-forward. Since only a few number of building blocks is required for parametrization and validation, fitting the parameters to experimental or *ab initio* values is feasible. For small organic molecules on the other hand, the situation is different. The size and diversity of just the drug-like chemical space is vast, making it difficult to construct building blocks and thus requiring an individual parametrisation of each ligand. The general approach is thereby either to inherit the parameters of the bonded and van der Waals (Lennard-Jones) parameters from a protein force field, or to parametrise them in a similar way based on experimental data and higher level calculations of a set of organic liquids. For a new molecule, partial charges are usually obtained *ad hoc* from semi-empirical or *ab initio* calculations of questionable accuracy. Examples of such force fields for organic molecules are the general Amber force field (GAFF) [1], or the OPLS all-atom force field (OPLS-AA) [2]. The quality of the net atomic charges (NACs) of small organic molecules generated in this fashion depends on the level of the quantum-chemical calculation as well as on the fitting procedure that is used to derive the NACs. The extraction of NACs from *ab initio* data is a long-standing problem, which has no unique solution. Here we present a machine-learning (ML) based approach for predicting NACs extracted from density function theory (DFT) electron densities via the DDEC6-scheme [3]. The training-set for the ML-model was chosen with the goal to cover the chemical space of drug-like molecules as far as possible. In addition to an instantaneous computation of the NACs, the charges are also less dependent on the molecular conformation than the ones obtained by fitting to the electrostatic potential (ESP). To assess the quality and compatibility with standard force fields like OPLS-AA and GAFF, we performed benchmark calculations for the free energy of hydration and liquid properties.

[1] M. J. Wang, *J. Comput. Chem.* **25**, 1157– 1174 (2005).

[2] W. L. Jorgensen, D. S. Maxwell, and J. Tirado-Rives, *J. Am. Chem. Soc,* **118**, 11225–11236 (1996).

[3] T. A. Manz and N. G. Limas, *RSC Adv.* **6**, 47771-47801 (2016).

Description and Modelling of Spectra, Structure and Function of Histidin Kinase Rhodopsin (HKR).

Franziska E. Beyle[1], **Marcus Elstner**[1], **Igor Schapiro**[2]

[1]*Department of Theoretical Chemical Biology, Institute of Physical Chemistry, KIT,*
Kaiserstrasse 12, 76131 Karlsruhe, Germany
[2]*Fritz Haber Center for Molecular Dynamics Research, Institute of Chemistry, The*
Hebrew University of Jerusalem, 9190401 Jerusalem

Rhodopsins are light-sensitive receptor proteins, they respond to light and enable the signal pathways of the cells. The discovery of the Channelrhodopsins in the last decade paved the way for a new technology in the field of neuroscience. These light-gated ion channels enable neuroscientists to selectively activate nerve cells in tissues with short laser pulses. This technique is called Optogenetics and is a milestone for the investigation of neural networks. However, the inactivation of the nerve cells is not yet possible, especially by moderate light intensities. One solution might be provided by the recent discovery of the bimodal switching Histidin Kinase Rhodopsin (HKR) [1]. In detail, irradiating the protein with two different wavelengths makes it switch between two stable states [2][3]. The mechanism has to be understood and clarified in order to adapt this unique feature on other rhodopsins. Thereby rhodopsins with new features can be developed for applications in the Optogenetic field. In this project, several structure models (homology models) are built and simulated on the molecular and quantum mechanic level in order to gain an equilibrium state and validate them by calculating the spectroscopic characteristics and compare them to experimental spectra. On the received structures, calculations in the excited state are performed and give an insight into the reactions which take place in the excited state. This information is important to get an idea about the lifetime and transition probability between the two stable states of the protein. Relax scans in the excited state are calculated in order to characterize the photochemical reaction path ways in Histidin Kinase Rhodopsins by using the quantum mechanical method CASSCF (Complete Active Space Self-Consitent Field) and molecular dynamic simulations in the excited state. Based on the data, we get an insight in the photochemical process in the HKR.

[1] M. Luck et al., *J. Biol. Chem.*, **287**, 40083 (2012).

[2] M. Luck, et al., *FEBS Lett.,* **589**, 1067 (2015).

[3] A. Penzkofer, et al., *Photoche Photobiol.*, **90**, 773 (2014).

Characterization of the intermediate states of transport cycle of sodium symporters via transition-path sampling methods

Ina Bisha[1,2], Alessandra Magistrato[3], Alessandro Laio[4], Iris Antes[2], Ville R. I. Kaila[1]

[1]*Department of Chemistry, Technical University of Munich, Lichtenbergstr. 4, 85747 Garching, Germany*
[2]*Protein Modelling Group, Technical University of Munich, Emil-Erlenmeyer-Forum 8, 85354, Freising, Germany*

[3]*CNR-IOM-Democritos National Simulation Center, SISSA, Trieste, Italy*

[4]*SISSA, Via Bonomea 265, 34165 Trieste, Italy*

Sodium symporters are membrane proteins that use Na^+ ions to co-transport a variety of substrates such as sugars, amino acids, neurotransmitters, across cellular membranes against their chemical concentration gradient [1-2]. This process is of fundamental biological importance, and therefore these proteins represent an important target for many diseases. Despite belonging to different gene families these symporters share a common structural core of 10 trans-membrane helices composed of two five-helix inverted repeat motifs, known as 'LeuT-fold' [3]. In order to explore the *alternating access mechanism* of sodium symporters, we investigate here the dynamics of these proteins in different conformational states, where substrate accessibility changes from one side to the other of the cellular membrane. To this end, we combine several computational techniques from advanced free energy sampling techniques to hybrid quantum mechanics/classical mechanics (QM/MM) calculations in order to quantitatively describe the transport mechanism, and to investigate how binding of ligands in intermediate states along the transport cycle is coupled to the global conformational protein changes.

[1] H. Krishnamurthy, C. L. Piscitelli, and E. Gouaux, *Nature*, **459**, 347-355 (2009).
[2] O. Jardetzky, *Nature*, **211**, 969–970 (1966).
[3] I. Bisha, A. Magistrato, *RSC Advances*, **6**(12), 9522-9540 (2016).

Implications of Axial Coordination on the Redox Behavior and H-Atom-Abstraction Reactivity of Compound I Analogues.

Mauricio Maldonado-Domínguez[1], **Martin Srnec**[1]

[1]*Department of Theoretical Chemistry, J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Dolejškova 2155/3, Prague 8-Libeň, Czech Republic.*

Abstract: Iron-oxo complexes are crucial for the function of many enzymes carrying out chemical transformations that are key to sustain life. In this work, we seek to correlate the redox properties and reactivity of iron systems with their electronic structure, applying theoretical methods calibrated with available electrochemical and spectroscopic data [1,2]. Our study is focused on porphiryn-based complexes where axial coordination tunes reactivity at the central iron-oxo moiety towards H-atom abstraction, aiming to shed light on the role of redox potential in the control of reactivity and selectivity towards activation of C-H and O-H bonds. With these results we strive to generalize the electronic and structural factors controlling reactivity in H-atom abstraction, as carried out by natural systems such as cytochrome P450, providing guidelines to foster the design of biomimetic catalysts to achieve difficult chemical transformations such as direct and selective hydrocarbon functionalization, of current interest to pharmaceutical and fuel industries.

[1] A. Takahishi, D. Yamaki, K. Ikemura, T. Kurahashi, T. Ogura, M. Hada, H. Fujii, *Inorg. Chem.* **51**, 678, (2012).

[2] C. V. Sastri, J. Lee, K. Oh, Y. J. Lee, J. Lee, T. A. Jackson, K. Ray, H. Hirao, W. Shin, J. A. Halfen, J. Kim, L. Que Jr., S. Shaik, W. Nam, *Proc. Natl. Acad. Sci. U.S.A.*, **104**, 19181, (2007).

Shedding UV-light on the Origins of RNA Nucleotides

Rafał Szabla[1, 2], Jiri Sponer[2], Robert W. Góra[3]

[1]*Institute of Physics, Polish Academy of Sciences, Warsaw*
[2]*Institute of Biophysics, Academy of Sciences of the Czech Republic, Brno*
[3]*Department of Physical and Quantum Chemistry, Wroclaw University of Technology*

Identification of prebiotically plausible pathways that could lead to RNA nucleotides has been one of the greatest challenges in the studies of the origins of life on Earth. Despite numerous efforts during the past 50 years, the first clean and highly efficient synthesis yielding β-ribocytidine and β-ribouridine nucleotides was published recently.[1] However, many related problems, e.g. the formation purine nucleosides, remain largely unsolved. Since UV irradiation played a central role in these syntheses, thorough understanding of the underlying photochemical reaction mechanisms might be crucial in putting the remaining elements of the puzzle together.

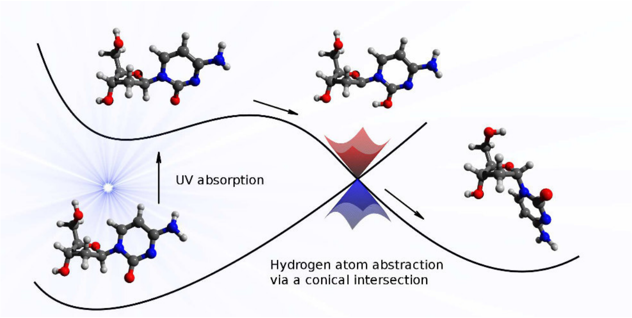


Figure 1: UV-induced C1′–H atom abstraction of 2′-dC, which explains its photoanomerisation.

Recent joint experimental and theoretical efforts provided important mechanistic insights into the photochemical processes governing the UV-assisted formation of pyrimidine nucleotides and the photodestruction of biologically irrelevant by-products. This was achieved by the detailed NMR analysis of the composition of product mixtures and state-of-the-art quantum chemical calculations employing multiconfigurational methods.[2, 3] With this knowledge we aim to address the remaining questions in the field in order to propose pathways that could have lead to the complete set of RNA building blocks on the Archean Earth.

[1] J.D. Sutherland, *Angew. Chem. Int. Ed.* **55**, (2016).

[2] R. Szabla, J. Campos, J.E. Šponer, J. Šponer, R.W. Góra, J.D. Sutherland, *Chem. Sci.* **6**, (2015).

[3] J. Xu, M. Tsanakopoulu, C.J. Magnani, R. Szabla, J.E. Šponer, J. Šponer, R.W. Góra, J.D. Sutherland, *Nature Chem.* **9**, (2017).

Domain-based Local Pair Natural Variant of Mukherjee's Multireference Coupled Cluster Method

Jiří Brabec[1], Masaaki Saitow[2], Jiří Pittner[1], Frank Neese[2] , Ondřej Demel[1]

[1]*J. Heyrovský Institute of Physical Chemistry, AS CR, Dolejškova 3, Prague, Czech Republic*
[2]*Max Planck Institute of Chemical Energy Conversion, Stiffstrasse 2-4, Mülheim an der Ruhr, Germany*

Multireference coupled cluster methods are an accurate approach for systems with quasidegeneracies. However, the applicability of these methods is limited due to the steep $O(n^6)$ scaling. This poster reports development of a local variant of Mukherjee's state specific multireference coupled cluster method [1] based on the domain based pair natural orbital approach (DLPNO) [2]. A common set of pair natural orbitals is constructed by the diagonalization of the density matrix, obtained at the DLPNO NEVPT2 level, for the each pair of internal and / or active orbitals. The active orbitals are kept unchanged. The current implementation in ORCA package is restricted to single and double excitations and mutually up to biexcited references. The resulting method has a near linear scaling, which is a significant improvement compared to previously reported LPNO MkCC method [3].
The performance of the DLPNO MkCC methods has been benchmarked on tetramethyleneethane, naphtynes, and β-carotene.

[1] U. S. Mahapatra, B. Datta, and D. Mukherjee, *J. Phys. Chem.* **110**, 6171 (1999).

[2] C. Riplinger and F. Neese, *J. Phys. Chem.* **138**, 034106 (2013).

[3] O. Demel, J. Pittner, and F. Neese, *J. Chem. Theory Comput.* **11**, 3104 (2015).

Modeling and NMR calculations of Oximes in Water and Ionic Liquids: Solvation Shell Structure implications

Faria, J. A.[1], de Castro, A. A.[1], Assis, L. C.[1], Mancini, D. T.[1], Costa, L. T.[2], da Cunha, E. F. F.[1], Ramalho, T. C.[1]

[1]Department of Chemistry, Federal University of Lavras, University Campus, PO Box 3037, CEP 37200-000, Lavras/MG, Brazil. [2]Department of Chemistry, Fluminense Federal University, Miguel de Frias's Street, 9, Icaraí, CEP 24220-900, Niterói/RJ, Brazil

Organophosphorus compounds (OP) have been employed in the agricultural activity for several decades and have neurotoxic effects on the central nervous system, and their toxicity is due to the irreversible inhibition of the acetylcholinesterase (AChE) enzyme. An antidote commonly employed to reactivate AChE is the so-called oxime. These compounds perform a nucleophilic attack on the phosphorus center of the OP reactivating the enzyme [1, 2]. Generally, the detection of OP is performed by employing expensive techniques such as GC and HPLC, but new techniques to detect them have been researched [3]. The use of Ionic Liquid as support for sensors, biosensors and as electrolyte is still little explored, but it is very promising [4]. This work aims to employ molecular dynamics and NMR calculations to investigate the solvent and thermal effects on NMR parameters of oximes in two different solvents, water and 1-Butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF4). By using the OPLS force field in the GROMACS 4.6.5 program, classical molecular dynamics simulations were performed for the oxime 3-fluoro-4-[(hydroxyimino)methyl]-1-methyl-pyridinium (3-Fluoro-4-PAM) in both solvents, at times of 1ns and 10ns, respectively. Due to the large number of conformations generated, quantum dynamics calculations were performed to obtain 1000 points using ADMP and B3LYP/6-31G at 310K temperature, starting from the last frame. For NMR calculations, the GIAO method was performed for both the dynamics and static systems, which were obtained through systems optimized at B3LYP/6-31G by using the Gaussian 09 program. The methods were tested for the vacuum optimized oxime on the dynamic and thermal effects employed, without the presence of the solvent, and with the use of explicit and implicit solvent (PCM). Calculations using the 4-PAM oxime were employed to validate the methodology, and with the theoretical NMR results, it was possible to notice that the ^{13}C chemical shift values were very close to those reported experimentally [5], being the best results from the employment of dynamic, thermal and solvent effects. The same was observed for the 3-Fluoro-4-PAM oxime that presented the best results in the presence of the solvent, with the thermal and dynamic effects. When the solvent is BMIM-BF4, the ^{19}F chemical shift values were about 6 units lower than when water is used, which shows that the OP poisoning detection is best observed when there is an ionic solvent used. According to those data, the use of fluorinated oximes assists in the detection process; this is related to their smaller chemical shift when exposed to solvents.

[1] K. Kuca, D. Jun, K. Musilek, *Mini. Rev. Med. Chem.* **6**, 269-277 (2006).
[2] F. P. Carvalho, *Environ. Sci. Policy*. **9**, 685-692 (2006).
[3] A. Beyer, M. Biziuk, *Food. Chem.* **108**, 669-680 (2008).
[4] L.-G. Zamfir, L. Rotariu, C. Bala, *Biosens. Bioelectron.* **46**, 61-67 (2013).
[5] D. Waysbort, D. Balderman, G. Amitai, *Org. Magn. Resonance*. **16**, 7-10 (1981).

Mechanistic insights into the selective hydrolysis of Asp-X peptide bonds in proteins by Zr(IV)-substituted polyoxometalates

Tzvetan T. Mihaylov, Hong Giang T. Ly, Tatjana N. Parac-Vogt, Kristine Pierloot

Department of Chemistry, KU Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium

Several resent investigations have shown that metal-substituted polyoxometalates (MSPs) consisting of highly Lewis acidic metal ions, such as Zr(IV) and Ce(IV), embedded into W(VI)-oxygen frameworks induce hydrolytic cleavage of proteins in a regioselective manner [1-2]. A common feature of the MSP-promoted hydrolysis of proteins is that the hydrolytic cleavage occur exclusively at peptide bonds located at (or in the vicinity of) positively charged patches of the protein surface, regardless of the size, three dimensional folding and surface charge density of the protein. In addition, the MSPs tend to cleave preferentially peptide bonds linking amino acids with carboxylate groups in their side chains (Asp and Glu). A remarkable selectivity has been observed for the hydrolysis of horse heart myoglobin (HHM) catalyzed by a series of Zr(IV)-substituted polyoxometalates (POMs). Although this protein contains also 13 Glu residues a hydrolytic cleavage was observed exclusively at Asp-X type peptide bonds [3].

Here, we report on another example of highly selective protein cleavage by MSPs. In the presence of Zr(IV)- and Ce(IV)-substituted POMs bovine hemoglobin (Hb) was selectively cleaved under mild conditions. Eleven cleavage sites were identified as in all of them the hydrolysis occurs next to Asp residues (Asp-X) located in the vicinity of positively charged patches of the protein surface. This high specific selectivity seems does not depend on the nature of the X amino acid residue, as the later can be either aliphatic, positively charged or negatively charged, and cannot be explained in terms of non-bonding MSP-protein interactions alone. In order to provide an explanation for the observed selectivity at atomistic level DFT calculations were performed on a model system. Based on this we propose a mechanism of MSP-promoted hydrolysis which may explain why Asp-X type peptide bonds are exclusively cleaved while Gly-X, X-Asp and X-Glu type peptide bonds remain intact.

[1] K. Stroobants, G, Absillis, E. Moelants, P. Proost, T. N. Parac-Vogt, *Chem. Eur. J.* **20**, 3894 (2014).

[2] K. Stroobants, E. Moelants, H. G. T. Ly, P. Proost, K. Bartik, T. N. Parac-Vogt, *Chem. Eur. J.* **19**, 2848 (2013).

[3] H. G. T. Ly, G. Absillis, R. Janssens, P. Proost, T. N. Parac-Vogt, *Angew. Chem. Int. Ed.* **54**, 7391 (2015).

Excitons and charge transfer states in light-harvesting antenna complexes

Lorenzo Cupellini[1], **Sandro Jurinovich**[1], **Stefano Caprasecca**[1], **Ciro A. Guido**[2],
Marco Campetella[3], **Thomas Renger**[4], **Benedetta Mennucci**[1]

[1]*Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Moruzzi 13, Pisa, Italy*
[2]*CEISAM, UMR CNRS 6230, Université de Nantes, 2 rue de la Houssinière, Nantes, France*
[3]*MSC, ENSCP - Chimie ParisTech, 11 rue Pierre et Marie Curie, Paris, France*
[4]*Institute of Theoretical Physics, Johannes Kepler University Linz, Linz, Austria*

Antenna complexes of photosynthetic organisms are pigment-protein aggregates, whose spectroscopic and photophysical properties are determined by the interaction between the pigments and the protein matrix, as well as the interactions among the pigments themselves. The complexity of the interactions and the dimension of such systems hamper the application of standard electronic structure methods. Instead, their properties can be described through an excitonic approximation, in which the properties of single pigments and the couplings among pigments are joined to describe the full system. Nevertheless, a faithful description of the properties and couplings needs to account for the presence of the protein matrix surrounding the pigments.[1] Recently, two-dimensional electronic spectroscopy has revealed that charge-transfer states have a role in the excited-state dynamics of the LH2 antenna complex, by mixing into the bright locally excited states.[2] However, a complete theoretical modelling of such states in the antenna complexes is still a challenge.

Starting from our previous description of the excitonic states in LH2,[3, 4] we present an exciton model that includes charge-transfer states to describe the exciton structure of the LH2 antenna complex. The charge-transfer couplings are obtained along a molecular dynamics simulation employing the Fragment Charge Difference diabatization scheme in its multistate formulation. [5] We show that the mixing to charge-transfer states significantly red-shifts the lowest bright exciton states of the antenna complex. Moreover, the disorder in the energies and couplings of charge-transfer states causes inhomogeneous broadening of the lowest exciton absorption band.

[1] C. Curutchet, B. Mennucci, *Chem Rev.* **2017**, *117*, 294–343.

[2] M. Ferretti, R. Hendrikx, E. Romero, J. Southall, R. J. Cogdell, V. I. Novoderezhkin, G. D. Scholes, R. van Grondelle, *Sci. Rep.* **2016**, *6*, 20834.

[3] L. Cupellini, S. Jurinovich, M. Campetella, S. Caprasecca, C. A. Guido, S. M. Kelly, A. T. Gardiner, R. Cogdell, B. Mennucci, *J. Phys. Chem. B* **2016**, *120*, 11348–11359.

[4] F. Segatta, L. Cupellini, S. Jurinovich, S. Mukamel, M. Dapor, S. Taioli, M. Garavelli, B. Mennucci, *Journal of the American Chemical Society* **2017**, *139*, 7558–7567.

[5] C.-H. Yang, C.-P. Hsu, *The Journal of chemical physics* **2013**, *139*, 154104.

$\mathcal{O}(n)$ Concentric Atomic Density Fitting for Hartree-Fock Exchange

Cannada Lewis[1], **Edward Valeev**[1]

[1]*Department of Chemistry, Virginia Tech, Blacksburg, Virginia, USA*

Concentric Atomic Density Fitting[1] (CADF), also known as Pair Atomic Resolution of the Identity[2] (PARI), yields a drastic approximation of the two-electron four-center integrals, that allows for $\mathcal{O}(n)$ storage of the density fitting coefficients. Even though the approximate of the electron repulsion integrals is poor, CADF can be safely used to compute the exchange contribution to the Fock matrix with acceptable errors in $\mathcal{O}(n^3)$ operations.[3] To reduce the operation complexity we explore a novel screening method that skips small contributions to the exchange (K) matrix by exploiting the sparsity of both the CADF coefficients and localized molecular orbitals. In doing so we can readily achieve $\mathcal{O}(n)$ operation complexity while having a smaller prefactor than the traditional $\mathcal{O}(n)$ algorithm for exchange LinK.[4] Our approximations greatly improve the performance of CADF exchange (CADF-K) while introducing new errors much smaller than the error already present in the CADF-K approach.

Furthermore we show how the Clustered Low-Rank (CLR) tensor framework[5] can be used to massively reduce the storage required for the three-center two-electron integrals, allowing us to avoid their direct computation further reducing the prefactor associated with CADF-K. Our new screening approximation coupled with the use of the CLR framework yields a highly performant Hartree-Fock exchange algorithm with acceptable accuracy, requiring relatively small amounts of memory and only $\mathcal{O}(n)$ operations within each iteration of the SCF algorithm.

Finally, these algorithms were implemented in the TiledArray framework, a distributed memory massively parallel tensor contraction library, allowing them to scale to thousands of cores. We show the parallel scaling of traditional CADF-K along with our $\mathcal{O}(n)$ implementation across multiple nodes and hundreds of processors.

[1] D. S. Hollman, H. F. Schaefer, and E. F. Valeev, *J. Chem. Phys.* **140**, 064109 (2014).

[2] P. Merlot, T. Kjærgaard, T. Helgaker, R. Lindh, F. Aquilante, S. Reine, and T. B. Pedersen, *J. Comput. Chem.* **34**, 1486 (2013).

[3] S. F. Manzer, E. Epifanovsky, and M. Head-Gordon, *J. Chem. Theory Comput.* **11**, 518 (2015).

[4] C. Ochsenfeld, C. A. White, and M. Head-Gordon, *J. Chem. Phys.* **109**, 1663 (1998).

[5] C. A. Lewis, J. A. Calvin, and E. F. Valeev, *J. Chem. Theory Comput.* **12**, 5868 (2016).

The intricate case of tetramethyleneethane

Libor Veis[1], Andrej Antalík[1], Ali Alavi[2, 3], Örs Legeza[4], Jiří Pittner[1]

[1] *J. Heyrovský Institute of Physical Chemistry, ASCR, 18223 Prague, Czech Republic*
[2] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom*
[3] *Max Planck Institute for Solid State Research, Heisenbergstrasse 1, 70569 Stuttgart, Germany*
[4] *Strongly Correlated Systems "Lendület" Research group, Wigner Research Centre for Physics, H-1525, Budapest, Hungary*

Tetramethyleneethane (TME) represents the simplest disjoint non-Kekulé diradical structure. Although the system might seem simple at the first sight, correct calculation of its electronic structure poses a very challenging problem, indeed. It has been shown that the accurate description of its potential energy surface with respect to rotation around the central carbon-carbon bond requires well-balanced treatment of both, static and dynamic correlation, as well as a large-enough basis set [1].

In this study, we follow the work of Pozun *et al.* [1] and provide new benchmark data calculated by the full configuration interaction quantum Monte Carlo (FCIQMC) method using the active space of 60 molecular orbitals. Our FCIQMC results, which agree well with the available experimental data, are then used for testing of the accuracy of state-of-the-art multireference coupled cluster methods, namely the Mukherjee's multireference coupled clusters (MR CC) [2] and the coupled clusters with singles and doubles tailored by the density matrix renormalization group method (DMRG-TCCSD).

[1] Z. D. Pozun, X. Su, K. D. Jordan, *J. Am. Chem. Soc.* **135**, 13862 (2013).

[2] D. I. Lyakh, M. Musial, V. F. Lotrich, R. J. Bartlett, *Chem. Rev.* **112**, 182 (2012).

[3] L. Veis, A. Antalik, J. Brabec, F. Neese, Ö. Legeza, J. Pittner, *J. Phys. Chem. Lett.* **7**, 4072 (2016).

DFT investigation on the trans–cis C–Pd–C rearrangement in heteroleptic Pd-hemichelates

S. Dohm[1], C. Werlé[2], A. Hansen[1], S. Grimme[1*] and J. P. Djukic[2]

1. Mulliken Center for Theoretical Chemistry, Institut für Physikalische und Theoretische Chemie, Universität Bonn, Beringstraße 4, D-53115 Bonn, Germany

2. Institut de Chimie de Strasbourg, UMR 7177 CNRS, Université de Strasbourg, 4 rue Blaise Pascal, 67000 Strasbourg Cedex 08, France

Hemichelation is understood as a mode of metal chelation with a heteroditopic ligand where a covalent coordinative bond is supplemented with a predominantly non-covalent stabilizing delocalized interaction of the metal with another metal centered moiety. The ready trans-to-cis isomerization of such a hemichelate was investigated by dispersion corrected density functional theory. Variable temperature NMR experiments reveal, that the isomerization process requires a rather low activation barrier and that the two systems follow a first-order kinetic law. DFT-D calculations confirm that, in spite of the more important contribution of covalence to the Pd···$Cr(CO)_3$ in the *trans*-complex, the latter is metastable and converts readily into the cis isomer in a single elementary reaction step.

It can be shown, that this isomerization is facilitated dynamically because hemichelation by an arenetricarbonylchromium-ligand dynamically offers in the transition state of the *trans* →*cis* isomerization process alternative coordination positions to the Pd center, which preserves its square planar coordination and keeps the energetic barrier payload low. Instead, in the isomerization of conventional homoleptic trans-bispalladacycles involves partial chelate decoordination and an unfavorable high-lying Y-shaped-Pd(II) transition state.

We demonstrate the application of a multilevel composite scheme of decent methods applicable to a wide range of compounds, to obtain reasonable free energies within feasible times. A new tight-binding semiempirical method[1] is used locate stationary points including transition states. Geometries are refined with the fast, yet accurate PBEh-3c[2] composite method. Solvation contributions are obtained with the COSMO−RS[3] continuum solvent model. The presented scheme allows the calculation of such reactions with reasonable errors of ≈3 kcal/mol within several days even on regular desktop computers.

[1] S. Grimme, C. Bannwarth, P. Shushkov, J. Chem. Theory Comput. (2017), **13**, 1989-2009.

[2] S. Grimme, J. G. Brandenburg, C. Bannwarth, A. Hansen, J. Chem. Phys. (2015), **143**, 054107

[3] A. Klamt, J. Chem. Phys. 1995, 99, 2224–2235

Coarse Grained Cross-scale Expression of Complex Combustion Reaction Mechanism Based on Master Equation

Lin Ji, An Ning

Department of Chemistry, Capital Normal University, Beijing 100048, China

Combustion chemistry is a special branch of chemistry that aims at getting stable effective combustion condition as the target. Therefore, the key task of combustion chemistry mechanism investigation is to effectively represent the detail combustion mechanism as simplified phenomenological mechanism. Common mechanism reduction method usually “select“ the important reactions from the detailed reaction network, trying to improve the simulation efficiency by at the cost of least information lost. Based on the “coarse grained” idea, we propose to develop a three-level coarse grain ansatz, including the statistic of “microscopic state” clustering, the “fluctuationize” expression of multi-channel reaction in mesoscopic level, and extraction of feedback loop in the macroscopic level. Master equation is the expression of law of mass conservation in the Markov stochastic processes. Depending on the defination of “state“ at different scale, master equation have different name and form in different area, such as Energy Grained Master Equation[1] in RRKM/ME theroy, Markov State Model[2] in protein dynamics and Chemical Master Equation[3] in stochastic reaction dynamics. Altogether, we would develop a set of “information loss free” multiscale coarse grained combustion reaction mechanism expression method, so that we can effectively “simplify” the reaction mechanism model and connect the elementary reaction mechanism investigation with those of fluid dynamics in turbulence combustion research

[1] JA Miller, SJ Klippenstein; *J. Chem. Phys.* ***110**:1052.*(2006)
[2] CR Schwantes, RT McGibbon, VS Pande; *J. Chem. Phys.* ***141**:090901* (2014)
[3] DT Gillespie; *Annu. Rev. Phys. Chem.* ***58**: 35* (2007)

Soft X-ray Spectroscopy of Transition Metal Compounds: A Theoretical Perspective

Sergey I. Bokarev[1]

[1]Institute of Physics, Rostock University, Albert-Einstein-Str. 23-24, Rostock, Germany

To date, X-ray spectroscopy has become a routine tool that can reveal highly local and element-specific information on the electronic structure of atoms in complex environments. Here, we aim at the development of an efficient and versatile theoretical methodology for the treatment of soft X-ray spectra of transition metal compounds mainly based on the multi-configurational self-consistent field electronic structure theory combined with a perturbative LS-coupling scheme for spin-orbit coupling [1]. A special focus is put on the L-edge photon-in/photon-out and photon-in/electron-out processes, i.e. X-ray absorption, resonant inelastic scattering, partial fluorescence yield, photoelectron and Auger spectroscopy treated on the same theoretical footing [2-4]. We address the application of the X-ray metal L-edge and ligand K-edge spectroscopy to unraveling electronic structure and nature of chemical bonds [5-7], oxidation and spin-states [4], the interplay of radiative and non-radiative decay channels [3], fingerprints of nuclear dynamics [8,9] as well as ultrafast electron dynamics triggered by X-ray light [10,11]. The investigated systems range from the small prototypical coordination compounds and catalysts [1-7] to the aggregates of biomolecules [12].

[1] S.I. Bokarev et al. *Phys. Rev. Lett.*, **111**, 083002 (2013).
[2] G. Grell et al. *J. Chem. Phys.* **143**, 074104 (2015).
[3] R. Golnak et al. *Sci. Rep.*, **6**, 24659 (2016).
[4] S.I. Bokarev *J. Phys. Chem. C*, **119**, 19192 (2015).
[5] E. Suljoti et al. *Angew. Chem. Int. Ed.*, **52**, 9841 (2013).
[6] N. Engel et al. *J. Phys. Chem. B*, **118**, 1555 (2014).
[7] K. Atak et al. *J. Phys. Chem. B*, **117**, 12613 (2013).
[8] S. Karsten et al. *J. Phys. Chem. Lett.* **8**, 992 (2017).
[9] S. Karsten et al. *J. Chem. Phys.* **146**, 224203 (2017).
[10] H. Wang et al. *Phys. Rev. Lett.* **118**, 023001 (2017).
[11] H.Wang et al. *Mol. Phys.* doi:10.1080/00268976.2017.1294267 (2017).
[12] M. Preuße et al. *Struct. Dynamics* **3**, 062601 (2016).

Elucidating the structure of merocyanine dyes with the ASEC-FEG method

Leandro R. Franco, Idney Brandão, Tertius L. Fonseca, Marcos A. Castro, Herbert C. Georg

Instituto de Física, Universidade Federal de Goiás, Campus Samambaia, 74690-900, Goiânia, GO, Brazil

Merocyanine dyes form an interesting class of materials with many applications. They are used as indicators of polarity, acidity and other properties, as fluorescent probes of macromolecules, as biomarkers, etc. They have also been investigated as possible sensitizers for photodynamic therapy and for solar cells.

Due to their importance in several applications, it is relevant to investigate how the environment affects the structure of merocyanine dyes. However, because of the extended π-electron system connecting the electron donor and acceptor groups, these molecules have sensitive electronic and conformational structure, making the modeling of such systems in medium a difficult task.

In the present work we have applied the ASEC-FEG method (which combines the sequential QM/MM method [1] with the Free Energy Gradient method [2]) to elucidate the structure of Phenol Blue, a typical merocyanine dye, in several solvents, both protic and aprotic, covering a wide range of dielectric constant [3]. The structure of this molecule has been object of some debate in the literature. Some authors suggest that the molecule is mostly in the neutral state whereas other authors point that it is mostly in the zwitterionic state, in solutions of different polarities.

Our results show that the molecule is mostly in the neutral state in aprotic solvents and is displaced to a cyanine-like structure in polar protic solvents. The results also illustrate the important role played by the hydrogen bonds in the conformation of merocyanine dyes.

Acknowledgements: The authors gratefully acknowledge the financial support given by the brazilian agencies CAPES, CNPq and FAPEG.

References:

[1] K. Coutinho, S. Canuto, *J. Chem. Phys.* 113, **9132** (2000).

[2] N. Okuyama-Yoshida, K. Kataoka, M. Nagaoka, T. Yamabe, *J. Chem. Phys.* **113**, 3519 (2000).

[3] L. R. Franco, I. Brandão, T. L. Fonseca, H. C. Georg, *J. Chem. Phys.* **145**, 194301 (2016); I. Brandão, L. R. Franco, T. L. Fonseca, M. A. Castro, H. C. Georg, *J. Chem. Phys.* in press (2017).

Accelerating equilibrium isotope effect calculations by stochastic change of mass

Konstantin Karandashev[1], **Jiří Vaníček**[1]

[1]*Laboratory of Theoretical Physical Chemistry, Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015, Lausanne, Switzerland*

Accurate path integral Monte Carlo or molecular dynamics calculations of isotope effects have until recently been expensive because of the necessity to reduce three types of errors present in such calculations: statistical errors due to sampling, path integral discretization errors, and thermodynamic integration errors. While the statistical errors can be reduced with virial estimators and path integral discretization errors with high-order factorization of the Boltzmann operator, here we propose a method for accelerating isotope effect calculations by eliminating the integration error [1]. In particular, we show that the error of thermodynamic integration [2, 3] can be removed entirely by changing particle masses stochastically during the calculation (a trick closely related to lambda-dynamics [4, 5]) and by using a piecewise linear umbrella biasing potential. Moreover, we demonstrate numerically that this approach does not increase the statistical error. An alternative approach to remove the integration error is based on so-called direct estimators [6]. We demonstrate that combining the stochastic change of mass with the direct estimators results in a method with a lower statistical error, and therefore, in more efficient simulations [7]. The resulting acceleration of isotope effect calculations is demonstrated on a model harmonic system and on deuterated species of methane.

[1] K. Karandashev, J. Vaníček, *J. Chem. Phys.* **146**, 184102 (2017).

[2] J. Vaníček, W. H. Miller, J. F. Castillo, F. J. Aoiz, *J. Chem. Phys.* **123**, 054108 (2005); T. Zimmermann, J. Vaníček, *J. Chem. Phys.* **131**, 024111 (2009); M. Buchowiecki, J. Vaníček, *Chem. Phys. Lett.* **588**, 11 (2013).

[3] O. Marsalek, P.-Y. Chen, R. Dupuis, M. Benoit, M. Méheut, Z. Bačić, M. E. Tuckerman, *J. Chem. Theory Comput.* **10**, 1440 (2014); M. Ceriotti, T. E. Markland, *J. Chem. Phys.* **138**, 014112 (2013).

[4] Z. Liu, B. J. Berne, *J. Chem. Phys.* **99**, 6071 (1993).

[5] A. Pérez, O. A. von Lilienfeld, *J. Chem. Theory Comput.* **7**, 2358 (2011).

[6] B. Cheng, M. Ceriotti, *J. Chem. Phys.* **141**, 244112 (2015).

[7] K. Karandashev, J. Vaníček, in preparation.

Describing Chemical Reactions in Explicit Solvent Using Adaptive QM/MM Models

J.M. Boereboom[1], P. Fleurat–Lessard[2], R.E. Bulo[1]

[1]*Inorganic Chemistry and Catalysis group, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands*
[2]*Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB), 9 avenue Alain Savary, 21078 Dijon Cedex, France*

Solvation plays an important role in chemical reactivity: Changing the solvent can drastically change the mechanism of a reaction. This is especially true for polar protic solvents that can strongly interact with charged intermediates. Taking these effects into account accurately requires an explicit description of the solvent molecules. To obtain reliable insights into the thermodynamics and kinetics of bond formation in the presence of (explicit) solvent, very long and computationally intensive simulations are required. This is only feasible if a multi-scale description of the solvent is adopted. The presented work is two-fold: We compare and test recent multi-scale explicit solvation models [1-3], and present new insights into the role of solvent in an illustrative bond-breaking reaction. The reaction features the solvated $Me_2N–(CH_2)_3–CH=O$ molecule. In its closed form, this molecule contains a five-membered ring with a short $N|\cdots C=O$ bond. The molecule was selected for this unusual $N|\cdots C=O$ bond that mimics the transition states of nucleophilic additions onto a carbonyl moiety [4]. The multi-scale models all define two spherical domains in which the solvent molecules are described at the quantum mechanical level. One such domain is centered on the oxygen atom while the second one is centered on the nitrogen.

The accuracy of the models is benchmarked against a reference simulation describing the structural features of the solvated $Me_2N–(CH_2)_3–CH=O$ molecule in its closed form. We show that the closed state is best described by multi-scale solvation models that change smoothly between the QM and MM description. Surprisingly, a micro-solvation model can describe the structure of the closed $N|\cdots C$ state with similar accuracy. Using the best adaptive QM/MM model, we then obtain the first reliable energy for the $N|\cdots C$ bond breaking reaction. This binding energy is around 6.0 kcal/mol, which is stronger than an average hydrogen bond. The micro-solvation model fails to describe this bond formation process. Indeed, only an explicit dual-sphere approach can accurately account for the long-range solvation changes along the reaction path.

[1] R.E. Bulo, B. Ensing, J. Sikkema, L. Visscher. *J. Chem. Theory Comput.* **5**, 2212 (2009)

[2] N. Bernstein, C. Varnai, I. Solt, S.A. Winfield, M.C. Payne, I. Simon, M. Fuxreiter, G. Csanyi. *Phys. Chem. Chem. Phys*. **14**, 646 (2012)

[3] C.N. Rowley, B. Roux, *J. Chem. Theory Comput.* **8**, 3526 (2012)

[4] J. Pilmé, H. Berthoumieux, V. Robert, P. Fleurat–Lessard. *Chem. Eur. J.* **13**, 5388 (2007)

Time-resolved X-ray scattering by non-stationary states in atoms and molecules

Mats Simmermacher[1], **Andrés M. Carrascosa**[2], **Adam Kirrander**[2], **Niels E. Henriksen**[1], **Klaus B. Møller**[1]

[1]*Department of Chemistry, Technical University of Denmark, Kemitorvet 207, 2800 Kongens Lyngby, Denmark*
[2]*School of Chemistry, University of Edinburgh, David Brewster Road, Edinburgh EH9 3FJ, Scotland*

Modern pulsed X-ray sources permit time-dependent measurements of dynamical changes in atoms and molecules via non-resonant scattering. The planning, analysis, and interpretation of such experiments, however, require a firm and elaborated theoretical framework. Appropriate expressions for the X-ray scattering signal have previously been derived by use of first-order perturbation theory and a quantized description of the electromagnetic radiation [1–3]. In the present work, this approach is applied to non-stationary electronic wave packets in atoms [4] as well as to molecules that undergo rapid dynamics subsequent to excitation. It is demonstrated how the time-resolved X-ray scattering signal can be described and understood in terms of electronic scattering matrix elements, which are Fourier transformed expectation values of the one-electron density operator. Since these elements are obtainable from multi-configurational electronic wave functions in a Gaussian-type orbital basis [5], the scattering signal can be simulated by integration of available electronic structure and quantum dynamics codes into the framework of an appropriate program. Furthermore, a general analytic solution to the scattering signal by electronic wave packets in the hydrogen atom is derived [4]. This establishes an accurate benchmark for numerical calculations and permits further insights into the physics of time-resolved X-ray scattering.

[1] N. E. Henriksen, K. B. Møller, *J. Phys. Chem. B* **112**, 558 (2008).

[2] U. Lorenz, K. B. Møller, N. E. Henriksen, *Phys. Rev. A* **81**, 023422 (2010).

[3] G. Dixit, O. Vendrell, R. Santra, *Proc. Natl. Acad. Sci. U.S.A.* **109**, 11636 (2012).

[4] M. Simmermacher, N. E. Henriksen, K. B. Møller, *Phys. Chem. Chem. Phys.*, DOI: 10.1039/C7CP01831B (2017).

[5] A. M. Carrascosa, A. Kirrander, *Phys. Chem. Chem. Phys.*, DOI: 10.1039/C7CP02054F (2017).

Towards highly accurate correlation energies for molecular systems

Jian-Hao Li[1], **Clémence Corminboeuf**[1]

[1]*Institute des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland*

Novel ab initio approaches based on the GW approximation are proposed and validated for improving the correlation energies of molecular systems. GW-based methods have been implemented for solid state computations but have become increasingly popular for the description of molecules [1-3]. In the language of diagrammatic many-body perturbation theory, these methods take into account bubble diagrams to all orders via a screened Coulomb interaction. Here, we combine traditional quantum chemistry and GW, with the goal of achieving robust and cost-effective methods that go beyond conventional quantum chemistry for computing the energies of molecules in both the ground and excited state.

[1] D. Jacquemin, I. Duchemin, X. Blase, *J. Chem. Theory. Comput.* **11**, 3290-3304 (2015).
[2] F. Caruso, M. Dauth, M. J. van Setten, P. Rinke, *J. Chem. Theory. Comput.* **12**, 5076-5087 (2016).
[3] F. Bruneval, T. Rangel, S. M. Hamed, M. Shao, C. Yang, J. B. Neaton, *Comput. Phys. Commun.* **208**, 149-161 (2016).

Mechanistic investigation of solvent-controlled CO_2 reduction by triphos-iron-hydride complex

Abhishek Khedkar[1, 2], **Anette Petuker**[3], **Linda Iffland**[3] , **Maurice Van Gastel**[4] ,
Michael Roemelt[* 1, 2], **Ulf-Peter Apfel**[* 3]

[1]*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany*
[2]*Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany*
[3]*Fakultät für Chemie und Biochemie, Anorganische Chemie I,Ruhr-Universität Bochum, 44780 Bochum, Germany*
[4]*Max-Planck-Institut für Chemische Energiekonversion, Mülheim an der Ruhr, Germany*

There has been increasing interest for converting the greenhouse gas CO_2 into valuable fuels and small organics. The selective reduction of CO_2 is of high value towards a future application as a C1-building block. Existing catalysts used to overcome the low reactivity of CO_2 reduction are mainly based on noble transition metals like ruthenium, rhodium and iridium. First-row transition metals, however, provide the advantage of being less expensive, more abundant and less toxic. As a consequence, the replacement of noble metals with nonprecious metals such as iron, as catalysts for CO_2 reduction is an important target. Recently, we found that a triphos-based iron-hydride complex that is capable of performing solvent-controlled reduction of CO_2. In THF, the complex reduces CO_2 to CO selectively whereas in acetonitrile, the reduction reactions exclusively afford formate, $HCOO^-$. Here we present the results of a theoretical investigation based on density functional theory (DFT) and coupled cluster (CC) calculations that was aimed at elucidating reaction mechanisms of the selective reduction. Importantly, the theoretical studies demonstrate the crucial role of the applied solvent in altering the course of the reaction.

[1] A. Khedkar, A. Petuker, L. Iffland, M. V. Gastel, M. Roemelt and U. Apfel *manuscript in preparation* (2017)

PO3-240

Detailed Mechanistic Studies on Palladium/Norbornene Catalyzed C-H Amination of Aryl Halide

Ping Chen, Xinhao Zhang* and Yun-Dong Wu *

Lab of Computational Chemistry and Drug Design, Peking University Shenzhen Graduate School, Shenzhen, China

C-H functionalization of aryl halides have had an important impact on modern organic chemistry[1]. Different types of bonds can be constructed through Pd/NBE co-catalyzed C-H activation of aryl halide, but the mechanism is still unclear. A catalytic cycle involving three different oxidation states of palladium ($Pd^{0}/^{II}/^{IV}$) was proposed[2]. Inspired by Catellani reaction, Dong and coworkers developed a novel ortho C-H amination reaction[3]. In the reaction, two oxidants, i.e. aryl iodide and BzO-NR_2, are involved. Aryl iodide is preferred in the oxidative addition of Pd^0, while BzO-NR_2 is favored in the oxidative addition of Pd^{II} intermediate **C**. In mass spectrometric experiment, a Pd^{IV} intermediate containing Cs atom was observed. Therefore, a Cs model that Cs_2CO_3 assist oxidative addition to Pd^{II} intermediate was proposed. The computational results show that Pd^{II} intermediate selectively react with benzoxyl morpholine, which is consistent with experimental results. Distortion-interaction analysis show that the reduction of the distortion energy of benzoxyl morphpline in Cs model is the key factor for the change of the substrate selectivity.

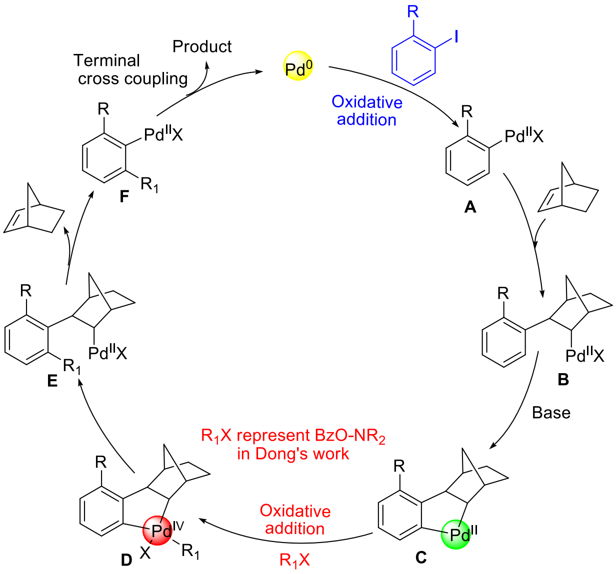


Figure 1. Proposed mechanism of Catellani reaction.

[1] J. Ye, M. Lautens, *Nat. Chem.* **7**, 863-870 (2015).
[2] M. Catellani, F. Frignani, A. Rangoni, *Angew. Chem. Int. Ed.* **36**, 119-122 (1997).
[3] Z. Dong, G. Dong, *J. Am. Chem. Soc.* **135**, 18350-18353 (2013).

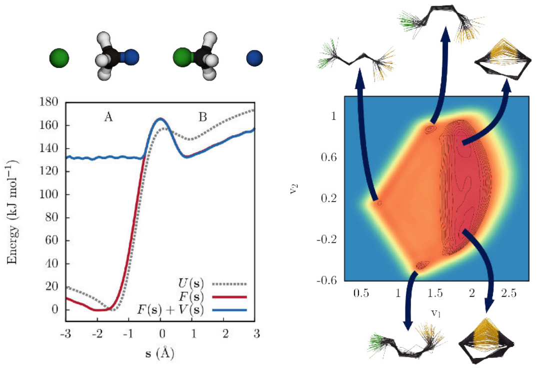
Enhancing fluctuations in chemical reactions

GiovanniMaria Piccini[1], **Michele Parrinello**[1]

[1]*Department of Chemistry and Applied Biosciences, ETH Zurich, c/o USI Campus, Via Giuseppe Buffi 13, CH-6900, Lugano, Ticino, Switzerland*

Molecular dynamics is a powerful tool to study the evolution of complex chemical systems. However, reactant and product states are often separated by very large activation energy barriers. Beacuse of this fact, the typical time scales of a chemical transition cannot be reached in a standard simulation. This limitations can be overcome by applying a bias potential to the underlying potential energy surface have been proposed, thus enhancing the fluctuations between reactants and product states.

Here we show how to different enhanced sampling methods, namely variationally enhanced sampling[1] (VES) and Metadyamics, can be used to study chemical reactions characterized by large energy barriers and involving rather complex degrees of freedom. We studied the asymmetric $CH_3F + Cl^- \leftrightarrow CH_3Cl + F^-$ S_N2 reaction using VES to obtain the Free-energy profile (see Fig. 1a) and calculate the rates.[2] We then studied the cyclization reaction of deprotonated 4-chloro-1-butanethiol to tetrahydrothiophene (see Fig. 1b) using metadynamics. Within this framework we applied the variational approach for conformation dynamics (VAC) to identify the best combination of variables allowing a proper Free-energy sampling.



1a 1b

Figure 1: a), Flooded Free-energy profile for the $CH_3F + Cl^- \leftrightarrow CH_3Cl$, b), FES of the tetrahydrothiophene cyclization reaction showing the different conformers of reactants and products.

[1] O. Valsson, M. Parrinello, *Phys. Rev. Lett.* **2014**, *113*, 90601.

[2] G. Piccini, J. J. McCarty, O. Valsson, M. Parrinello, *J. Phys. Chem. Lett.* **2017**, *8*, 580–583.

Ultrafast spin-flip dynamics in transition metal complexes triggered by soft X-ray light

Huihui Wang[1], **Sergey I. Bokarev**[1], **Saadullah G. Aziz**[2], **Oliver Kühn**[1]

[1]*Institute of Physics, Rostock University, Albert-Einstein-Str. 23-24, Rostock, Germany*
[2] *Chemistry Department, Faculty of Science, King Abdulaziz University, 21589 Jeddah, Saudi Arabia*

Recent advances in attosecond spectroscopy open the door to understanding the correlated motion of valence and core electrons on their intrinsic timescales. For valence excitations, processes related to the electron spin are usually driven by nuclear motion. When going, however, to the core-excited states where the core hole has a nonzero angular momentum, a strong spin-orbit coupling starts to play a role [1-3]. In this work, we present a theoretical simulation of an ultrafast spin-flip dynamics driven solely by spin-orbit coupling and electron correlation in the L-edge (2p→3d) excited states of a prototypical Fe(II) complex, which occurs faster than the core hole lifetime (about 4 fs) [4,5]. The non-equilibrium electron dynamics is studied by means of time-dependent restricted active space configuration interaction recast in the form of reduced density matrix propagation. The spin-orbit coupling between electronic states of different multiplicity is considered within the LS-coupling limit employing atomic mean-field integral approximation. Dissipative effects of electronic and vibrational origin are considered as well. A detailed analysis of such phenomena will help to gain a fundamental understanding of spin-crossover processes and build up the basis for their control by light.

[1] S.I. Bokarev, M. Dantz, E. Suljoti, O. Kühn, E.F. Aziz *Phys. Rev. Lett.* **111**, 083002 (2013).

[2] S.I. Bokarev, M. Khan, M.K. Abdel-Latif, J. Xiao, R. Hilal, S.G. Aziz, E.F. Aziz, O. Kühn *J. Phys. Chem. C* **119**, 19192 (2015).

[3] R. Golnak, S.I Bokarev, R. Seidel, J. Xiao, G. Grell, K. Atak, I. Unger, S. Thürmer, S.G. Aziz, O. Kühn, B. Winter, E.F. Aziz *Sci. Rep*. **6**, 24659 (2016).

[4] H. Wang, S.I. Bokarev, S.G. Aziz *Phys. Rev. Lett.* **118**, 023001 (2017).

[5] H. Wang, S.I. Bokarev, S.G. Aziz *Mol. Phys.* doi: 10.1080/00268976.2017.1294267 (2017).

Theoretical Investigations of Sigma-Hole Interaction in Condensed Halogen Systems

Carsten Müller[1]

[1]Theoretical Chemistry, Institute for Chemistry and Biochemistry, Freie Universität Berlin,
Takustr. 3, 14195 Berlin, Germany

Sigma-hole interaction determines the crystal structures of Cl_2, Br_2 and I_2 and of many polyhalogen compounds. Here we investigate more recently explored polyhalogen crystals of chlorine [1-2], bromine [3] and iodine monobromide [4]. By means of theoretical periodic density functional theory calculations, we not only confirm experimental X-Ray structures and vibrational spectra but also interpret the bonding pattern in the polyhalogen network and explore the influence of different cations.

In the two modifications of solid F_2 – on the other hand – sigma hole interaction does not appear to be important and solids based on polyfluorine networks seem not to exist due to the less developed sigma hole in F_2. Here we investigate α- [5] and β-F_2 [6] at coupled cluster level applying an incremental scheme to understand why F_2 behaves differently in solids than other halogens and to confirm experimentally observed X-Ray structures from literature.

[1] R. Brückner, H. Haller, S. Steinhauer, C. Müller, S. Riedel, *Ang. Chem. Int. Ed.* **54**, 15570 (2015).

[2] R. Brückner, P. Pröhm, A. Wiesner, S. Steinhauer, C. Müller, S. Riedel, *Ang. Chem. Int. Ed.* **55**, 10904 (2016).

[3] K. Sonnenberg, P. Bröhm, S. Steinhauer, A. Wiesner, C. Müller, S. Riedel, *Z. Anorg. Chem.* **643**, 101 (2017).

[4] L. Mann, P. Voßnacker, C. Müller, S. Riedel, *Chem. Eur. J.* **23**, 244 (2017).

[5] S. Mattsson, B. Paulus, C. Müller, *in preparation.*

[6] C. Müller, *in preparation.*

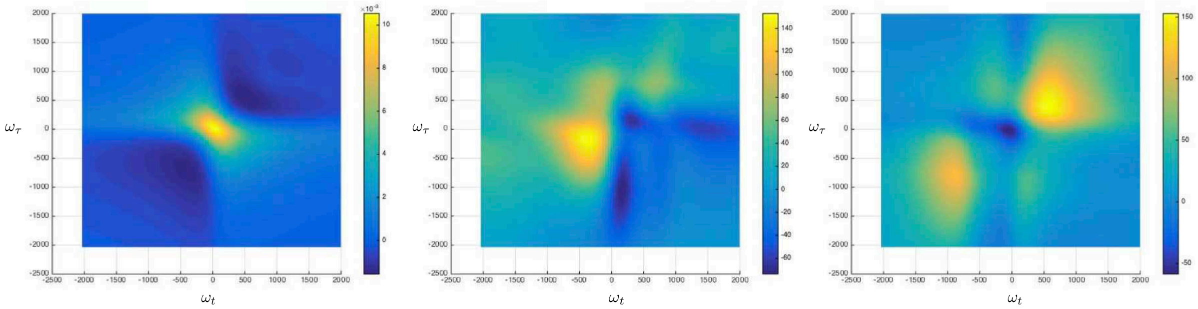
Theory of Strong-Field Effects in Femtosecond Electronic Two-Dimensional Spectroscopy

Elisa Palacino-González*, Lipeng Chen, Maxim F. Gelin and Wolfgang Domcke
Department of Chemistry, Technical University of Munich, D-85747 Garching, Germany
*Corresponding author: elisa.palacino@ch.tum.de

Usually, femtosecond spectroscopic experiments are performed in the regime of weak coupling between the chromophore and the applied laser fields. The goal of femtosecond time-resolved spectroscopy is to obtain information on the photoinduced dynamics of the molecule under study rather than to manipulate its dynamics. Nevertheless, a growing number of experimental and theoretical studies reveal that the signals induced by suitably chosen comparatively strong laser fields may provide more information on the photoinduced dynamics than weak-field signals. For example, it was demonstrated that strong pump and probe pulses in femtosecond pump-probe spectroscopy can significantly enhance weak transitions which cannot be detected with pump-probe spectroscopy in the weak-field regime [1].

Electronic two-dimensional (2D) spectroscopy is currently one of the most popular techniques in coherent femtosecond spectroscopy. In the present work, we theoretically investigate the application of this technique beyond the weak-field limit. We consider a model consisting two electronic states which are linearly coupled to a single vibrational mode, assuming that the displacement of the potential-energy function of the excited electronic state relative to the electronic ground state is relatively small. This situation is typical, for example, for porphyrins and related molecules.

Strong matter-field coupling causes a breakdown of theories which are based on perturbation theory in the matter-field coupling. We therefore evaluate the nonlinear polarization in the rephasing and non-rephasing phase matching directions in a nonperturbative manner, solving the relevant driven master equations numerically. In the limit of weak matter-field coupling, the polarization obtained in this way reduces to the third-order polarization. For intermediate and strong matter-field coupling, on the other hand, the thus-obtained polarization contains all relevant higher-order contributions beyond the weak-field limit.



Typical computed non-rephasing 2D spectra for a two-state one-mode model are presented in the figure. The left panel shows the weak-field signal which is indistinguishable from that of the electronic two-level system without electron-vibration coupling. Stronger pulses enhance the effective electron-vibration coupling of the system, revealing vibrational transitions in the 2D spectra (middle and right panels). Our analysis shows that the strength of the laser field at the peak of the pulses and the duration of the pulses can be fine-tuned to enhance the information content of the 2D spectra.

References

[1] Gelin, M. F., Belyaev, A. K. and Domcke, W. Pump-probe spectroscopy with strong pulses as a tool to enhance weak electronic transitions, Phys. Rev. A **87,** 063416 (2013).

Virtual screening through molecular fingerprinting of existing antipsychotic drugs.

Ashish Radadiya[1b], Harshika Patel[3], Payal Bhalodia[3], Hardevsinh Vala[2], Anamik Shah[2]* and Nigel Richards[1]

[1]*School of Chemistry, Cardiff University, Cardiff, UK*

[2]*National Facility for Drug Discovery Centre, Department of Chemistry, Saurashtra University, Rajkot-360005, Gujarat, India*

[3]*Department of Pharmacology, R. K. College of Pharmacy, Rajkot, Gujarat, India.*

E-mail: *anamik_shah@hotmail.com*

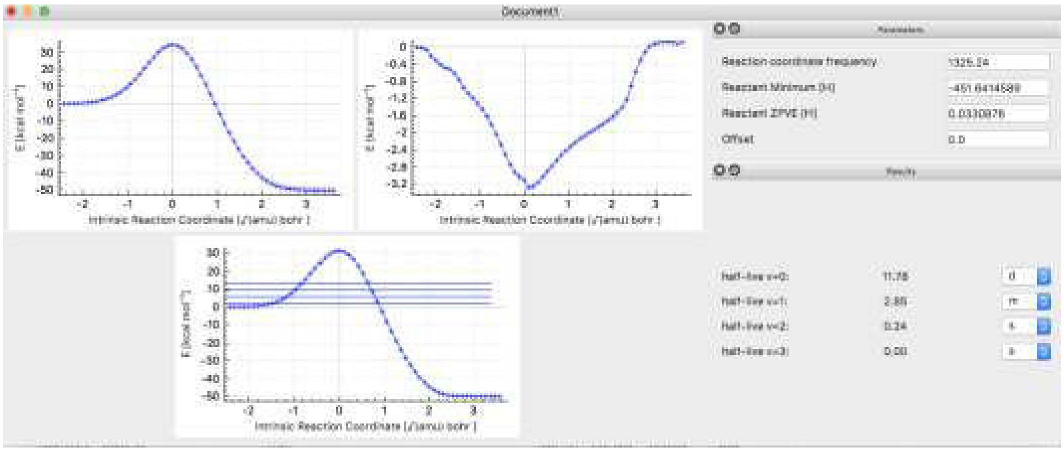
Abstract: Use of molecular fingerprinting in virtual screening is easier and faster but yet powerful technique in medicinal chemistry research for initial hit identification. Here, an attempt has been made for finding similar compounds from the FPMD library (an in-house collection of 7000 small organic molecules) based on approved antipsychotic drugs targeting D2 receptors, serotonin receptors and 5-HT_{2A}. Different molecular fingerprints like FCFP, ECFP, ECFC were used for comparative studies of Drug database. Top 20 ranked molecules were identified and among them HKV-54, 68, 71, 86, 102 and 115 were screened for their in vivo antipsychotic activity against rat model of 48 mice. The study includes Catalepsy, Inhibition of Apomorphine induced stereotypic reaction, Pole climbing avoidance and sedative effect. Results obtained were comparable with existing antipsychotic drugs available in market.

Tunnex: A user-friendly program to compute tunneling kinetics

Henrik Quanz[1] and Peter R. Schreiner[1]

[1]*Institute of Organic Chemistry, Justus-Liebig University, Heinrich-Buff-Ring 17, 35392 Gießen, Germany*

Since the discovery of *tunneling control* in our group [1], demands for computing tunneling kinetics have increased significantly.[2-4] Tunnex is a is a cross-platform free open-source program under development to estimate reaction rates from electronic structure packages (ESPs). Transition state theory (TST), Variational TST (VTST), tunneling corrections, including the Wigner, Eckart as well as the Wentzel, Kramers and Brillouin (WKB) approximations, will be included in the final version. The program consists of two parts: a graphical user interface (GUI) to visualize and compute the results and a command line tool to collect the data from ESPs. Currently, only Gaussian is supported, but the interface will be made extendable by script languages through plugins. Tunnex offers customizable 2d plots and the data are accessible in tables; data export is also supported. The goal is to combine the GUI and the command line tool to one final program including project management and server support.



Reaction coordinate frequency 1325.24
Reactant Minimum [H] -451.6414589
Reactant ZPVE [H] 0.0330876
Offset 0.0

half-live v=0: 11.78 d
half-live v=1: 2.88 m
half-live v=2: 0.24 s
half-live v=3: 0.00 s

[1] P. R. Schreiner, H. P. Reisenauer, D. Ley, D. Gerbig, C.-H. Wu and W. D. Allen, *Science* **332**, 1300 (2011)

[2] M. Schäfer, K. Peckelsen, M. Paul, J. Martens, J. Oomens, G. Berden, A. Berkessel and A. J. Meijer, *J. Am. Chem. Soc.* (2017)

[3] S. Karmakar and A. Datta, *J. Org. Chem.* **82**, 1558 (2017)

[4] C. M. Nunes, S. N. Knezz, I. Reva, R. Fausto and R. J. McMahon, *J. Am. Chem. Soc.* **138**, 15287 (2016)

Activation of the GTP Hydrolysis by the Switch I region in the Elongation Factor EF-Tu

Gülşah Çifci[1], Şeref Gül[2], Mehtap Işık[3], Selami Ercan[4], Viktorya Aviyente[1], Neş'e Bilgin[5], Bülent Balta[6]

[1] *Bogazici University, Department of Chemistry, 34342 Bebek, Istanbul*
[2] *Koç University, Department of Chemical and Biological Engineering, 34450 Sariyer, Istanbul*
[3] *Tri-Institutional PhD Program in Chemical Biology, Weill Cornell Graduate School of Medical Sciences, 1300 York Ave, New York, NY 10065*
[4] *Batman University, School of Health, 72060 Batman*
[5] *Boğaziçi University, Department of Molecular Biology and Genetics, 34342 Bebek, Istanbul*
[6] *Istanbul Technical University, Department of Molecular Biology and Genetics, 34469 Maslak, Istanbul*

Elongation factor Tu (EF-Tu) is responsible of the delivery of the aminoacyl-tRNA to the ribosome. EF-Tu is a G-protein with a low intrinsic GTPase activity, but this activity can be accelerated by ≈ 6 - 7 orders of magnitude by programmed ribosomes. The stimulation of the GTP hydrolysis is thought to be triggered by a conformational rearrangement of EF-Tu, which is in turn caused by a conformational rearrangement of the ribosome and tRNA.

Molecular dynamics simulations, 200-300 ns long, have been carried out on the wild type and mutant EF-Tu·GTP complexes from *T. aquaticus* and *E. coli*. The Amber ff03 force field has been used, together with a periodic box of TIP3P water molecules.

In *T. aquaticus*, the Switch I region has been found to be very mobile and R57 of Switch I enters the active site like the catalytic arginine in other G-proteins. While in the wild type *E. coli* EF-Tu, the corresponding K56 has remained out of the active site, in the simulations at a higher temperature or using the K56R mutant, this residue has come close to GTP.

pK_a calculations via thermodynamic integration simulations show that an important fraction of H85, a residue known to mediate the stimulatory effect of the ribosome, is doubly protonated. When doubly protonated, H85 spends a considerable time in the active site even in the absence of ribosomes.

We also show that the T62-γ-phosphate and T62-Mg^{2+} interactions are necessary to maintain the GTP bound conformation of Switch I, whereas D51 is not crucial.

Q-Chem 5: Facilitating Worldwide Scientific Breakthroughs

Evgeny Epifanovsky[1]

[1]*Q-Chem, Inc. 6601 Owens Drive, Suite 105, Pleasanton, California 94588, USA*

Founded in 1993, Q-Chem strives to bring its customers state-of-the-art methods and algorithms for performing quantum chemistry calculations. Cutting-edge innovation, performance, and robustness are Q-Chem's distinguishing features. Q-Chem is an open-teamware project, and the latest release includes contributions from more than 100 developers in 9 countries.

This poster presents methodological advances and algorithmic improvements contained in the new release of our software, Q-Chem 5:

- Quantum chemistry's broadest range of density functionals. Over 200 functionals!
- New parallel capabilities. The new occ-RI-K method significantly speeds up hybrid DFT calculations of the energy and gradient in large basis sets. OpenMP parallel DFT frequency is available. Improved parallel RI-MP2 and coupled cluster gradients.
- All-new effective core potential library. Vital for heavy elements, it provides higher angular momentum capabilities for energies, analytical gradients and analytical frequencies. Also improved precision and support for OpenMP parallel evaluation.
- New solvation and QM/MM capabilities. The CMIRS solvation method is available. New capabilities to model solvation effects on excited states and NMR are included.
- New energy decomposition analysis (EDA) methods. The DFT-based second generation ALMO-EDA with stable basis set limits is implemented, and its single bond extension is available. The adiabatic EDA and MP2 ALMO-EDA are included.
- New anharmonic methods. The uncoupled mode model is available for more accurate anharmonic thermochemistry than harmonic analysis. A new anharmonic vibrations module is included for accurate spectroscopic prediction.
- New electron correlation methods. For strongly correlated molecules, unique new methods, include NOCI-MP2, spin-flip extensions, CCVB for open shells, CCVB-SD energies and gradients for closed shells. Traditional CASSCF is now available.
- General improvements. Greatly expanded basis set library. New visualization capabilities in IQmol front end.

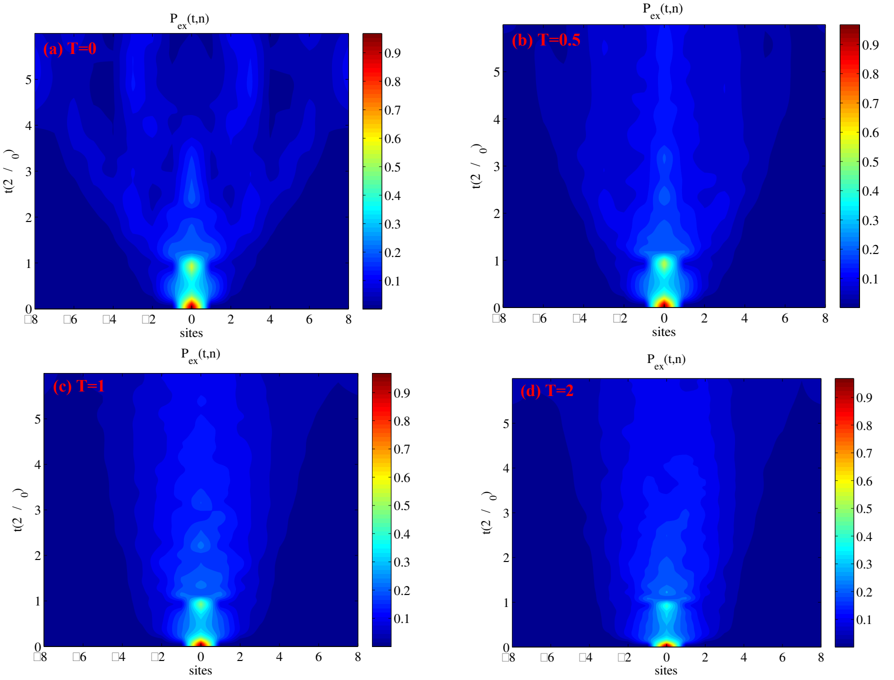
Finite temperature dynamics of a Holstein polaron: Thermo Field dynamics approach

Lipeng Chen

Department of Chemistry, Technische Universität München, D-85747 Garching, Germany

Organic solar cells (OSCs) offer the advantage of wide-ranging chemical functionalities which render tunable their optical, electrical, electrochemical, and morphological properties. However, OSCs have yet to possess the photocurrent efficiencies of their inorganic counterparts, thereby limiting their large-scale commercial applications. It is thus imperative that uncovering the mechanisms of charge transport will immensely facilitate the design of solar-to-electronic energy conversion devices with high efficiency and robustness. Despite many intriguing facets of charge transport uncovered in recent years, a consensus has yet to emerge on fundamental mechanisms of charge transport in organic semiconductors.

Theoretical study of charge transport in organic molecular crystals has a long and rich history dating back to as early as 1950s when Holstein pioneered the concept of small-polaron movement. A large body of literature exists on the study of the conventional form of Holstein Hamiltonian with the diagonal coupling only. However simultaneous presence of diagonal and off-diagonal electron-phonon coupling seems crucial to characterize the charge carriers transport behavior in organic semiconductors. Previously, we have proposed a multitude of the Davydov trial states, i.e., a superposition of the D_1 or the D_2 Ansatze, referred to the 'multi-D_1' or 'multi-D_2' Anatze to systematically study the dynamics of a one dimensional Holstein polaron in the presence of simultaneous diagonal and off-diagonal exciton-phonon coupling at zero temperature. Here, we extend polaron dynamics described by multiple Davydov ansatz to finite temperature by seamlessly integrating the multi-D_2 ansatz into the thermo field dynamics (TFD) framework, a finite temperature representation of quantum mechanics employing temperature dependent 'vaccum' expectation values to treat statistical averages of observables.



The time evolution of the exciton probability at different temperatures T=0, 0.5, 1, 2 are displayed in Figure above. We have found that the increase of temperature inhibits polaron mobility for weak to moderate diagonal coupling, while off-diagonal coupling induce phonon-assisted transport which dominates at high temperature. It is also demonstrated that band-like transport features dominate the diagonal coupling case, and there exists a crossover from band-like to hopping transport with increasing temperature when including off-diagonal coupling.

Applicability of the Effective Oxidation State analysis

Verònica Postils, Carlos Delgado-Alonso, Josep M. Luis, Pedro Salvador*

Institut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona, Maria Aurèlia Capmany 69, 17003, Girona, Spain.
email: vpostils@gmail.com

Oxidation State (OS) is a relevant and worldwide-used concept in Chemistry defined as the charge an atom has (*might be imagined to have*) after applying an agreed-upon rules. However, conceptually, the OS is a property intrinsically related to the distribution of electrons around the atom. Thus, the electronic wave function of the system should contain this type of information if a proper partition and scheme is devised. In 2015, we introduced a general scheme to measure the OS from wave function analysis, the so-called effective oxidation state (EOS) analysis [1].

Here we present a systematic EOS analysis [2] taking into account, among others, the compounds described in the recent Karen's IUPAC Report on the revision of the OS concept [3]. Remarkably, the results of our quantum mechanical approach can be reconciled with the empirical rules given by Karen to calculate OSs in most cases and, in some difficult or unclear situations where Karen used special provisions to reproduce the expected OS, our approach is free of such considerations. For instance, when the more electronegative atom is bonded as a Lewis acid or when the molecule cannot be described by a single Lewis structure.
The determination of the OS in carbene structures represents another limitation of the *new* empirical rules reported in the IUPAC's report. Mainly, they cannot retrieve the different splitting of the carbene double bond and the different OSs Fischer- and Schrock-like carbenes have due to differences in their electronic structure and bonding. The empirical rules given by Karen, unlike EOS analysis, cannot describe the homolytic double bond cleavage is expected by Fischer-like carbenes.
Finally, the results obtained from EOS analysis on a large set of π-haptocomplexes will be presented, where a broader rule to determine the OS for these compounds can be devised: the π-haptoligand in the complex presents the OS that corresponds to an aromatic structure, according to Huckel's and Baird's aromaticity rules.

[1] E. Ramos-Cordoba, V. Postis, P. Salvador, *J. Chem. Theory Comput.* **11**, 1501 (2015).
[2] V. Postils, C. Delgado-Alonso, J. M. Luis, P. Salvador, *in preparation.*
[3] P. Karen, P. McArdle, J. Takats, *Pure Appl. Chem.* **86**, 1017 (2014). P. Karen, *Angew. Chem. Int. Ed.* **54**, 2 (2015).

Spectroscopy of Cooperative Laser Electron-γ-Nuclear Processes in Molecules and Clusters: New Effects in Cryogenic Molecules

A.V. Glushkov[1,2], **A.A. Kuznetsova**[2], **O.Yu. Khetselius**[1,2]

[1]*Department of Applied Mathematics and Quantum Optics, Odessa State University – OSENU, Lvovskaya str.,15, Odessa, 65016, Ukraine*
[2]*International Centre of Quantum Chemistry, Odessa State University – OSENU, Lvovskaya str.,15, Odessa, 65016, Ukraine*

In the modern molecular spectroscopy a great interest attracts studying a new class of phenomena, connected with modelling the cooperative laser-electron-γ-nuclear processes. It includes calculation of the probabilities of the mixed γ-optical transitions in molecules, intensities of the complicated γ-transitions due to the changing of the molecular excited state population due to a laser field effect. The first qualitative estimates of the cooperative effects parameters were earlier presented (e.g. [1] and refs. therein). We develop an advanced computational approach to calculation of laser-electron-γ-transition spectra (electron-vibrational-rotational satellites) of nucleus in diatomic and multiatomic molecules, based on density functional (one version) and model potential (second version) methods and energy approach [2]. Decay and excitation probability are linked with imaginary part of the molecule - field system. New data on the electron-nuclear γ-transition spectra of a nucleus in some molecules are presented, namely, for diatomics, 3-atomic XY_2 ($D_{\propto h}$), 5-atomic XY_4(T_d), 7-atomic XY_6(O_h) ones (HI, Hbr, OsO_4, UF_6, alkali dimers). As example, in fig.1 the theoretical emission (solid curve) and absorption spectrum of nucleus ^{127}I in $H^{127}I$ is presented. It is shown that studying cooperative electron-gamma-nuclear processes in cryogenic Rydberg molecules (such as ^{133}Cs nucleus; $E^{(0)}_{\gamma}$=81 keB; $^{85}Rb^{133}Cs$) allows to discover the cooperative effects experimentally for the first time.

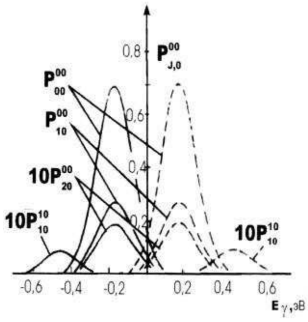


Fig.1 Emission and absorption spectrum of ^{127}I in $H^{127}I$ (ν_a=0, J_a=0)

[1] V. Letokhov, C.Moore, *Chemical and Biochemical Applications of Lasers*, Acad. Press, N-Y, 1979; V. Letokhov, V. Minogin, *JETP.Sov.Phys.***70**, 794 (1976); L.Ivanov, V. Letokhov, *JETP.Sov.Phys.***93**, 396 (1987); A. Glushkov, L. Ivanov, V. Letokhov, Preprint ISAN N-AS4, Moscow-Troitsk, 1992; *Phys.Lett.A.***170,** 33 (1992).

[2] A. Glushkov, O.Khetselius, S. Malinovskaya, *Molec. Phys.* **160,** 1257 (2008); *Frontiers in Quantum Systems in Chemistry and Physics, Ser.: Progress in Theor.Chem. and Phys.* Ed. S. Wilson, P. Grout, J. Maruani, G. Delgado-Barrio, P. Piecuch (Springer) **18**, 523 (2008).

A Detailed View into Structural and Functional Mechanism of the First Intermediate State of Channelrhodopsin-2

Beatrix M. Bold[1], Yanan Guo[1], Franziska E. Beyle[1], Peter Hegemann[2], Marco Marazzi[1,3] and Marcus Elstner[1]

[1]Department of Theoretical Chemical Biology, Institute of Physical Chemistry, KIT,
Kaiserstrasse 12, 76131 Karlsruhe, Germany
[2]Experimental Biophysics, Institute of Biology, Humboldt-Universität,
Invalidenstrasse 42, 10115 Berlin, Germany
[3]Université de Lorraine-Nancy & CNRS, SRSMC, Vandoeuvre-lès-Nancy, France

Channelrhodopsins (ChRs) are light-gated ion channels and widely used in the field of optogenetics, because of their easy expressibility in various host cells and their ability to generate photo currents in a very controlled fashion.

They consists of the light-isomerizable chromophore retinal. Light absorption of the dark-state of ChR causes the isomerization of retinal from all-*trans* to 13-*cis*. The isomerization triggers a cyclic reaction, where a sequence of different reactions like opening or closing of the channel take place. It is called photocycle and consists of several intermediate states, which are spectroscopically identified.

A QM/MM study of the dark state of ChR2 Wild-Type give already an insight into the active site [1]. A detailed atomistic knowledge of the active site is needed for further studies of the several intermediate states. The first intermediate state of ChR2 is called P1.

Spectroscopic results give an insight of changes happen in P1. However, a detailed atomistic description of P1 still lacks, which is important to understand the complete photocycle.

Several techniques are used to characterize the atomistic and functional mechanism of this first intermediate state. QM/MM and MM simulations were performed to study the P1 state. Calculation of excitation energies and vibrational frequencies are used to compare with spectroscopic data and to characterize changes in the active site and in the protein environment of the chromophore retinal in P1.

[1] Y. Guo, *Chemical Science* ***7***, 3879 (2016).

Spectroscopy Interatomic Potentials, Collisional Spectral Line Shift and Broadening for molecular pairs “heavy atom- noble gas atom”

O.Yu. Khetselius[1,2], **A.A. Kuznetsova**[2], **V. F. Mansarliysky**[2]

[1]*Department of Applied Mathematics and Quantum Optics, Odessa State University – OSENU, Lvovskaya str.,15, Odessa, 65016, Ukraine*
[2]*International Centre of Quantum Chemistry, Odessa State University – OSENU, Lvovskaya str.,15, Odessa, 65016, Ukraine*

We present new advance computational approach and new data for interatomic potentials and collisional spectral lines shifts and broadening for moelecular systems, which include heavy elements atoms (alkali, alkali-earth, lanthanides and others) in an atmosphere of the noble gas atoms. Besides, computing the spectral line (including the hyperfine structure) shift allows to determine a quality of the electron wave functions and study a contribution of the relativistic and correlation effects. In order to calculate, for example, the hyperfine spectral lines collision shift one should use the expression from kinetical theory of the spectral lines and computational code [1]:

$$f_p = \frac{D}{p} = \frac{4\pi w_0}{kT} \int_0^\infty dw(R) \exp(-U(R)/kT) R^2 dR$$

where $U(R)$ is an effective potential of the inter atomic interaction, which has a central symmetry in a case of the pairs A-B; T is temperature, w_0 is a frequency of the hyperfine transition in the isolated active atom; $d\omega(R)=Dw(R)/w_0$ is the relative local shift of the hyperfine lines, which is due to the disposition of atoms of the A and B on a distance R. The relativistic many-body perturbation theory [2] is used to determine the relativistic Dirac functions for studied atoms. We present new data on the interatomic potentials, local and observed collisional f_p shifts and widths for pairs: A-B (A=Rb,Cs,Tl,Yb; B=He,Ar, Kr,Xe) in dependence on temperature T. Our results are compared with the available experimental data and other theoretical results (see Refs. in [2]), which are obtained within a perturbation theory with the Hartree-Fock or Dirac-Fock zeroth approximation.

[1] A. Glushkov, O. Khetselius et al, Theory and Applications of Comput. Chem. (AIP) **1102,** 172 (2009); *Int. J. Quant. Chem.* **109**, 3325 (2009). .

[2] O. Khetselius, *Frontiers in Quantum Methods and Applications in Chem. and Phys., Ser.: Progress in Theor. Chem. and Phys.,* ed. M.Nascimento, J.Maruani, E.Brändas, G.Delgado-Barrio (Springer).**29**, 54 (2015).

Exploring the Structure of Dialkyl and Diallyl Magnesium Clusters by Means of Global Search Algorithm

S. Bouaouli[1], **L. Perrin**[1], **P. Carbonnière**[2]

[1]ICBMS UMR 5246, Université de Lyon, Bat Curien, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne cedex, France
[2]IPREM/ECP UMR CNRS 5254, Université de Pau et des Pays de l'Adour, 2 Avenue du Président Pierre Angot, F-64000 Pau, France

Organomagnesium reagents occupy a central position in organometallic chemistry, not only in organic synthesis but also in coordinative chain transfer polymerization, in which they are used, in combination with a catalyst, as a chain transfer agent [1]. Formally, the chain exchange reaction relies on a associative / dissociative mechanism that involves hetero-polymetallic complexes, either as transition states or reaction intermediates [2].

The modeling of this type of reaction, that is formally a transmétallation, is critical in order to depict and understand the mechanism of polymerizations that are carried out under chain transfer condition. Currently no mechanistic study provides a rational basis for the research and development of catalytic chain transfer polymerization systems, and especially the match or mismatch between the active catalyst and the chain transfer agent [3]. This most probably originates from (i) the lack of information on the nature and structure of the homo- and heteropolymetallic systems involved in the polymerization, (ii) the conformational heterogeneity of such systems.

In order to raise information on the clusters involved in alkene and conjugated diene polymerization, a global search algorithm of minima (GSAM) [4] has been used in order to identify the most stable clusters and to assess their conformational heterogeneity. This method, which is based on the sampling of the topological form generated on the basis of a set of molecular fragments, allows an efficient exploration of the most stable polymetallic clusters.

In this communication we present an unprecedented exhaustive sampling of two organomagnesium systems: $[Mg(Allyl)_2]_n$ and $[Mg(Bu)_2]_n$, n varying from 1 to 6. In addition to the structural information collected from this sampling, the stability of the n-mers is discussed and the most relevant structures isolable in solution are proposed. Based on this sampling, precise energy profiles for ethylene and butadiene polymerization, under change exchange conditions can be computed and will be presented.

[1] A. Valente, A. Mortreux, M. Visseaux, P. Zinck, *Chem. Rev.* ***113***, 3836 (2013).

[2] R. Ribeiro, R. Ruivo, H. Nsiri, S. Norsic, F. D'Agosto, L. Perrin, C. Boisson, *ACS Catal*. ***6***, 851 (2016).

[3] G. J. P. Britovsek, S. A. Cohen, V. C. Gibson, M. van Meurs, *J. AM. CHEM. SOC.* ***126***, 10701 (2004).

[4] R. Marchal, P. Carbonnière, C. Pouchan, *Int. J. Quantum Chem.* ***110***, 2256 (2010).

New Electron-β-Nuclear Spectroscopy of Molecules and Chemical Bond Effect on The β-Decay Parameters

V.V. Buyadzhi[1,2] , **A.V. Glushkov**[1,2], , **Y.V.Dubrovskaya**[1,2], **O.Yu. Khetselius**[1,2]

[1]*Department of Applied Mathematics and Quantum Optics, Odessa State University – OSENU, Lvovskaya str.,15, Odessa, 65016, Ukraine*
[2]*International Centre of Quantum Chemistry, Odessa State University – OSENU, Lvovskaya str.,15, Odessa, 65016, Ukraine*

We present the theoretical fundamentals of electron-beta-nuclear computational spectroscopy of molecules and discuss the cooperative electron β-nuclear processes in molecules, including the excitation, ionization, electronic rearrangement, induced by the nuclear reactions and β-decay [1]. The many-body perturbation theory (PT) with the optimized Kohn-Sham zeroth approximation [1] is used to calculate the β-decay parameters for a number of allowed (superallowed) transitions (^{33}P-^{33}S, ^{241}Pu-^{241}Am etc) and study a chemical bond effect on β-decay parameters. There are taken into account the following effects: i) Changing the electron wave functions because of the changing molecular electric field; changing the valence shell occupation numbers in different chemical substances; ii) The integration limits (calculating the Fermi integral function) changing due to different chemical substances; iii) additional channel, when β-electron occupies a free state in the bound molecular spectrum and other decay channels. We calculated the final-state probability distribution for excitations to the electronic continuum of $^3HeT^+$ resulting from the β-decay of T_2. We studied the electronic rearrangement induced by nuclear transmutation in the β-decay $^{6}_{2}He_4 \rightarrow (^{6}_{3}Li^{+}_{3})^* + e^- + \bar{\nu}_e$. The half-life period $T_{1/2}$ for β-decay of tritium atom (molecule) has been estimated while taking into account the bound β-decay channel and some other accompanying effects. The estimated values of $T_{1/2}$ for the tritium β-decay and free triton decay are: $(T_{1/2})_a$=12.26 years (correction due to the electron-atomic-molecular effects $(\Delta T_{1/2}/T_{1/2})_a$=0.8%) for the tritium atom and $(T_{1/2})_t$ =12.36 years for the triton decay. We firstly present the value $T_{1/2}$ in a case of the β-decay in the halogen-containing molecular tritium (^{3}HCl): $(T_{1/2})_m$=12.28 years (^{3}HCl); the correction due to the chemical bond effect is $(\Delta T_{1/2})_{am}$=0.024 (i.e. 0.20%).

[1] A. Glushkov, O. Khetselius, L. Lovett, *Advances in the Theory of Atomic and Molecular Systems: Dynamics, Spectroscopy, Clusters, and Nanostructures. Series: Progr. in Theor. Chem. and Phys*, Eds. P. Piecuch, J. Maruani, G. Delgado-Barrio, S. Wilson (Springer). **20**, 125 (2009).

A Theoretical Study of the Interaction of Calcite with Amino Acids

Robert Stepić[1, 2], **Zlatko Brkljača**[1, 2, 3*] , **Ana-Sunčana Smith**[1, 2, 3], **David M. Smith**[2, 3]

[1] *PULS Group, Institute for Theoretical Physics I, FAU, Nägelsbachstraße 49b, Erlangen, Germany*
[2] *Cluster of Exellence: Engineering of Advanced Materials, Nägelsbachstraße 49b, Erlangen, Germany*
[3] *CLS Group, Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia*

Calcite is one of the most widespread minerals on earth which interacts favourably with a variety of biomolecules. This interaction can mediate the growth of calcite resulting in formation of biominerals with remarkable mechanical properties useful in a number of applications [1]. In this work we utilize a bottom-up approach and study the interaction of protein building blocks, amino acids, with the stable (104) surface of calcite. We also probe the interactions with different morphologies deriving from (104) surface which incorporate kinks and edges. Amino acids are studied in their native zwitterionic and protected forms. Our method of choice for this study encompasses fully atomistic molecular dynamics simulations using two different state of the art force fields for these types of systems [2, 3]. We employ enhanced sampling techniques with biasing potentials to obtain free energy profiles for binding of amino acids to the surface. This enables us to estimate the free energies of binding of amino acids to the calcite as well as the molecular details of the interaction. Importance of polar groups for binding to the stable (104) surface is illustrated. These results provide a force field benchmark and reference data on binding energies and conformations of specific amino acids which could help interpret the experimental data on peptide and protein mediated calcite functionalization and growth.

[1] J. H. Harding, D. M. Duffy, M. L. Sushko, P.M. Rodger, D. Quigley, J. A. Elliot, *Chem. Rev.* **108**, 4823 (2008).

[2] C. L. Freeman, J. H. Harding, D. J. Cooke, J.A. Elliot, J. S. Lardge, D. M. Duffy, *J. Phys. Chem. C* **111**, 11943 (2007).

[3] P. Raiteri, J. D. Gale, D. Quigley, P.M. Rodger, *J. Phys. Chem. C* **114**, 5997 (2010).

---

[*] currently at Faculty of Science, Department of Physical Chemistry, Zagreb, Croatia

Solid-state and molecular size depending on variation of fundamental constants.

L. F. Pašteka[1,2], A. Borschevsky[3], Y. Hao[3], P. Schwerdtfeger[1], V. Flambaum[4,1]

[1]*Centre for Theoretical Chemistry and Physics, Massey University, New Zealand*
[2]*Department of Physical and Theoretical Chemistry, Comenius University, Slovakia*
[3]*Van Swinderen Institute, University of Groningen, The Netherlands*
[4]*School of Physics, University of New South Wales, Australia*

The size-dependence of molecules or bulk materials on fundamental constants offers a new and promising direction in the study of variations of fundamental constants (VFC) and the detection of scalar dark matter to probe the physics beyond the Standard Model [1-3]. Precise experimental setups involved in the detection of VFC, scalar dark matter and gravitational waves, such as laser interferometers, resonant-mass detectors and cryogenic oscillators now reach precisions far exceeding any other spectroscopic apparatus and their performance is directly connected to material size depending on changes in fundamental constants.

We investigate the dependence of crystal lattice parameters and molecular bond lengths on the fine structure constant α and proton-to-electron mass ratio μ. We present calculated and experiment-derived estimates of α- and μ-dependence of these parameters for selected systems inspired by contemporary experimental setups. We show the sensitivity of this approach may reach several orders of magnitude smaller VFC than the current most stringent experimental constraints.

[1] A. Derevianko, M. Pospelov, *Nature Phys.* **10**, 933 (2014)
[2] Y. Stadnik, V. V. Flambaum, *Phys. Rev. Lett.* **115**, 201301 (2015)
[3] Y. Stadnik, V. V. Flambaum, *Phys. Rev. Lett.* **116**, 031102 (2016)

Relativistic Quantum Chemistry of Heavy Elements and Hadronic Atoms and Molecules

V. Ternovsky[1,2], **A. Glushkov**[1,2], **O. Khetselius**[1,2], **I. Serga**[1], **A. Kvasikova**[2]

[1]Department of Applied Mathematics and Quantum Optics, Odessa State University – OSENU, Lvovskaya str.,15, Odessa, 65016, Ukraine
[2]International Centre of Quantum Chemistry, Odessa State University – OSENU, Lvovskaya str.,15, Odessa, 65016, Ukraine

The gauge-invariant relativistic many-body perturbation theory approach [1] to consistent calculation of the spectra for heavy and superheavy elements (isotopes) and hadronic atomic and molecular systems with an account of relativistic, correlation, nuclear, radiative effects is presented. The wave functions zeroth basis is found from the Klein-Gordon (pion system) or Dirac (electron subsystem) equation. The potential includes the core ab initio potential, the electric and polarization potentials of a nucleus (the Fermi models for charge distribution in a nucleus is used). For superheavy ions the correlation corrections of high orders are accounted for within the Green function method. The magnetic inter-electron interaction is accounted for in the lowest order, the Lamb shift polarization part is calculated in the generalized Uhling-Serber approximation and the self-energy part is calculated on the basis of the Green's function method of Dirac equation with complex energy and singular nuclear potential. There are listed the results of calculations: 1).energy levels, hfs parameters, shifts and widths of some transitions for heavy atoms (Tl. Pb, U). It is proposed a new approach to describe the characteristics of the vibrational transitions of the molecular systems based on the numerical solution of the Schrödinger (Klein-Gordon-Fock) equation with realistic Simons-Parr-Finlan potential and carried out computing the Rb, Cs, Cs2 vibrational transition frequencies. The scheme developed has attractive perspectives in studying energy, radiative and spectral parameters of pion-(adron)-molecular systems such π-, K-AB systems and other exotic ones, which are of a great interest for modern molecular spectroscopy and pionic chemistry.

[1] A.V. Glushkov and L.N. Ivanov, Phys. Lett. A**170**, 33 (1992); A.V. Glushkov, Adv. in the Theory of Quantum Systems in Chem. and Phys. (Berlin, Springer) **26**, 231 (2012); Frontiers in Quantum Systems in Chem. And Physics (Berlin, Springer) **18**, 505 (2008).

[2] A.V.Glushkov, In: Low Energy Antiproton Phys., AIP Serie.**796**, 206 (2005); Recent Advances in Theory of Phys. and Chem. Systems (Springer), **15**, 285 (2006).

Consistent approach to Raman scattering of the light on metastable levels of diatomic molecules

E.V. Ternovsky[1,2], **A.V. Glushkov**[1,2], **A.A. Svinarenko**[1,2]

[1] *Department of Applied Mathematics and Quantum Optics, Odessa State University – OSENU, Lvovskaya str.,15, Odessa, 65016, Ukraine*
[2] *International Centre of Quantum Chemistry, Odessa State University – OSENU, Lvovskaya str.,15, Odessa, 65016, Ukraine*

Laser action on molecules leads to different non-linear processes, including multi-photon ionization, excitation and dissociation, Raman scattering. The elementary two-photon processes are linear coherent and combinational scattering. The intensities and polarization of lines in these spectra are defined by polarizability and derivative on inter-nuclear distance. In this paper it is considered a process of Relay and Raman vibration scattering of the light on metastable levels of molecules (H_2, HD, D_2, Li_2, Rb_2, Cs_2, Fr_2). On the example of polarizability of metastable molecules it has been studied an effect of nuclear motion in processes of the second order of the perturbation theory. New numerical method for construction of the Green electron functions for optical electrons and electron wave functions is developed within the model potential approach in the spheroid coordinates system that allows to take into account non-spherical character of molecular field. We have carried out the calculations of molecular polarizability, its derivative on inter-nuclear distance, depolarization degree under Relay and Raman light scattering on the frequencies of the Rb, Nd lasers. Relativistic generalization of proposed approach is carried out within QED perturbation theory with account of relativistic, correlation effects [1,2]. Analysis of results of the calculation of a polarizability, its derivative on inter-nuclear distance, for example, for excited triple metastable $c^3\Pi_n$, states of the H_2, HD, D_2 molecules on the frequencies of the Rb (1,78eV) and Nd (1,18eV) lasers shows that the main contribution into polarization of the cited metastable molecules is provided by changing the electron shell under action of the external electromagnetic field. An influence of the nuclear notion terms is also studied and found to be quite little.

[1] A. Glushkov, O. Khetselius, L. Lovett, *Advances in the Theory of Atomic and Molecular Systems: Dynamics, Spectroscopy, Clusters, and Nanostructures. Series: Progr. in Theor. Chem. and Phys*, Eds. P. Piecuch, J. Maruani, G. Delgado-Barrio, S. Wilson (Springer). **20**, 125 (2009).

[2]. A.V.Glushkov et al, Int. Journ. Quant.Chem. **99**, 879 (2004); **99**, 936 (2004); **109**, 3325 (2009); A.V.Glushkov, O.Yu. Khetselius, L. Lovett, Progr. Theor. Chem. & Phys. (Springer) 20, 125-152 (2009).

Theoretical Photoelectron Spectroscopy: A Versatile Tool to Understand the Electronic Structure

Gilbert Grell[1], **Sergey I. Bokarev**[1], **Tobias Moehle**[1] , **Oliver Kühn**[1]

[1]*Institut für Physik, Universität Rostock, Albert-Einstein-Strasse 23-24, Rostock, Germany*

Photoelectron spectroscopy (PES) is a popular tool to probe the electronic structure in different aggregation states mapping bound electronic states to the continuum. To assign and understand experimental PES data which are usually rich of features, application of advanced theoretical modelling is required. This especially applies to highly correlated systems like transition metal (TM) complexes. In this work, we employ a Dyson orbital approach [1] to estimate photoionization cross sections in conjunction with the multi-configurational restricted active space self-consistent field (RASSCF) technique and linear response TDDFT with optimally-tuned range-separated hybrid density functionals. Our protocol [2] is capable to include spin-orbit coupling which is a prerequisite for the description of core-level PES and Auger spectra.

This contribution demonstrates applications of our protocol addressing different aspects of electronic structure and photoinduced dynamics of prototypical TM compounds. For instance, in L-edge X-ray PES of TM compounds, the interplay of radiative and autoionization channels as well as solute–solvent interactions were studied [3]. Further, the interpretation of UV/vis pump - XUV photoemission probe experiments has been conducted in [4] (RASSCF) and [5, 6] (TDDFT) unraveling ultrafast photoinduced dynamics of charge transfer states in iron complexes with a special focus on spin crossover. This procedure can be also extended for description of the resonant photoemission of Auger electrons complementing the toolkit for theoretical prediction of X-ray photoionization processes.

[1] C. M. Oana and A. I. Krylov *J. Chem. Phys* **127**, 234106 (2007)

[2] G. Grell, S. I. Bokarev, B. Winter, R. Seidel, et al. *J. Chem. Phys.* **143**, 7 (2015)

[3] R. Golnak, S. I. Bokarev, R. Seidel, J. Xiao, G. Grell et al. *Sci. Rep.* **6**, 24659 (2016)

[4] A. Moguilevski, M. Wilke, G.Grell, S. I. Bokarev et al. *Chem. Phys. Chem.* **18**, 465 (2017)

[5] N. Engel, S. I. Bokarev, A. Moguilevski et al. *Phys. Chem. Chem. Phys.* **19**, 14248 (2017)

[6] A. A. Raheem, M. Wilke, M. Borgwardt, N. Engel, S. Bokarev, G. Grell et al. *Struct. Dyn.* (manuscript submitted)

Theoretical determination of the ground state of CsS and CsO

S. Koudjeti[a], **K. Merabti**[a], **S. Azizi**[a], **B. Mehnen**[b], **S. Ben Yaghlane**[b], **N.E. Jaidane**[b] **and M. Hochlaf**[c]

[a] *Laboratoire de Physique Théorique, Université Abou Bekr Belkaïd, Tlemcen Algérie.*

[b] *Laboratoire de Spectroscopie Atomique, Moléculaire et Applications – LSAMA, Université de Tunis, Tunisie.*

[c] *Université Paris-Est, Laboratoire Modélisation et Simulation Multi Echelle, ,77454 Marne-La Vallée, Paris, France*

The electronic structure calculations were performed using the MOLPRO program[1]. We calculated the potential energies using highly correlated ab initio methods, namely the complete active space self-consistant field (CASSCF) approach [2] followed by the internally contracted multireference configuration interactions (MRCI) method [3].

In these calculations, different basis sets have been used for oxygen, sulfur and cesium atoms.

The spectroscopic constants such as vibrational harmonic frequency ω_e, the internuclear distance at equilibrium R_e, the rotational constant $B_e$and the electronic transition energy T_e of the ground and the excited electronic states have been calculated by fitting the energy values around the equilibrium position to a polynomial in terms of the internuclear distance [4] and compared with litterature values [5-6].

[1] MOLPRO is a package of ab initio programs written by H.J.Werner and P.J.Knowles.

[2] P.J.Knowles and H.J.Werner, *Chem.Phys.Lett.* **115**, 259, (1985).

[3] H.J.Werner and P.J.Knowles, *J.Chem.Phys.***89**, 5803, (1988).

[4] B. Numerov, Publs. *observatoire central astrophys. Russ.* **2**, 188, (1933).

[5] D.Kaeen, M.Korek and S.N.Abdulal, *J. Mod. Phys*, **6**,1889 (2015).

[6] Partridge, H., Langhoff, S. R., & Bauschlicher Jr, C. W. *J. Chem. Phys.* **88**, 6431, (1988).

Algorithm for calculating Bethe logarithm for two- or three- centered molecules

Ewa Palikot[1], **Monika Stanke**[1]

[1]*Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, ul. Grudziądzka 5, Toruń, Poland*

Bethe logarithm is one of the leading quantum electrodynamic energy correction of the order of α^3. Method of calculating expectation value of Bethe logarithm in alternative way to Schwartz [2] is presented. The theoretical base paper for the work was [3]. The method proposed in [3] was extended for calculate multi-electron atoms and two- or three-centered homo- or hetero-nuclear molecules. Calculations was done in Born-Oppenheimer approximation using explicitly correlated Gaussian functions. Expectation value of Bethe logarithm for H2 and HeH+ molecules are presented.

[1] H. A. Bethe, *Phys. Rev.* **72**, 339 (1947),
[2] C. Schwartz, *Phys. Rev.* **123**, 1700 (1961),
[3] M. Stanke, L. Adamowicz, D. Kędziera, *Mol. Phys.* **111**, 9 (2013),
[4] K. Piszczatowski *et al.*, J. *Chem. Theory Comput.* **5**, 3039 (2009),
[5] V. I. Korobov, *Phys. Rev. A* **69**, 505 (2004).

PO3-263

Studys of anorganic biradicals: Dependancy of computational methods, electronical and sterical effects

E. Welz[1], **B. Engels**[1]

[1]*Department of Theoretical and Physical Chemistry, University of Wuerzburg, Emil-Fischer-Straße 42, Wuerzburg, Germany*

The CAAC liganded diborene and diborane show an interesting behavior concerning their chemical behavior. Depending on the sterical effects of the ligands they appear coplanar or orthogonal. A huge role plays the CAAC ligand which causes of its sterical and electronical effects very often an open shell structure.

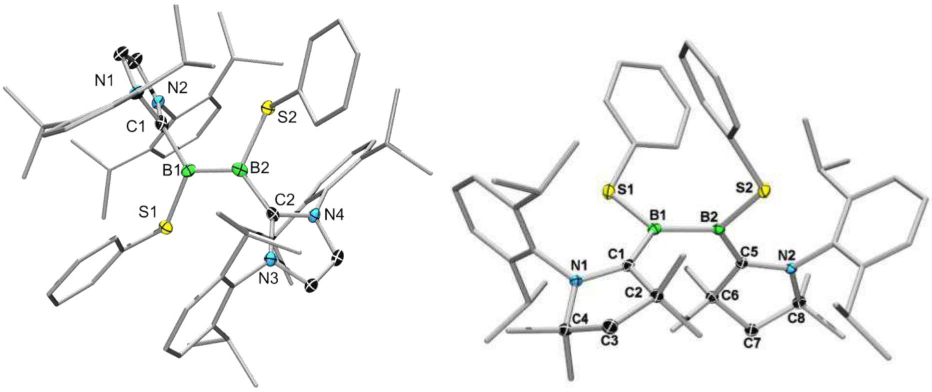


Figure 1: Shows a coplanar liganded diborene on the left site and an orthogonal liganded diborane on the right side.

For the coplanar substituted diborene it is proven that it appears as a B=B double bond, in contrast the diborane with orthogonal standing substitutes a B-B single bond is found. Now it is on great interest in what way it is possible to describe a biradical character with low cost DFT functionals, and which funstionals give the best performance compared to high level CASSPT2, MR-CI methods. Another interesting point is the influence of the ligand on the boron. Therefor we take a closer look at different substituted boron systems and their influence on the structure. To get an overview over the influence of the electronic behavior we take the same skeletal structur and verify the eletronical behavior of the ligands.

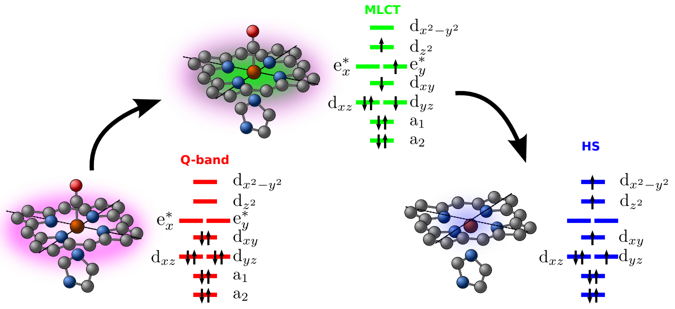
Competition between photolysis and spin-crossover : quantum wavepacket dynamics on heme-CO organometallic complex

Miquel Huix-Rotllant[1], **K. Falahati**[2], **I. Burghardt**[2]

[1]*Institut de Chimie Radicalaire, CNRS - Aix-Marseille University, Avenue Escadrille Normandie-Niemen, Marseille, France.*

[2]*Intitut für Phys. u. Theor. Chemie, Goethe University, Max-von-Laue-Str., Frankfurt am Main, Germany.*

Hemoproteins are well known metalloproteins involved in storage and transport of small diatomic molecules. Recent time-resolved X-ray spectra with ultrashort pulses have revealed that the photolysis of carbon monoxide (CO) from myoglobin occurs in <50-70 fs [1]. Still, there is a discussion whether photolysis occurs before (low-spin dissociation) or after (high-spin dissociation) the spin-crossover mechanism. To resolve this, we have developed a vibronic Hamiltonian containing both the dissociation coordinate and the intersystem crossing for a manifold of singlet, triplet and quintet states. The Hamiltonian has been fitted to CASPT2 PES using a 5th-order Taylor expansion on the vibrational coordinates in addition to Morse and exponential potentials to account for anharmonicities. The model has been fitted to reproduce 180 electronic states along 12 principal vibrational coordinates, including all vibronic and spin-orbit couplings. The Hamiltonian is used to propagate wavepackets using multi-layer formulation of multi-configuration time-dependent Hartree (ML-MCTDH) method [2]. Our model reveals that strong (pseudo-)Jahn-Teller couplings induce an ultrafast transfer from the porphyrin to the metal-ligand charge transfer band (MLCT), from where dissociation occurs [3]. After photolysis, the spin-crossover acts relaxing the remaining system to a quintet state.



[1] M. Levantino et al., *Nat. Chem.* **6**, 6772 (2015).

[2] H. Wang, M. Thoss, *J. Chem. Phys.* **119**, 1289 (2003).

[3] M. Huix-Rotllant, K. Falahati, I. Burghardt, (in preparation).

Multilevel coupled cluster theory with Cholesky- and correlated natural transition orbitals for core-excited states.

Sarai Dery Folkestad[1], Ida-Marie Høyvik[1], Henrik Koch[1]

[1]*Department of Chemistry, NTNU, Høgskoleringen 5, 7049 Trondheim, Norway*

In multilevel coupled cluster (MLCC) theory[1] the active regions of a molecular system, with respect to some size-intensive property, is treated at a higher level of coupled cluster (CC) theory than the inactive region. The molecular system is partitioned by a convenient selection of molecular orbitals, such as the local Cholesky orbitals[2] or by use of correlated natural transition orbitals (CNTOs)[3]. MLCC is well adapted to the treatment of size-intensive properties and facilitates computational savings while still retaining the accuracy of the higher level method, for the property of interest. The MLCC framework sets no restriction on the number of active regions, and any combination of coupled cluster methods can in theory be used to treat the system at hand.

In this work an MLCC code is implemented, with full flexibility as to the choice of system partitioning and treatment at CCS, CC2, CCSD and CC3 level of theory. Core excitations, which are local in nature and thus well suited for study with MLCC, are treated by use of the CVS approximation[4, 5]. Both Cholesky orbitals and CNTOs are used to partition the orbitals into active and inactive regions.

[1] R. H. Myhre, A. M. Sánchez de Merás, H. Koch *J. Chem. Phys.* **141**, 224105 (2014).

[2] A. M. Sánchez de Merás, H. Koch, I. G. Cuesta, L. Boman, *J. Chem. Phys.* **132**, 204105 (2010).

[3] I-M. Høyvik, R. H. Myhre, H. Koch *J. Chem. Phys.* **146**, 144109 (2017).

[4] L. S. Cederbaum, W. Domcke, J. Schirmer, *Phys. Rev. A* **22**, 206 (1980)

[5] S. Coriani, H. Koch *J. Chem. Phys.* **143**, 181103 (2015).

Interrogating the "B05" density functional for non-locality information.

Stephen G. Dale, Erin R. Johnson, Axel D. Becke

Department of Chemistry, Dalhousie University, 6274 Coburg Rd, Halifax, Canada

In two papers[1, 2], Becke introduced Kohn-Sham density-functional approximations for static and dynamic correlation to be partnered with 100 percent exactly-computed exchange. Known as "B05", this was the first non-local correlation model designed to work with the full non-locality of exact (or Hartree-Fock) exchange. Non-locality issues, often referred to as the "delocalization" problem, have emerged as one of the most vexing problems in DFT today. Questions such as... how much exact exchange should be used in a hybrid functional, or... what value of the range parameter should be used in a long-range corrected functional, abound, and the answers are system dependent. The physics of non-locality is built into the B05 functional in a natural way and one wonders, therefore, if B05 might provide a mechanism to answer such questions. We are exploring a procedure, "B05min", to do this.

[1] A. D. Becke, *J. Chem. Phys.* **119**, 2972 (2003).

[2] A. D. Becke, *J. Chem. Phys.* **122**, 064101 (2005).

High-accuracy extrapolated ab initio thermochemistry of the cyanonitrene radical

Michael E. Harding

Institut für Nanotechnologie, Karlsruher Institut für Technologie (KIT), Campus Nord,
Postfach 3640, D-76021 Karlsruhe, Germany

Theoretical and experimental determinations of the heat of formation of the cyanonitrene radical, NCN, span a range of 443 to 501 kJ mol^{-1} (see ref. [1] and references therein). Due to the fact that such discrepancies are unacceptable for a triatomic molecule, which is likely to play a key role in the formation of so-called prompt NO in combustion under fuel-rich conditions, enthalpies of formation at both 0 and 298 K were computed according to the HEAT (High-accuracy Extrapolated Ab initio Thermochemistry) protocol. [2–4]
The recommended enthalpy of formation for NCN is 451.7 ± 1.7 kJ mol^{-1} at 0 K and 452.2 ± 1.7 kJ mol^{-1} at 298 K, thus resolving discrepancies among the available values. The computed values are in agreement with some of the experimental values and previous computations, but the uncertainties associated with the HEAT values are considerably smaller than those based on experimental studies and earlier theoretical estimates. The study also reveals conceptual problems with the inclusion of theoretical estimations and their confidence limits into the thermochemical network of the Active Thermochemical Tables (ATcT) approach [5, 6], which is widely used as a reference for experimental and theoretical thermochemistry.

[1] E. Goos, C. Sickfeld, F. Mauß, L. Seidel, B. Ruscic, A. Burcat, T. Zeuch, *Proc. Combust. Inst.* **34**, 657 (2013).

[2] A. Tajti, P.G. Szalay, A. G. Császár, M. Kállay, J. Gauss, E. F. Valeev, B. A. Flowers, J. Vázquez, and J. F. Stanton, *J. Chem. Phys.*, **121**, 11599 (2004).

[3] Y. J. Bomble, J. Vázquez, M. Kállay, C. Michauk, P. G. Szalay, A. G. Császár, J. Gauss, and J. F. Stanton, *J. Chem. Phys.*, **125**, 064108 (2006).

[4] M. E. Harding, J. Vázquez, B. Ruscic, A. K. Wilson, J. Gauss, and J. F. Stanton, *J. Chem. Phys.*, **128**, 114111 (2008).

[5] B. Ruscic, R. E. Pinzon, M. L. Morton, G. von Laszewski, S. Bittner, S. G. Nijsure, K. A. Amin, M. Minkoff, and A. F. Wagner, *J. Phys. Chem. A* **108**, 9979 (2004).

[6] http://atct.anl.gov/

Can wavefuntion analysis support the (new) definition of oxidation state?

Verònica Postils, Carlos Delgado-Alonso, Pedro Salvador

Institut de Química Computacional i Catàlisi i Departament de Química, Universitat de Girona, Maria Aurèlia Capmany 69, 17003, Girona, Spain.

Oxidation state (OS) is a concept of utmost relevance in Chemistry that has been lacking a proper, clear cut definition. IUPAC's Gold Book still discusses a set of "agreed upon" rules, but no formal definition. Consequently, considerable debate can be found in the literature discussing over inconsistencies and alternative OS assignation in non-trivial bonding situations. Quite recently, Karen lead a IUPAC's Report [1] on the revision of the OS concept, providing a new generic definition, namely "The OS of a bonded atom equals its charge after ionic approximation", as well as algorithms for OS assignation and a vast number of illustrative examples. Despite OS is intrinsically related to the distribution of electrons around atom, the report tiptoes around the role of quantum-chemical calculations for OS assignation. The wavefunction of the system, however, should contain this type of information; one just needs to devise proper schemes to retrieve it.

Almost at the same time as Karen's work, we had introduced [2] a new and general scheme to derive OS from wavefunction analysis, the so-called effective oxidation state (EOS) analysis. It is formally applicable to any molecular system and for any level of theory. Here we present a systematic analysis of the molecular examples described in (or related with) Karen's report (more than 80 systems) using the EOS approach. Remarkably, the results of the quantum mechanical approach can be reconciled with the improved OS definition in most cases, even though the EOS analysis considers explicitly neither bonds nor Lewis structures. Moreover, no special provisions are needed when the practical application of Karen's algorithms comes with exceptions or leads to ambiguities.

Discrepancies occur and are expected when the individual bond polarization, tuned by the chemical environment, does not match with reference pairwise atomic electronegativities. Also, the rule *bonds between two atoms of the same element are divided equally* cannot always be recovered from first principles, unless the involved atoms are symmetry-equivalent.

Our analysis already reveals limitations of the new OS definition, e.g. in the assignation of OS of hapto-complexes (fundamental role of aromaticity and local spin states of the ligands), and in Fisher-type carbenes.

[1] P. Karen et al, *Pure Appl. Chem.* **86** 1017 (2014); *Angew. Chem. Int. Ed.* **54**, 2 (2015).
[2] E. Ramos-Cordoba et al. *J. Chem. Theory Comput* **11**, 1501 (2015).

Excited states for orbital-optimized second-order perturbation theory

Eloy Ramos-Cordoba[1,2], **Martin Head-Gordon**[1]

[1]*University of California, Berkeley, Berkeley, California 94720, (USA)*
[2]*Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU) and Donostia International Physics Center (DIPC), 20080 Donostia, (Spain)*

Unrestricted Hartree-Fock (UHF) wave functions with spin contamination are usually poor zero-order approximations for second-order Moller-Plesset perturbation theory (MP2). Orbital-optimized second-order perturbation theory (OOMP2) tackle this problem by using approximate Brueckner orbitals. In OOMP2 the orbitals are optimized in the presence of the mean-field energy plus the second-order many-body correlation energy. Since in OOMP2 the energy is fully minimized with respect to orbital rotations, a Hellman-Feynman condition is fulfilled and first-order properties do not present discontinuities. This method improves the description of geometries, vibrational frequencies, and relative energies. Additionally, in OOMP2 the response function does not show spurious second order poles, making it suitable for linear-response excited state properties. In this contribution, we present an extension of the OOMP2 method to excited states and we report test calculations for closed-shell systems and doublet radicals. The performance of method is compared with other second-order methods for excitation energies such as the approximate coupled-cluster singles and doubles model (CC2), configuration interaction with doubles corrections (CIS(D)), and the algebraic diagrammatic construction through second order (ADC(2)).

[1] R. C. Lochan and M. Head-Gordon, *J. Chem. Phys.* ***126***, 164101 (2007).
[2] D. Stuck and M. Head-Gordon, *J. Chem. Phys.* ***139***, 244109 (2013).
[2] E. Ramos-Cordoba and M. Head-Gordon, *in preparation*

Energetic parameters of the $Pt(SCN)_6^{2-}$ complex

Vladislav V. Yudanov

Laboratory of Photochemistry, Voevodsky Institute of Chemical Kinetics and Combustion of SB RAS, 3 Institutskaya Str., Novosibirsk, Russian Federation

Photosolvation of $Pt(SCN)_6^{2-}$ in water can have several possible reaction mechanisms, which are very difficult, almost impossible, to establish by experimental methods. The choice in favor of a certain mechanism of the reaction can be made only after comparing the results of quantum-chemical calculations of the intermediates with experimental spectra.

The quantum-chemical calculations of the $Pt(SCN)_6^{2-}$ complex were performed in two stages. First, the geometry of the complex in the ground state was optimized for the singlet state by RHF/LANL2DZ method. Further, the energies of the excited states, the wavelengths and strengths of the oscillators were obtained by CIS method. The most significant of them (with large oscillator strengths) are presented in the table below.

Excitation energies, eV	*Wavelengths, nm*	*Oscillator strengths*
0.1214	*10213.91*	*0.1490*
0.2102	*5898.24*	*0.3913*
4.8845	*253.83*	*0.0921*
4.9804	*248.94*	*0.0859*
5.1073	*242.76*	*0.0492*
5.1371	*241.35*	*0.0309*
5.2085	*238.04*	*0.0115*

Financial support from the Russian Science Foundation (Grant No. 15-13-10012) is gratefully acknowledged.

Theoretical Study of the Methanamine Formation as Glycine Precursor in the ISM: Role of Water-Ice

Francisca Cid, Alejandro Toro-Labbé, Soledad Gutiérrez-Oliva

Laboratorio de Química Teórica Computacional (QTC), Facultad de Química,
Pontificia Universidad Católica de Chile, Av. Vicuña Mackenna 4860, Santiago, Chile

Experimental studies have shown the possibility to hydrogenate C≡N bond until full saturation (See Figure 1) under interstellar conditions, to form methylamine (CH_3NH_2) from hydrogen cyanide (HCN) [1]. The relevance of the methylamine formation is because it is a precursor to amino acids formation process in the Interstellar Medium (ISM). This theoretical study explore the gas-phase and also the process that takes place on the surface of icy particles from the reaction force perspective [2], this allow us identify different structural and electronic events through a rational partition along the reaction coordinate (ξ). Electronic characterization of transition states are given by reaction electronic flux analysis (REF) [3].

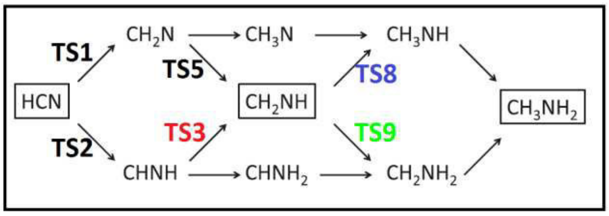


Figure 1. Hydrogenation reaction network [1]

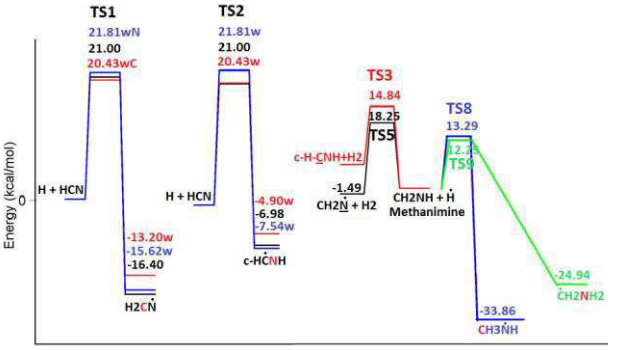


Figure 2. Energy parameters of hydrogenation reactions.

As it is shown in Figure 2, the hydrogenation reaction through carbon (TS1, TS3 and TS8) is thermodynamically favored. The reaction force analysis indicates that energy barriers are basically of structural nature. The reaction force analysis and the reaction electronic flux explain the mechanism of CH_2NH formation induced first by the weakening of the C≡N bond that strengthen the H-C interaction leading to the bond formation.

Acknowledgments. This work was supported by FONDECYT through project N° 1141098.

Key words: hydrogenation, water-ice, reaction force, glycine, interstellar medium.

References

[1] P. Theulé, F. Borget, et. al., *Astronomy and Astrophysics*, **534**, A64 (2011).
[2] A. Toro-Labbé, *J. Phys. Chem. A*, **103,** 4398-4403 (1999).
[3] P. Flores-Morales, S. Gutiérrez-Oliva et. al., *Comp. Theor. Chem.*, **943,** 121-126 (2010).

Squaramide polymerization of lactide:

Crucial role of a weak interactions network.

Christophe Gourlaouen[1], **Samuel Dagorne**[2]

[1]Laboratoire de Chimie Quantique, Institut de Chimie UMR 7177 CNRS/Université de Strasbourg 4, rue Blaise Pascal, 67000, Strasbourg France, gourlaouen@unistra.fr

[2]Laboratoire de Synthèse, Réactivité et Catalyse Organométalliques, Institut de Chimie UMR 7177 CNRS/Université de Strasbourg 4, rue Blaise Pascal, 67000, Strasbourg France,dagorne@unistra.fr

Newly synthesized substituted squaramides have been successfully used as organocatalyst for lactide ring-opening polymerization (ROP) [1]. The amino-functionalized squaramide [Figure 1] leads to ROP of L-lactides under mild conditions in the presence of benzyl alcohol. Experimental data prove that both Hydrogen-bond acceptor and donor sites are critical for the catalyst activity: the absence of amino group inhibits the reaction. The catalyst is also selective; it is inactive in the presence of other cyclic molecules such as ε-caprolactone. DFT calculations were undertaken to determine the precise mechanism of the ROP. We successfully computed a three main steps mechanism and highlighted the role played by each part of the molecule. As proposed by the experimentalist the three nitrogen atoms act as anchor to fix the alcohol and the monomer. However, we put in evidence the more active role played by the amino group. Then we also prove that the fluorinated part also contribute to the thermodynamic balance of the reaction. Finally, the selective activity of the catalyst was explained through the modification of the H-bond network induced by the change of the monomer.

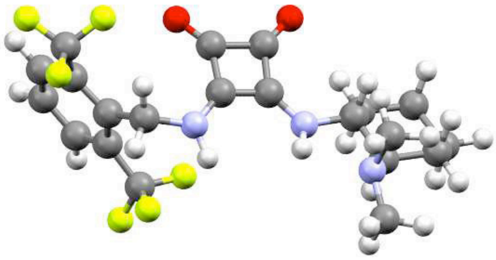


Figure 1: Structure of the amino-squaramide

[1] S. Dagorne, *ChemCatChem.* **9**, accepted (2017).

Excited State Transition Energies and Properties in Solution from a Smooth Dielectric Model

J. Coleman Howard[1], **James C. Womack**[2], **J. Dziedzic**[2], **Chris-Kriton Skylaris**[2], **T. Daniel Crawford**[1]

[1]*Department of Chemistry, Virginia Tech, Blacksburg, Virginia, United States*
[2]*School of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, United Kingdom*

A quantum mechanical solvation model is presented for a solute embedded in a polarizable dielectric medium, where the solute cavity is determined from an electronic isodensity surface in a smooth two-parameter model previously implemented in plane-wave-based density functional theory computations. In this work, solvent-solute interactions are incorporated into a Hartree-Fock framework and captured via numerical solution of the nonhomogenous Poisson equation on a real-space grid through an interface between PSI4 and the DL_MG multigrid solver library. The method is applied here to compute excited state transition energies and properties with the equation-of-motion coupled-cluster singles and doubles method (EOM-CCSD). Results are presented for solvated water, as well as formaldehyde, acetone and *trans*-acrolein, which have low-lying $n \rightarrow \pi^*$ transitions and associated blue shifts in aqueous solution. Comparisons are made with other theoretical approaches, including popular implicit solvation models and QM/MM methods, in addition to available experimental data.

On the Chirality of Antimalarial Drug Candidates

Kirk C. Pearce[1], Yongle Du[1], Yumin Dai[1], Priscilla Krai[3], Seema Dalal[3], Maria B. Cassera[2,3], Michael Goetz[4], T. Daniel Crawford[1], David G. I. Kingston[1,2]

[1]*Department of Chemistry, Virginia Tech, Blacksburg, Virginia, United States*
[2]*Virginia Tech Center for Drug Discovery, Virginia Tech, Blacksburg, Virginia, United States*
[3]*Department of Biochemistry, Virginia Tech, Blacksburg, Virginia, United States*
[4]*Natural Products Discovery Institute, Doylestown, Pennsylvania, United States*

A dichloromethane extract of *Trichospira verticillata* from the Natural Products Discovery Institute was discovered to have good antiplasmodial activity. After purification, four new germacranolide-type sesquiterpene lactones named trichospirolides A-D (**1** - **4**) were isolated from *Trichospira verticillata*. The structures of the new compounds were elucidated by analysis of their 1D and 2D NMR spectra and MS data. The relative and absolute configurations were assigned based on a comparison of calculated and experimental ECD and UV spectra, specific rotations, and internuclear distances for all possible diastereomers for each compound. Herein, we report the stereochemical assignment of these four compounds.

Electrochemistry via Liquid Photoemission Spectroscopy: Insight from Molecular Simulations

Veronika Jurásková[1], **Petr Slavíček**[1, 2]

[1]*Department of Physical Chemistry, University of Chemistry and Technology Prague,*
Technická 5, Prague 6, Czech Republic
[2]*J.Heyrovský Institute of Physical Chemistry, Academy of Science of the Czech Republic, v.v.i.,*
Prague 8, Czech Republic

Photoemission spectroscopy (PES) with liquid microjets represents relatively new powerful method enabling measurements of photoemission spectra in liquid phase. It opens a way to study electronic structure of liquid water and aqueous solutions of different molecules in general. [1] PES can also provide information on the oxidation half reactions.

In this presentation, we focused on modeling of photoemission spectra in aqueous solution using *ab initio* molecular dynamics simulations (AIMD) combined with static calculations of vertical ionization energy. [2] Our main goal was to invent a protocol reproducing the measured spectra and enabling the calculations of redox potentials. The redox potentials are directly connected with the Gibbs free energy of oxidation. This quantity can be estimated from the calculated vertical ionization energy and reorganization energy which is related to the spectral width. In our calculations, we studied the effect of different solvent models and nuclear quantum effects on these properties.

Due to the relation between reorganization energy and spectral width, we discuss the possibility of direct extraction of redox potentials from photoemission spectra. This represents a complex problem requiring the information on the solute and solvent reorganization energy and the characteristic vibrational frequencies responsible for the reorganization. Here, we calculated the solvent reorganization using the equilibrium and non-equilibrium continuum models. We also showed the possibility of the estimation of the solvent frequency from experimental data on refractive index of liquid water.

[1] B. Winter; M. Faubel, *Chem. Rev.* **106**, 1176 (2006).

[2] M. Rubešová; V. Jurásková; P. Slavíček *J. Comput. Chem.* **38**, 427 (2017).

Numerically converged Hyperfine Coupling Constants using a similarity transformed Hamiltonian and a Multiwavelet basis set

Stig Rune Jensen[1,2], **Luca Frediani**[1,2]

[1] *Centre for Theoretical and Computational Chemistry*
[2] *Department of Chemistry, UiT - The Arctic University of Norway, N-9037 Tromsø*

Hyperfine coupling constants (HFCCs) are among the most challenging molecular properties to compute when it comes to basis set convergence. The reason for this is that the property depends explicitly on the spin density at the nuclear position (through the Fermi-Contact operator), where it is well known that the standard basis sets of computational chemistry are inadequate. Even the fully adaptive and highly flexible multiwavelet basis[1] shows a rather slow convergence for the density value at the nuclear cusp, and very large computational resources are needed to reach numerically converged results in a brute force manner. The spin density is particularly challenging as is it computed as the difference between two large and almost equal numbers (the spin-up and spin-down density values), putting hard demands on the absolute precision of the calculation.

Using a similarity transformed Hamiltonian[2] we can analytically remove the nuclear cusps of the wavefunction, leaving only a smoothly varying part to be represented in the numerical basis set. We show that this retains the fast convergence of the density value also at the nuclear positions, which makes it possible to obtain numerically converged values for HFCCs within Density Functional Theory using a multiwavelet basis set.

[1] S. R. Jensen, *et al.*, *J. Phys. Chem. Lett.* **8**, 7 (2017).

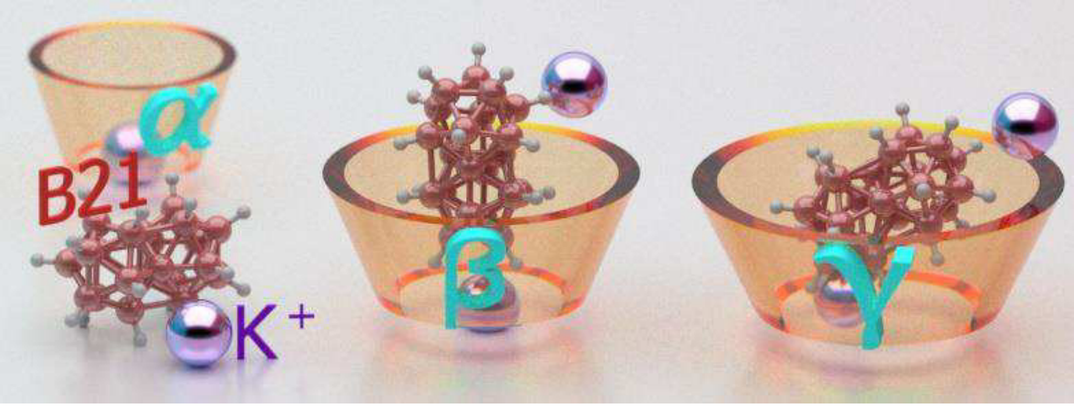
[2] F. Bischoff, *J. Chem. Phys.* **141**, 184105 (2014).

Interactions of binary twinned-icosahedral $[B_{21}H_{18}]^-$ with cyclodextrins

Saltuk M. Eyrilmez[1,2], **Martin Lepsik**[1], **Pavel Hobza**[1,3], **Jindřich Fanfrlik**[1], **Drahomír Hnyk**[4]

[1]*Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Flemingovo nam. 2, CZ-16610 Prague 6, Czech Republic*
[2]*Department of Physical Chemistry, Palacký University, CZ–77146 Olomouc, Czech Republic*
[3]*Regional Center of Advanced Technologies and Materials, Department of Physical Chemistry, Palacký University, CZ–77146 Olomouc, Czech Republic*
[4]*Institute of Inorganic Chemistry of the Czech Academy of Sciences, v.v.i. CZ-25068 Husinec-Řež, Czech Republic*

In this project, we study the spectroscopic evidence of gas-phase complexes of *closo,closo*-$[B_{21}H_{18}]^-$ (B21; D_{3h} symmetry) with β- and γ-cyclodextrin (CD) by using quantum-chemical computations, showing that β- and γ-CD are able to interact with B21 due to their larger cavities, in contrast to the smaller α-CD. The hydridic B–H vectors of the B21 anion interact with K^+ counterions and, *via* dihydrogen bonding, also with the partially positively charged hydrogens of the CD sugar units in the modeled β- and γ-CD complexes. In summary, the combination of spectrometric and computational analysis shows that macropolyhedral boron hydride anions with two counter-ions can form stable complexes with β- and γ-CD in the gas phase, offering a new perspective for the future investigation of this remarkable anion in the areas of supramolecular and medicinal chemistries [1].



[1] S. M. Eyrilmez et al., *Phys. Chem. Chem. Phys.* **19**, 11748, (2017).

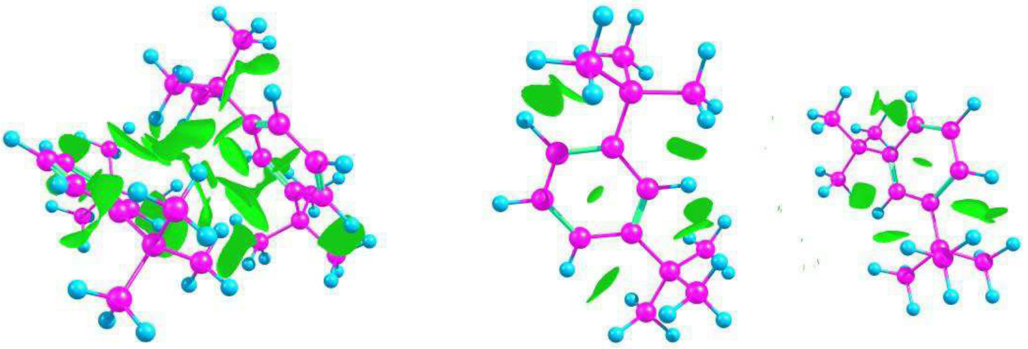
Understanding and Utilizing the Role of London Dispersion Interactions in Catalysis

Lijuan Song[1], **Henrik Quanz**[1], **and Peter R. Schreiner**[1]

[1]*Institute of Organic Chemistry, Justus-Liebig University, Heinrich-Buff-Ring 17, Giessen, Germany*

London dispersion (LD) interactions constitute the attractive part of the van-der-Waals potential and they have been found to provide decisive stabilization in sterically bulky molecules and to enhance catalytic reactivity.[1]

We present a systematic study on quantifying LD interactions by correlating LD interactions energies with the intrinsic properties (size and polarizability) of so-called dispersion-energy donors (DEDs).[2] We employed dispersion-corrected density functional theory that allows to size the significance of LD contributions.[3] A group scan of various DEDs illustrates the "DED-strength", which can be applied to catalyzed chemical reactions as LD helps understand the contribution of DEDs in the reactivity and selectivity of chemical reactions. The notion of selectivity control by specific rate acceleration through LD stabilization rather than by inhibitory means enables LD interaction to be developed as a control element in the design of catalyzed chemical reactions.



(a) B3LYP-D3 (b) B3LYP

Figure 1. NCI plot of 1,3-Di-tert-butylbenzene dimer with and without dispersion correction.

[1] **Review:** J. P. Wagner, P. R. Schreiner, *Angew. Chem. Int. Ed.* ***54***, 12274 (2015).
[2] S. Rösel, C. Balestrieri, P. R. Schreiner, *Chem. Sci.* ***8***, 405 (2017).
[3] S. Grimme, A. Hansen, J. G. Brandenburg, C. Bannwarth, *Chem. Rev.* ***116***, 5105 (2016).

Molecular dynamics simulations on the aggregation of Keggin-type polyoxometalate ions in aqueous solution.

A. Chaumont and G. Wipff

[1]Universite de Strasbourg, UMR 7140, Chimie de la Matiere Complexe,
4, rue B. Pascal, 67000 Strasbourg, France

Aqueous solutions of polyoxometallate (α-$PW_{12}O_{40}^{3-}$) Keggin anions have been simulated by molecular dynamics, comparing between solutions with different neutralizing M^{n+} counterions (Cs^+, NBu_4^+, UO_2^{2+}, Eu^{3+}, H_3O^+ and $H_5O_2^+$). They reveal marked counterion effects. While the hydrophobic NBu_4^+ cations tend to surround α-$PW_{12}O_{40}^{3-}$ anions via loose contacts, leading to "phase separation" between water and an overall neutral humid salty domain, the other studied cations are more hydrophilic and generally separated from the α-$PW_{12}O_{40}^{3-}$ anions. The most important finding concerns the aggregation of α-$PW_{12}O_{40}^{3-}$ anions, mostly as dimers with short contacts but also as higher $(\alpha\text{-}PW_{12}O_{40}^{3-})_n$ oligomers (n = 3 to 5) with the proportion of the aggregates ranging from ca. 9 to 46%, depending on the counterion. While Eu^{3+} and UO_2^{2+} are fully hydrated and interact at short distances with α-$PW_{12}O_{40}^{3-}$ as solvent-separated ion pairs, Cs^+ can form contact ion pairs, as well as solvent-separated ions.

Free energy profiles, obtained via potential of mean force "PMF" calculations, as a function of the P ... P distance show a flat profile with a tiny minimum at ca. 11 Å as the anions approach each other, showing that the anions can form "contact ion pairs" in the presence of either H_3O^+, UO_2^{2+} or Eu^{3+} counterions.

The role of water is demonstrated by comparing PMFs in water and in methanol solution where there is no contact ion pair, but a free energy minimum at ca. 17 Å, corresponding to an ion separated pair α-$PW_{12}O_{40}^{3-}$...$Eu(MeOH)_9^{3+}$...α-$PW_{12}O_{40}^{3-}$.

Spin-orbit coupling matrix elements from the Hermitian formulation of coupled cluster response theory

Aleksandra Tucholska[1]**, M. Lesiuk**[1]**, Robert Moszynski**[1]

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

In high resolution spectroscopy, the interpretation of experimental spectra requires inclusion of both the relativistic effects and electron correlation at a high level. Relativistic effects, especially the spin-orbit interaction, are responsible for the fine structure splitting, existence of intercombination transitions, and phosphorescence. They also affect the shape of the potential energy surfaces of systems containing heavy atoms.

In this work we are focused on the computation of the spin-orbit coupling matrix elements using the Hermitian formulation of coupled cluster response theory [1,2]. In contrast to the existing coupled cluster approaches, the resulting electron transition moments satisfy the necessary symmetry conditions.

We present a derivation and implementation of the spin-orbit coupling matrix elements within the CC3 approximation of the coupled cluster amplitudes. The results are obtained with Gaussian and Slater basis sets. We present preliminary numerical results and compare them with the MRCI values and experimental data. Additionally, we present computed lifetimes for various states of atomic and diatomic closed-shell systems.

The code for spin-orbit matrix elements, transition moments between excited states, as well as the previously implemented code for transition moments from the ground state, will be incorporated into KOŁOS: A general purpose ab initio program for the electronic structure calculation with Slater orbitals, Slater geminals, and Kołos-Wolniewicz functions.

Acknowledgments: This work was supported by the The National Science Centre within the grant No. D112/501/66GR5365

[1] A. M. Tucholska, M. Lesiuk, R. Moszynski *J. Chem. Phys.* **146** (2017) 034108
[2] A. M. Tucholska, M. Modrzejewski and R. Moszynski *J. Chem. Phys.* **141** (2014) 12409
[3] B. Jeziorski and R. Moszynski, *Int. J. Quantum Chem*. **48** (1993) 161.
[4] R. Moszynski, P. S. Zuchowski and B. Jeziorski, *Collect. Czech. Chem. Commun.* **70** (2005) 1109.

Upgrading existing GGA functionals to range-separated hybrid meta-GGAs

Marcin Modrzejewski[1], **Michał Hapka**[1], **Małgorzata M. Szczęśniak**[2], **Grzegorz Chałasiński**[1]

[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*

We present a general scheme for converting an existing exchange functional into its range-separated hybrid form with long-range Hartree-Fock exchange. The main difference with the existing approaches is that the underlying Becke-Roussel-type exchange hole has the exact second-order expansion in the interelectron distance. Consequently, the short-range part of the range-separated exchange energy depends on the kinetic energy density and the Laplacian even if the base functional is a simple GGA. The range-separation parameter can be fixed by the requirement that the spurious self-interaction energy of the hydrogen atom vanishes. An example constructed using this scheme is LC-PBETPSS, which combines the PBE exchange and the TPSS correlation energies. Numerical tests show remarkably robust performance of the method for noncovalent interactions, barrier heights, excitation energies, and energy differences involving compounds with transition metals.

Acknowledgments: This work was supported by the The National Science Centre within the grant No. 2014/15/N/ST4/02170.

[1] M. Modrzejewski, M. Hapka, G. Chalasinski, and Malgorzata M. Szczesniak, *J. Chem. Theory Comput.* ***12***, 3662 (2016).

High-energy photochemistry in liquid solutions: Ultrafast proton and electron transfer initiated by X-rays

Daniel Hollas[1], Marwin Pohl[2], Bernd Winter[3], Tsveta Miteva[4], Nicolas Sisourat[4], Petr Slavíček[1]

[1]*Department of Physical Chemistry, University of Chemistry and Technology Prague, Technická 5, Prague, Czech Republic*
[2]*Department of Physics, Freie Universität Berlin, Arnimallee 14, D-141595, Berlin, Germany*
[3]*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195, Berlin, Germany*
[4]*UMR 7614, Laboratoire de Chimie Physique Matière et Rayonnement, Sorbonne Universités, UPMC University Paris 06, France*

High energy radiation is routinely used in various areas of science and technology yet the ultrafast processes following the core ionization of atoms or molecules remain poorly understood. In addition to well-known Auger decay and X-ray fluorescence, new non-local relaxation processes such as Intermolecular Coulombic Decay (ICD) were discovered only recently. In collaboration with liquid beam photoemission experiments, we investigated ultrafast electronic and nuclear relaxation pathways in liquid solutions.

A new relaxation pathway in liquid water was recently identified (so called PTM-CS process).[1] We have shown that the same process is taking place also in other hydrogen bonded systems such as hydrogen peroxide[2], glycine[3] and ammonia solutions[3, 4]. Since the different relaxation pathways result in different transient reactive species, our findings may lead to a better understanding of biomolecular radiation damage.

[1] S. Thürmer, M. Ončák, N. Ottosson, R. Seidel, U. Hergenhahn, S. E. Bradforth, P. Slavíček, B. Winter, *Nat. Chem.* **5**, 590 (2013).

[2] I. Unger, S. Thürmer, D. Hollas, E. F. Aziz, B. Winter, P. Slavíček, *J. Phys. Chem. C* **118**, 29142 (2014).

[3] I. Unger, D. Hollas, R. Seidel, S. Thürmer, E. Aziz, P. Slavíček, B. Winter, *J. Phys. Chem. B* **119**, 10750 (2015).

[4] D. Hollas, M. Pohl, R. Seidel, E.F. Aziz, P. Slavíček, B. Winter, *Sci. Rep.* **7**, 756 (2017).

Lewis acid bulkiness effect on the stereoselectivity of cycloaddition reactions between acyclic dienes and α,β-enals.

Diana Yepes[1], Patricia Pérez[1], Pablo Jaque[1], Israel Fernández[2]

[1]*Departamento de Ciencias Químicas, Facultad de Ciencias Exactas, Universidad Andres Bello, Av. República 275, Santiago, Chile.*

[2]*Departamento de Química Orgánica I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040-Madrid, Spain.*

The factors controlling the reactivity and endo/exo selectivity of Lewis acid-catalyzed Diels–Alder reactions between highly substituted open-chain 1,3-dienes and α,β-enals have been explored computationally by means of density functional theory calculations. In agreement with previous experimental observations [1], it is found that the $B(C_6F_5)_3$-catalyzed cycloaddition reaction leads almost exclusively to the corresponding exo-cycloadduct, whereas the analogous $AlCl_3$-mediated process is highly endo-selective. The effect of Lewis acid bulkiness on stereoselectivity has been quantitatively analyzed by means of a combination of the activation strain model of reactivity and the energy decomposition analysis methods [2,3]. In contrast to the current view, the exo-selectivity promoted by the bulky $B(C_6F_5)_3$ catalyst does not result from the steric destabilization of the corresponding endo-transition state but from the interplay between the less destabilizing strain energy and the stronger interaction between the deformed reactants along the entire reaction coordinate. In addition, non-covalent interactions are found to play a crucial role in stabilizing the exo-approach. These results allow us to not only quantitatively understand the effect of the Lewis acids in the process, but also predict new catalysts leading to highly exo-selective Diels–Alder reactions [4].

[1] J.-H. Zhou, B. Jiang, F.-F. Meng, Y.-H. Xu, T.-P. Loh, *Org. Lett.* **17**, 4432 (2015).
[2] F. M. Bickelhaupt, *J. Comput. Chem.* **20**, 114 (1999).
[3] K. Morokuma, *J. Chem. Phys.* **55**, 1236 (1971).
[4] D. Yepes, P. Pérez, P. Jaque, I. Fernández, *Org. Chem. Front.* DOI: 10.1039/c7qo00154a.

Acknowledgments

The authors acknowledge financial support from the FONDECYT (No. 3150249 to D. Y., No. 1140341 to P.P. and No. 1140340 to P. J.) and the Spanish MINECO-FEDER (Grant No. CTQ2013-44303-P, CTQ2014- 51912-REDC and CTQ2016-78205-P to I. F.).

NMR magnetic shielding in halogen bonding and cooperative effects in $(BrF)_n$ clusters.

Blatter, Sandra Patricia[1, 2], **Maldonado, Alejandro**[1], **Aucar, Gustavo**[1, 2]

[1] *FaCENA - UNNE - Corrientes - Argentina*
[2] *Physics Department, Natural and Exact Science Faculty, Northeastern University of Argentina and Institute of Modelling and Innovative Technology, IMIT, Corrientes, Argentina*

In this work we study the NMR nuclear magnetic shielding linear moelcules containing halogen atoms XY (X, Y= F, Cl, Br, I) and the magnitud of relativistic effects in such property. We also analyze dimer molecules with the same linear molecules in order to find a relationship among the strength of halogen bonding and the NMR parameter. As a particular case, we study deeper the cooperative effects on the magnetic shielding constant in cyclic clusters FBr_n (n = 1 - 5) molecular systems.
We appplyed the relativisticc polarization propagator approach (Rel-PPA)[1] for the nuclear magnetic shielding constant as implemented in Dirac code.[3] We also performed nonrelativistic calculations making the sepped of light (c) tend to infinity in order to obtain such a values with the same scheme of calculations.
The bond lenght of monomers,XY (X, Y = F, Cl, Br, I), used in this work were taken from experimental measurements. The gauge atomic including orbitals (GIAO) was used in shielding calculations to avoid the gauge dependence and ensure the basis set convergency. In the firs step we analized the magnetic shielding of halogen in monomers, and after that the same properties in dimers in order to analize the the effect of halogen bonding. The next step was the calculations of the magnetic shielding in $(FBr)_n$ clusters taken from early study[2] and the look for cooperative effects on one nucleus due the rest of halogen atom conforming the clusters.

Keyword: Relativistic effects; Cooperative effects; Magnetic shielding; Polarization propagators

[1] G. A. Aucar, R. H. Romero, and A. F. Maldonado. *Int. Rev. on Phys. Chem.*, 29:1, 2010.

[2] R. D. Parra. *Comp. Theor. Chem.*, 1066:47, 2015.

[3] DIRAC, a relativistic ab initio electronic structure program, Release DIRAC13 (2013), written by L. Visscher, H. J. Aa. Jensen, R. Bast, and T. Saue. (see http://www.diracprogram.org).

[4] K. Sutter, G. A. Aucar, and J. Autschbach. *Chem. European J.*, 21:18138, 2015.

Reaction Force Constant Analysis Applied in Organic and Organometallics Multi-Bond Reactions.

Pablo Jaque[1]

[1]Departamento de Ciencias Química, Facultad de Ciencias Exactas, Universidad Andres Bello, Santiago, Chile; e-mail: pjaque@unab.cl

A main goal in chemistry is to rationalize the controlling factors on the reaction barrier heights, thermodynamic driving force and the reaction mechanisms of a chemical interconversion since this can lead to an improved capability for guiding the chemical processes. In this regard, several interpretative models have been proposed and successful applied in a large variety of chemical reactions. The potential energy profile $V(\xi)$ along any reaction coordinate ξ (typically the intrinsic reaction coordinate) contains the kinetical and thermodynamical information. In addition, the exploration of the shape of $V(\xi)$ through its derivative allows to describe what physically happens in a chemical reaction. Therefore, the reaction force $\mathbf{F}(\xi)$ [1] and the reaction force constant $\kappa(\xi)$ [2] defined, respectively, as the first- and the second-order derivative of $V(\xi)$ of the reacting system along ξ, provide a useful frame to characterize the "mechanic" aspects. While the former provide a rational partition of the energy barrier into structural and electronic factors [3] the latter has been proposed as a suitable indicator of the degree of synchronicity/asynchronicity in bond-breaking/bond-forming processes [4]. In the present communication we will present the last results of organic and organometallic multi-bond reactions.

Acknowledgments. The authors acknowledge FONDECYT project number 1140340.

[1] A. Toro-Labbé, *J. Phys. Chem. A* **103**, 4398 (1999).
[2] P. Jaque, A. Toro-Labbé, P. Politzer, P. Geerlings, *Chem. Phys. Lett.* **456**, 135 (2008).
[3] P. Politzer, A. Toro-Labbé, S. Gutiérrez-Oliva, J. S. Murray, *Adv. Quantum Chem.* **64**, 189 (2012).
[4] D. Yepes, J. S. Murray, P. Politzer, P. Jaque, *Phys. Chem. Chem. Phys.* **14**, 11125 (2012). D. Yepes, O. Donoso-Tauda, P. Pérez, J. S. Murray, P. Politzer, P. Jaque, *Phys. Chem. Chem. Phys.* **15**, 7311 (2013). D. Yepes, J. S. Murray, P. Pérez, L. R. Domingo, P. Politzer, P. Jaque, *Phys. Chem. Chem. Phys.* **16**, 6726 (2014).

DLPNO-CCSD(T) based compound methods for accurate thermochemistry

Dimitrios G. Liakos[1] **and Frank Neese**[1]

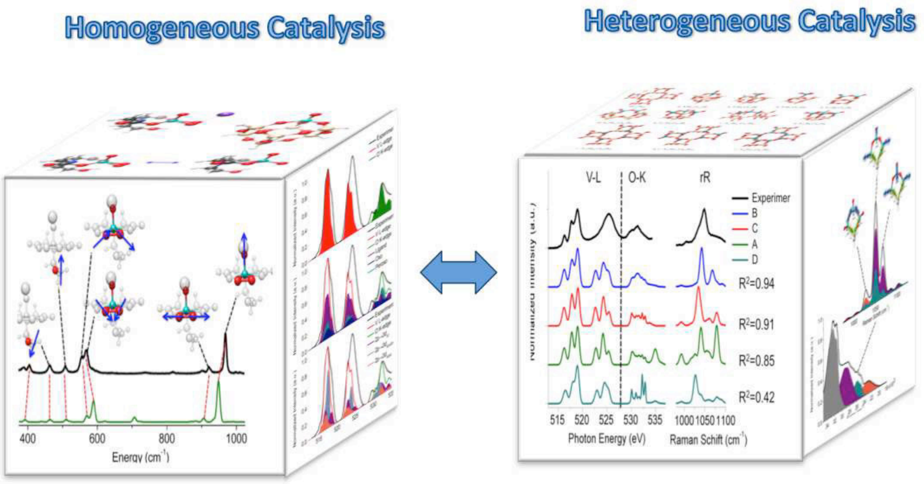
[1]Max-Planck Institute for Chemical Energy Conversion, Stiftstr. 34-36 D-45470 Muelheim a.d. Ruhr Germany

DLPNO-CCSD(T) methods provide an efficient way to calculate energies with CCSD(T) accuracy. Nevertheless, sources of error still remain that need to be addressed in order achieve experimental accuracy. In an attempt to reach thermochemical accuracy, we present a combination of methods that attempts to address most of the potential errors like the basis set incompleteness, inaccurate initial geometries and relativistic effects. The resulting methods are all implemented in ORCA package and can be used in a black box manner. The calculated energies can now be used as a reference for calibration of approximate methods

Insights into heterogeneous catalysts from theoretical spectroscopy and accurate binding energies

Dimitrios Maganas and Frank Neese
[1] *Max Planck Institute for Chemical Energy Conversion, Stiftstr. 34-36, D-45470 Mülheim an der Ruhr*
**: presenting author, email: dimitrios.manganas@cec.mpg.de*

The structural characterization of catalytically active structures in heterogeneous catalysis is a particularly difficult problem. In many cases, spectroscopic data taken under in-situ conditions is available. However, developing the full information content of these spectroscopic data has been proven to be exceptionally difficult. This is partially due to the fact that many different structural motifs contribute to the spectra and partially is due to a lack of reliable theoretical tools that are able to simulate spectra with predictive accuracy and therefore allow for structure/spectra correlations. In addition entry into the field of catalytic reactivity is required in order to cross-correlate spectroscopic properties with accurate energetics in an effort to identify key reaction functionalities of a particular catalytic system. We will present herein illustrative examples on metal oxide[1,2] based catalysts.



(1) A unified view on heterogeneous and homogeneous catalysts through a combination of spectroscopy and quantum chemistry Dimitrios Maganas, Annette Trunschke , Robert Schlögl and Frank Neese Faraday Discuss.**, 2016**, 188*, 181-197*

(2) Surface Adsorption Energetics Studied with “Gold Standard” Wave-Function-Based Ab Initio Methods: Small-Molecule Binding to TiO_2(110) Adam Kubas, Daniel Berger, Harald Oberhofer, Dimitrios Maganas, Karsten Reuter, and Frank Neese J. Phys. Chem. Lett., **2016**, 7, *4207–4212*

Energy decomposition analysis for studying covalent bonds.

Daniel S. Levine, Martin Head-Gordon

Kenneth S. Pitzer Center for Theoretical Chemistry, Department of Chemistry, University of California, Berkeley, California 94720, United States

Energy Decomposition Analysis (EDA) is a technique to describe the interactions between fragments of molecules in terms of chemically meaningful terms (e.g. electrostatics, dispersion, Pauli repulsion, charge transfer, etc.). Few EDAs are applicable to systems in which the fragmentation of the supersystem into separate interacting parts breaks covalent bonds. We present an EDA method specifically designed for this class of problem using absolutely localized molecular orbitals (ALMOs). This EDA method gives terms describable as frozen interactions (further decomposable into electrostatics, Pauli repulsion, dispersion components), spin-coupling, induced polarization, and charge-transfer stabilization. A variety of simple and complex molecules (including dispersion-assisted bonds and metal-metal bonds) are analyzed by this method and the results lend insight into the nature of the interactions.

Exact Single-Electron Approach to the Dynamics of Molecules in Strong Laser Fields

Axel Schild[1], **E.K.U. Gross**[2]

[1]*Laboratorium für Physikalische Chemie, ETH Zürich, Switzerland*
[2]*Max Planck Institute of Microstructure Physics, Halle (Saale), Germany*

We present an exact single-electron picture that describes the correlated electron dynamics in strong laser fields. The picture is based on the idea to factor the many-electron wavefunction as a product of a marginal amplitude and a conditional amplitude. The marginal amplitude is constructed such that it yields the exact one-electron density and current density. If the equation of motion for the many-electron wavefunction is a Schrödinger equation, then the equation of motion for the marginal amplitude is also a Schrödinger equation, albeit for a single effective particle (with the mass of an electron) and with the many-electron interaction given by a time-dependent effective potential. Thus, the resulting marginal amplitude may be called a single-electron wavefunction, but it yields properties of the full many-electron system.

Our approach is relevant for the description of strong field phenomena, because they are often interpreted in a single-electron picture. We present results for 2- and 3-electron model systems in strong laser fields and illustrate how an exact single-electron picture of ionization or high-harmonic generation looks like, and how many-electron interactions are represented as the time-dependence of an effective single-electron potential. Additionally, we present a first step towards a new computationally feasible approximation for the theoretical treatment of the dynamics of realistic molecules in laser fields.

[1] Axel Schild, E.K.U. Gross, *Phys. Rev. Lett.* **118**, 163202 (2017).

When magnetism meets reactivity: Hydrogen generation via a bi-metallic mechanism with spin exchange.

Nuno A. G. Bandeira[1,2,3], **Luís F. Veiros**[2], **Carles Bo**[1]

[1] *Institute of Chemical Research of Catalonia (ICIQ) - Avda. Països Catalans, 16- 43007 Tarragona, Spain.*

[2] *Centro de Química Estrutural - Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.*

[3] *Centro de Química e Bioquímica - Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal.*

The very recent report by Chirik and others [1] of a novel transition metal complex $[(^{Ph}Tpy)(PPh_2Me)_2Mo(XH_n)]^+$ (^{Ph}Tpy, 4′-Ph-2,2′,6′,2″-terpyridine, XH_n=NH_3, OH_2, NH_2NH_2) capable of generating molecular hydrogen from an XHn ligand as a hydrogen source is an interesting leap forward towards sustainable energy research in the homogeneous phase:

$$[(^{Ph}Tpy)(PPh_2Me)_2Mo^{I}(XH_n)]^+ \xrightarrow[60°C]{\Delta} [(^{Ph}Tpy)(PPh_2Me)_2Mo^{II}(XH_{n-1})]^+ + 1/2H_2$$

We explored three mechanistic routes for this process and examined their feasibility with Density Functional Theory (PBE-D3BJ/TZP+DZP) to pinpoint the most favourable one. The rate limiting step takes place initially by an oxidative addition of the X-H bond (Figure 1) but the subsequent step must involve a bi-metallic association with concomitant spin exchange.

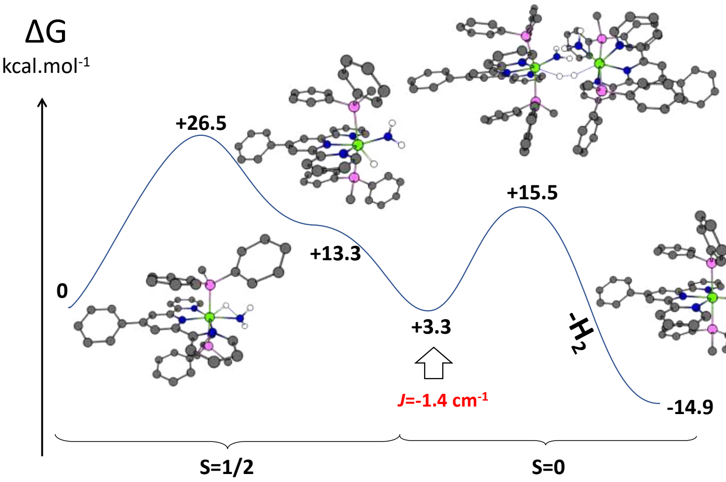


Figure 1 – The formation of H_2 from coordinated ammonia.

[1] M. J. Bezdek, S. Guo, and P. J. Chirik, *Science* **354**, 730 (2016).

$FeNO^{2+}$ as a model system for spin–state energetics.

Constantine N. Sakellaris[1], **Christoph R. Jacob**[1]

[1]*Institute of Physical and Theoretical Chemistry, TU Braunschweig,*
Gaußstr. 17, 38106 Braunschweig, Germany.

Iron–nitrosyl complexes, containing an NO ligand perpendicular to the plane of a porphyrin–like N_4 cavity, feature a rather complicated electronic structure; on top of an open–shell iron cation we have an NO ligand, a "non–innocent" ligand [1–3]. Consequently, iron–nitrosyl compounds provide a challenging test case for the development of quantum–chemical methods, particularly for the density functional theory.

Here, we propose a $FeNO^{2+}$ moity [4], embedded in a square grid of point–charges, q, as a model system for spin–state energetics [5]. The grid serves as a means of charge perturbations, resembling ligand fields of different strength in the actual complex. We report the CASSCF/CASPT2 and DFT spin–state energetic transitions between the high–intermediate and low–intermediate spin states, i.e. sextet to quartet and doublet to quartet. We span across a total charge of $Q = +3$ to -3, for which the three spin states are calculated with nine different active spaces.

It is shown that calculated energies for spin–state crossovers with relatively large active spaces become oblivious to any amelioration, expected to either be brought about by the CASPT2 correction, or to their increase in size by means of additional orbitals. Thus, we find that these active spaces are quenched, or energetically converged and can provide reliable excitation energies at least for such a model system.

In addition to the grid of fixed Fe–q distances, we expand (or shrink) the square–plane by varying the distance between the Fe atom and the four point charges. Moreover, we choose to perturb the point–charge perturbation grid itself by keeping its total charge fixed but the relative distribution over the individual four point–charges *not* uniform. As a final parameter in our study, we vary the Fe–N–O angle from 0 to 180 degrees.

The $FeNO^{2+}$ model system established here and the reference data obtained for a wide range of parameters can serve as a benchmark to guide future developments in spin–DFT.

[1] D. Sakow, B. Böker, K. Brandhorst, O. Burghaus and M. Bröring, *Angew. Chem. Int. Ed.* **52**, 4912 (2013).

[2] J. Conradie and A. Gosh, *J. Phys. Chem. B* **111**, 12621 (2007).

[3] M. Radon and K. Pierloot, *J. Phys. Chem. A* **112**, 11824 (2008).

[4] K. Boguslawski, Ch. R. Jacob and M. Reiher, *J. Chem. Theory Comput.* **7**, 2740 (2011).

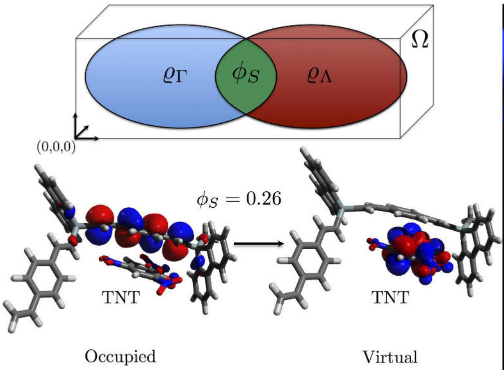
[5] C. N. Sakellaris and Ch. R. Jacob, *to be submitted for publication* (2017).

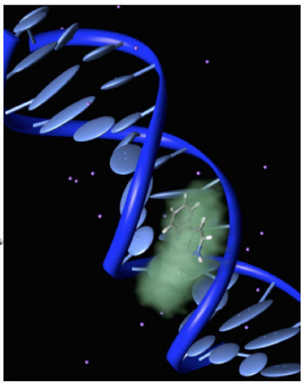
Orbital relaxation and electronic transitions
What is the nature of Handy's Z-vector?

Mariachiara Pastore[1,2], **Antonio Monari**[1, 2], **Xavier Assfeld**[1,2], **Thibaud Etienne**[3]

[1] *Université de Lorraine – Nancy, France (Théorie-Modélisation-Simulation SRSMC)*
[2] *CNRS (Théorie-Modélisation-Simulation SRSMC) – CNRS : UMR7565*
[3] *Chimie Théorique, Méthodologies, Modélisation – Institut Charles Gerhardt, Université de Montpellier, France*

Providing a quantitative insight into light-induced electronic structure reorganization of complex chromophores remains a challenging task that has attracted a substantial attention from theoretical communities in the past few years. Indeed, a potential knowledge related to the ability of a chromophore to undergo a charge transfer caused by photon absorption or emission is of seminal importance for designing novel dyes with highly competitive optoelectronic properties. These target systems are at the center of the main societal issues of our time such as public health with anti-cancer phototherapy, sustainable energy with high-performance solar cells, or homeland security with explosive probes for example. In this context, we elaborated systematic and tractable strategies for qualitatively and quantitatively assessing the electronic cloud polarization of complex molecular structures upon a transition to or from electronic excited states and improve our understanding of the electronic transition process[1, 2, 3]. In addition to providing a clear picture of complex charge transfer processes, our topological metrics are able to act as reliable diagnostic instruments for the exchange-correlation functionals used within the time-dependent density functional theory framework, and therefore constitute a precious tool for computational chemists. After introducing the theoretical elaboration of our strategy and applying it to the aforementioned hot topics, this contribution will detail for the first time the generalization of our topological analyses to fully relaxed excited states density matrices including the so-called Z-vector. Finally, the way our developments allowed us to unravel the physical nature of Handy's Z-vector itself [4] will be reported.





[1] T. Etienne, X. Assfeld, A. Monari, *J. Chem. Theory Comput.* **10**, 3896 & 3906 (2014).
[2] T. Etienne, *J. Chem. Theory Comput.* **11**, 1692 (2015).
[3] T. Etienne, *J. Chem. Phys.* **142**, 244103 (2015).
[4] M. Pastore, A. Monari, E. Mosconi, X. Assfeld, T. Etienne, *J. Chem. Phys.*, *Submitted.*

Stochastic-CASSCF and Multiconfiguration Pair-Density Functional Theory for Spin Challenges in organometallic and organic chemistry

G. Li Manni, N. Bogdanov, A. Alavi

Department of Electronic Structure Theory, Max-Planck Institute for Solid State Research,
Heisenbergstrasse 1, 70569 Stuttgart, Germany

Spin magnetism, of great relevance in the field of energy storage and conversions, poses enormous challenges to well established theoretical methods in quantum chemistry, due to the complex electronic structures of ground and excited states, often involving orbital and states degeneracies and in general multiconfigurational in nature. Advanced ab initio theoretical methods currently available are not able to meet this challenge and density functional theory (DFT) has been for a long time the only computational tool to complement experimental findings. Methods for strongly correlated systems are urged. In this talk, I will present two novel methods: **(a)** The Stochastic-CASSCF [1] approach, that uses a Quantum Monte-Carlo algorithm to solve the CI secular problem and the Super-CI scheme to variationally optimizing the molecular orbitals and **(b)** the Multiconfiguration Pair-Density Functional Theory (MC-PDFT) [2] method, a post-SCF scheme that combines the advantages of multiconfigurational wave function theory and density functional theory to recover static and dynamic electron correlation. The two methods are complementary and have been coupled together. By these approaches (a) much larger active spaces, easily up to 50 electrons and 50 orbitals, (b) larger basis set expansions (via density fitting techniques), up to several thousand contracted functions and, (c) molecular systems of a few hundred atoms are accessible and both non-dynamical and dynamic correlation effects can be recovered. These methods are completely general and can be applied to any kind of molecular system. In this talk, their application to several chemical systems of practical interest will be presented, with special focus on the Fe(II)-Porphyrin and the chain of polyacenes.

(a) (b)

Figure 1: Fe(II)-Porphyrin *(left)*, and dodecacene *(right)*, CAS(50,50) treated via Stochastic-CASSCF/MC-PDFT.

[1] G. Li Manni, S. D. Smart, A. Alavi, *J. Chem. Theory Comput.* **12**, 1245 (2016).

[2] L. Gagliardi, D. G. Truhlar, G. Li Manni, R. K. Carlson, C. E. Hoyer, J. L. Bao, *Acc. Chem. Res.* **50**, 66 (2017).

Putting the squeeze on: First-principles melting of Hg, Cd and Zn under pressure

K.G. Steenbergen[1], **F. Calvo**[2], **E. Pahl**[1], **P. Schwerdtfeger**[1]

[1] *Centre for Theoretical Chemistry and Physics, The New Zealand Institute for Advanced Study, Massey University (Auckland), Private Bag 102904, 0632 Auckland, New Zealand*
[2] *Laboratoire Interdisciplinaire de Physique, Université Grenoble Alpes and CNRS, St Martin d'Héres, France*

As the only elemental metal that exists in the liquid state at standard temperature and pressure, mercury's thermodynamic properties have been of significant interest to the scientific community for over 60 years. In Hg, scalar relativity leads to a significant contraction of mercury's 6*s* shell, which stabilises the 6*s* orbital while destabilising the 5*d* shell. Using density functional theory and the recently-developed interface pinning method for bulk melting (graphically illustrated in Figure 1),[1] we have recently proven that mercury is, in fact, a liquid at room temperature due to relativistic effects.[2] We obtain a relativistic simulated melting temperature (T_m) of 241 K, in excellent agreement with the experimental value of 234 K. The non-relativistic model melts at 402 K: an increase of 160 K! Here, we present the results of first-principles melting simulations at 0, 10 and 20 GPa, using the Hg relativistic and non-relativistic models, in order to compare how relativity effects solid state properties under pressure. We also include and compare results for cadmium and zinc at the same pressures. With a first glimpse at relativistic effects at nonstandard pressures and temperatures, as well as a comprehensive comparison of thermodynamic effects across the group-12 metals for the liquid and solid states, this work gives a deeper understanding of how relativity and pressure affect macroscopic properties of metals.

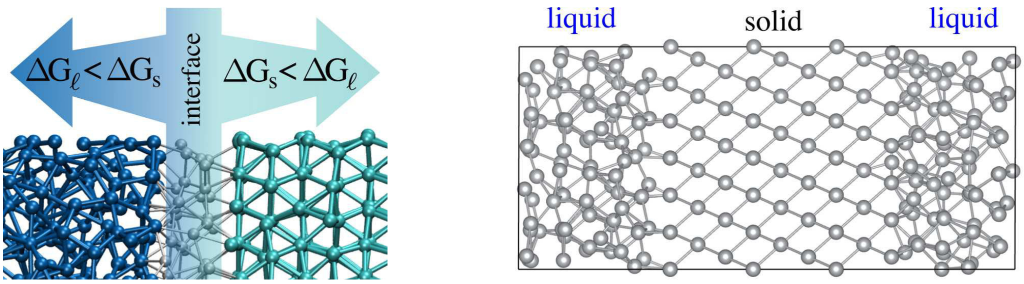


Figure 1: Interface pinning exploits the fact that the Gibbs free energy difference (ΔG) between the solid and liquid phase is zero at T_m: (left) graphical illustration of interface melting; (right) first-principles bulk melting supercell for Hg.

[1] UR Pedersen, F Hummel, G Kresse, G Kahl, C Dellago. *Phys. Rev. B* **88**, 094101 (2013).

[2] KG Steenbergen, E Pahl, P Schwerdtfeger. *J. Phys. Chem. Lett.* **8**, 1407–1412 (2017).

Oxygen Induced Diffusion of Ni Atoms in Ni-Au Clusters

Ralf Meyer[1], **Andreas W. Hauser**[1]

[1]*Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria*

Bimetallic nanoparticles are a topic of special interest due to their unique physical and chemical properties. Potential applications for this new class of materials range from optics and catalysis to biomedicine. Recent experimental results of the Ernst group, who is able to grow highly inert mixed-metallic nanoparticles in superfluid helium nanodroplets,[1, 2] caught our interest and triggered a series of theoretical investigations of Ni-core/Au-shell nanoclusters with the aim to explain the observed inversion of the core-shell structure after heating to 400°C and subsequent cooling. The experimental investigations were based on *in-situ* transmission electron microscopy and included spatially resolved EDX and EELS measurements allowing for an element-specific characterization of the nanoparticle structure as a function of temperature. However, the advantage of this direct imaging technique comes at the cost of an inevitable oxidation of the particles during observation, which leads to an interesting interplay between oxidation reactions and phase transitions. It is our aim to describe these features via a combination of Monte Carlo and molecular dynamics calculations with density functional theory. Preliminary results indicate that the oxidation of the nickel atoms at the surface is responsible for locking the bimetallic particles in a Au-core/Ni-shell structure. The diffusion of Ni atoms to the surface of the core-shell particle seems to be significantly enhanced by the adsorption of oxygen on the surface of the nanoparticles.

[1] P. Thaler, A. Volk, F. Lackner, H. Steurer, D. Knez, W. Grogger, F. Hofer, and W. E. Ernst, *Phys. Rev. B*, **90**, 155442 (2014).

[2] G. Haberfehlner, P. Thaler, D. Knez, A. Volk, F. Hofer, W. E. Ernst and G. Kothleitner, *Nat. Commun*, **6**, 8779 (2015).

Adsorption of post–Combustion Gases by *Mg–MOF–74*

F. Keshavarz, O. Sánchez, D. Bahamón, P. Gamallo, X. Giménez and R. Sayós
Departament de Ciència de Materials i Química Física
Universitat de Barcelona

Separation of CO_2 from gas streams is imperative in sour natural gas wells and power–plant flue gases [1]. Such separation may be performed during post–combustion, with the gas stream at 1 *atm.* and between 313 to 333 *K*, consisting of CO_2 (15%), N_2 (75%), H_2O (6%), O_2 (4%), NO_x (53 ppm) and SO_2 (80 ppm), al percentages being *v/v* [2]. An interesting candidate for the capturing task is a metal–organic framework, *Mg–MOF–74.* It exhibits exceptional CO_2 storage capacity, strong physisorption interaction, but facile CO_2 release and thermodynamic selectivity [3]. Despite these positive features, *Mg–MOF–74* capacity may decrease dramatically if exposed to mixtures of gases under dynamic conditions, as would be the case of post–combustion [4]. Though it has been revealed that SO_2 is a significant threat to CO_2 adsorption, and gases such as H_2O, NO_2, *NO* and O_2 are major concerns, most experimental and simulation studies have ignored the effect of these gases on the adsorption behavior.

Therefore, this study considers the influence of minor gases on CO_2 adsorption capability. The best force field, for isotherm analysis of post–combustion gases, was first verified through *Grand Canonical Monte Carlo* (GCMC) simulations (pressure: 0.1 to 1 *atm.*), including Lennard–Jones 6–12, Coulomb interactions and Ewald summation method for van der Waals, short– and long–range electrostatic interactions, respectively. The best force field parameters for *Mg–MOF–74*, reproducing both experimental and simulated isotherms, have been determined.

Then, pure gas isotherms at several temperatures above and below 323 *K* were retrieved for all the gases (except H_2O, that is usually trapped before the adsorption unit) from GCMC simulations. Two– and three–gas mixtures, corresponding to all combinations, at several pressure and temperatures, have been also studied, so that the influence on CO_2 adsorption could be determined in detail. Mixture results show a moderate to low ability of minor gases to diminish CO_2 adsorption on *Mg–MOF–74*, in contradiction to prior statements in the literature. More specific results will be presented at the meeting.

References:

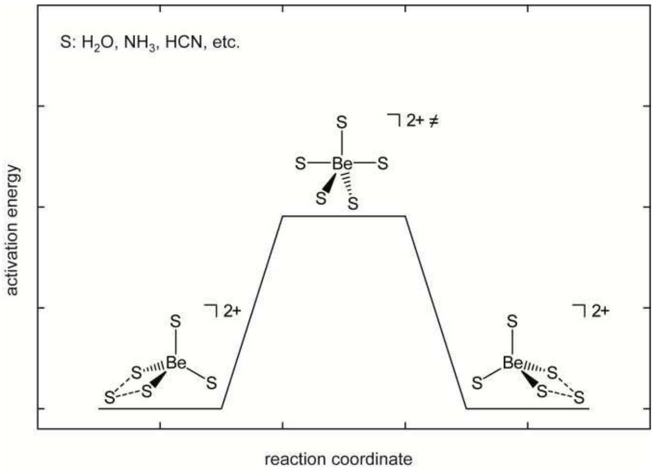
[1] Zou, R., et al. "*Storage and separation applications of nanoporous metal–organic frameworks*", *Cryst. Eng. Comm* 12 (2010) 1337-1353.
[2] Espinal, L., et al. "*Measurement, standards, and data needs for CO_2 capture materials: a critical review*", *Env. Sci. Technol.* 47 (2013) 11960-11975.
[3] Sircar, S., T. C. Golden, and M. B. Rao. "*Activated carbon for gas separation and storage*", *Carbon* 34 (1996) 1-12.
[4] Britt, D., et al. "*Highly efficient separation of carbon dioxide by a metal-organic framework replete with open metal sites*", *Proc. Nat. Acad. Sci.* 106 (2009) 20637-20640.
[5] Pham, T., et al. "*Capturing the H_2–Metal Interaction in Mg-MOF-74 Using Classical Polarization*" *J. Phys. Chem. C* 118 (2014) 22683-22690.

LiEBe^{2+} - Ligand Exchange at Beryllium dications

Ralph Puchta[1,2]

[1]*Department Chemie und Pharmazie, Institut für Anorganische Chemie,*
Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 1,
91058 Erlangen, Deutschland
[2] *Department Chemie und Pharmazie, Computer Chemie Centrum,*
Friedrich-Alexander-Universität Erlangen-Nürnberg, Nägelsbachstraße 25,
91052 Erlangen, Deutschland

Beryllium is supposed to be the most toxic non-radioactive metal in the periodic table, while parallel it is applied in various technical applications.[1] Due to the toxicological concerns only a few experimental studies in (bio)inorganic chemistry and related mechanisms are known. While solvent exchange reactions are the most fundamental substitution processes that a solvated metal ion can undergo and do not necessarily lead to a chemical conversion, they contribute fundamentally to our understanding of reactivity and substitution mechanisms. Experiments will lead to knowledge about reactions under realistic conditions, in contrast to quantum chemical calculations that permit detailed investigations unbiased by external effects.



In the presented work ligand exchange reactions on [BeS$_4$]$^{2+}$-ions were investigated and rationalized by DFT and MP2 calculations, focusing on solvent molecules (S),[2] bio-relevant ligands and ligands with differently hybridized donor atoms.

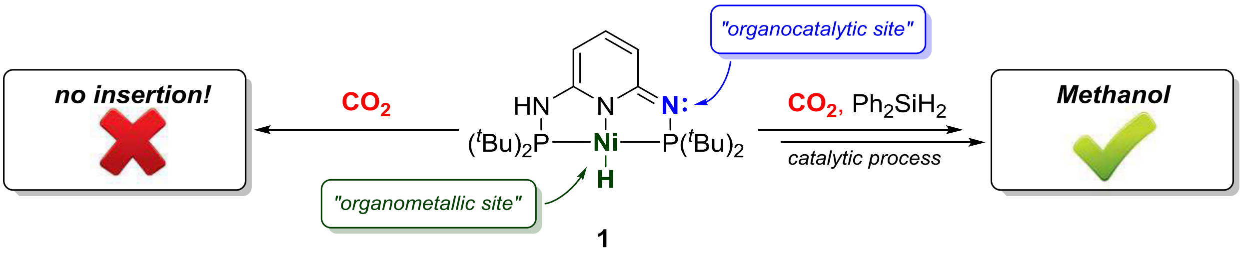
[1] R. Puchta, *Nat. Chem.* **3**, 413 (2011).
[2] R. Puchta, N. v. Eikema Hommes, R. v. Eldik, *Helv. Chim. Acta*, 88, 911, (2005).

Hydride-enhanced ligand nucleophilicity for metalloorganic catalytic reactivities

Theo P. Gonçalves[a], Huaifeng Li and Kuo-Wei Huang[b]

King Abdullah University of Science and Technology (KAUST)
KAUST Catalysis Center (KCC), and Physical Science and Engineering Division (PSE),
Thuwal, 23955-6900, Saudi Arabia
[a]*E-mail: theo.goncalves@kaust.edu.sa*
[b]*E-mail: hkw@kaust.edu.sa*

In this work, we disclose the computational study of unexpected reaction mechanism with our dearomatized Ni-H pincer complex **1** that promotes CO_2 reduction without direct participation of the metal center.[1] The reactivity has been attributed to the presence of the iminic arm moiety which acts as a strong electron donor, and in consequence, activates silane for hydride transfer. In contrast to commune observed reactivity,[2] our DFT and CCSD(T) calculations support that the complex itself is unable to perform CO_2 insertion to Ni-H bond in experimental conditions. Further analysis of the transition states confirm experimental finding that the nucleophilicity of the nitrogen is enhanced when electron donating spectator ligands are coordinating to the Ni metal. Therefore the dearomatized PN^3P nickel complexes are capable of catalyzed efficiently transformations which typically belongs to the organocatalyst domain.



Scheme 1. Reactivity of the **1**, PN^3P^*Ni-H complex.

References (use Times New Roman 10)

[1] H. Li, Q. Zhao, T. P. Gonçalves, D. Gong, B. Zheng, L. Yao, Z. Lai, Z. Wang, J. Zheng, K. W. Huang, *unpublished data*.

[2] a) S. Chakraborty, J. Zhang, J. A. Krause, H. Guan, *J. Am. Chem. Soc* **2010**, *132*, 8872-8873; b) K. J. Jonasson, O. F. Wendt, *Chem. Eur. J* **2014**, *20*, 11894-11902.

Influence of odd/even alkyl side-chain substitution on the morphology and charge-transport of benzothieno-benzothiophenes (BTBT)

M. Alkan, I. Yavuz[1]

[1] *Department of Physics, Marmara University, 34722, Ziverbey, İstanbul, Turkey.*

Recent measurements show that organic materials with a benzothieno-benzothiophene (BTBT) core exhibit unprecedented charge-carrier mobilities but dramatically influenced by the size of side-chains. Recently, the crystal structures of a series of even (C_n-X-C_n) and odd (C_n-X) alkylated BTBTs have been obtained [1]. Using a multitude of computational tools, we calculate the molecular ordering and charge-transport of these materials to understand the side-chain dependence. The mobilities are typically on the order of 1-100 cm^2/Vs, therefore we employ both band transport models using deformation-potential theory based on DFT-D3 methodology and hopping transport using kinetic Monte Carlo simulations employing Marcus-Levich-Jortner charge-transfer theory. Band transport calculations are performed in a perfect lattice, while hopping transport calculations are performed for both perfect lattices and disordered morphologies based on molecular dynamics simulations.

[1] H. Minemawari *et al.*, *Chem. Mater.* **29**, 1245−1254 (2017).

Calculation of Molecular Properties from Relativistic Electron Dynamics

Lukas Konecny[1], Marius Kadek[2], Stanislav Komorovsky[3], Olga L. Malkin[1, 3], Vladimir G. Malkin[3], Kenneth Ruud[2], Michal Repisky[2]

[1]*Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University, Ilkovicova 6, Bratislava, Slovakia*
[2]*The Centre for Theoretical and Computational Chemistry, Department of Chemistry, UiT The Arctic University of Norway, NO-9037, Tromsø, Norway*
[3]*Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dubravska cesta 9, Bratislava, Slovakia*

We present an implementation and applications of relativistic electron dynamics for molecular property calculations as an alternative to response theory approach. The electron dynamics methodology is based on a direct stepwise time propagation of an electronic state, represented by an one-electron density matrix. Time dependence of molecular properties can be obtained in the course of the simulation and afterwards processed to spectra in various regions including near resonant frequencies. This is possible without the need to explicitly evaluate the response kernels. If molecules of interest contain atoms of heavy elements or exhibit strong spin-orbit coupling, relativistic Hamiltonians have to be considered. Our implementation utilizes the matrix representation of the four-component Dirac–Coulomb Hamiltonian in the basis of restricted kinetically balanced Gaussian functions exploiting the noncollinear Kramers unrestricted formalism, as well as the quasirelativistic two-component X2C Hamiltonian. The latter leads to a 7-fold acceleration practically without the loss of accuracy.

The selected applications include the calculations of electron absorption and circular dichroism spectra by Fourier transform of the time-dependent induced electric or magnetic dipole moment, respectively. We focus on various spectral regions including the UV/Vis [1] and X-ray near L-edge structure [2]. Moreover, we compute molecular hyperpolarizabilities by a time-dependent finite-field method [3]. To overcome the absence of an analysis tool for spectra we have developed the dipole-weighted transition analysis to identify the nature of electronic transitions. In addition, to eliminate non-physical excitations that arise as artefacts of finite basis representation particularly in the high-frequency regions we propose the orbital-selective perturbation.

[1] M. Repisky, L. Konecny, M. Kadek, S. Komorovsky, O. L. Malkin, V. G Malkin, K. Ruud, *J. Chem. Theory Comput.* **11**, 980 (2015).

[2] M. Kadek, L. Konecny, B. Gao, M. Repisky, K. Ruud, *Phys. Chem. Chem. Phys.* **17**, 22566 (2015).

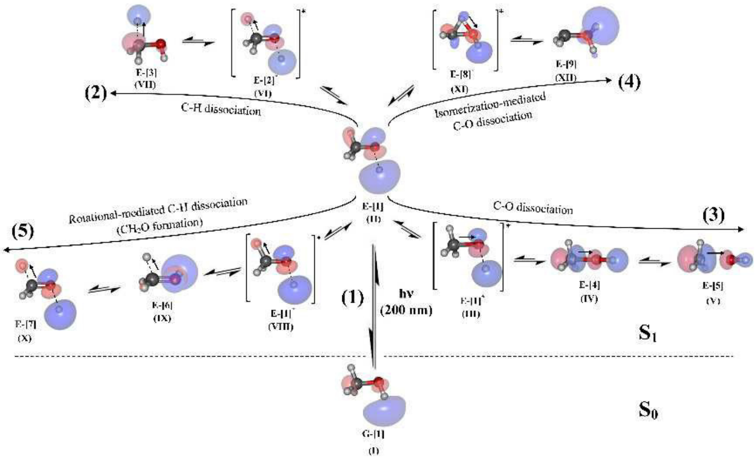
[3] L. Konecny, M. Kadek, S. Komorovsky, O. L. Malkin, K. Ruud, M. Repisky, *J. Chem. Theory Comput.* **12**, 5823 (2016).

Dynamics of Photo-fragmentation of Methanol

Pannipa Panajapo, Kittipan Siwawannapong, Kritsana Sagarik*

School of Chemistry, Institute of Science, Suranaree University of Technology,
111 University Avenue, Nakhon Ratchasima 30000,
Thailand.

ABSTRACT: Photo-fragmentation of methanol (CH_3OH) has been of interest, because the product radicals are reactive intermediates in industrial, combustion and atmospheric processes [1,2]. Based on a theoretical method [3], the photo-fragmentation of CH_3OH in the S_1 state was studied using TD-DFT and ADC(2) calculations with the aug-cc-pVDZ basis set and BOMD simulations over the temperature range of 200–2100 K. Because a minimum was found on the S_1 relax-scan potential energy surface, the photo-fragmentation processes were suggested for the first time to take place through the $[CH_3O]^{\cdot}$–$[H]^{\cdot}$ radical pair, which is also a common intermediate for the C-H and C-O bond dissociations, as well as for the formation of formaldehyde (CH_2O) through a rotational-mediated dissociation process. These findings are different from the previous theoretical study [2], in which a homolytic cleavage of the O-H bond along a purely repulsive potential surface was predicted from a freeze-scan method. The BOMD results suggested that in the S_1 state, the photo-fragmentation of CH_3OH and the formation of CH_2O are kinetic-control processes.



[1] M. Yang, P. D. Nightingale, R. Beale, P. S. Liss, B. Blomquis, C. Fairall, *Environ. Sci.* **110**, 20034 (2013).

[2] R. J. Buenker, G. Olbrich, H. P. Schuchmann, B. L. Schuermann, C. V. Sonntag, *J. Am. Chem. Soc.*, **106**, 4362 (1984).

[3] J. Thisuwan, P. Suwannakham, C. Lao-ngam, K. Sagarik, *Phys. Chem. Chem. Phys.*, **18**, 5564 (2016).

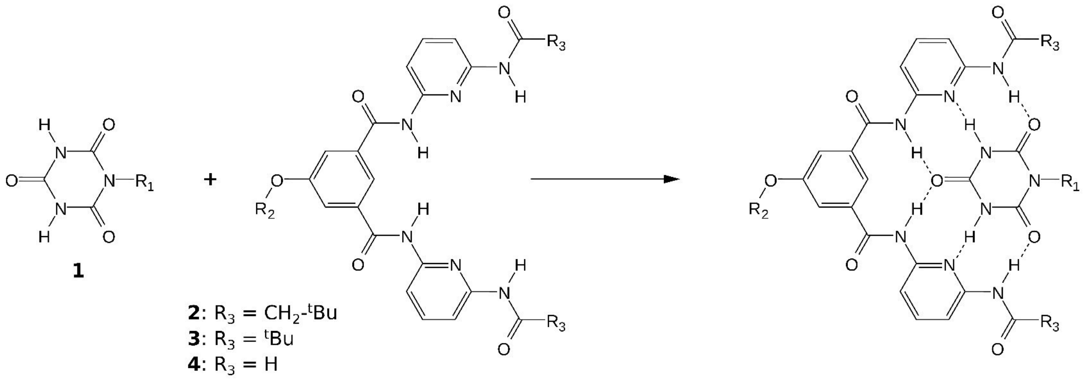
Acknowledgement: The Royal Golden Jubilee (RGJ) Ph.D. Program of the Thailand Research Fund (TRF) (Grant No. PHD/0139/2554) and the Development and Promotion of Science and Technology Talents Project (DPST).

Investigating the molecular structure and hydrogen bonding in single-chain polymer nanoparticle self-assembly binding motifs

Peter A. Limacher[1] , **Wim Klopper**[1]

[1]*Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany*

Figure 1 shows the intermolecular binding between a Hamilton wedge and cyanuric acid, frequently employed binding motifs to achieve self-assembly of single-chain polymer nanoparticles.



1

2: R_3 = CH_2-^{t}Bu
3: R_3 = ^{t}Bu
4: R_3 = H

Figure 1: The hydrogen bonding pattern in a Hamilton wedge/cyanuric acid binding motif

In a recent study, we performed a conformational analysis of the isolated compounds and the hydrogen-bonded complex.[1] We found several low-energy structures, which are characterized based on their non-planarity and binding energy. New hypothetical binding motifs are proposed and proven to possess a superior binding energy, when becoming planar.

In addition, we compared NMR chemical shifts calculated on the B3LYP, BP86 and MP2 level with experimentally available data with a good qualitative agreement. Cases of quantitative disagreement between experiment and theory are traced back to solvent effects for isolated substituents or to thermally stretched intermolecular bonds for hydrogen-bonded species. When comparing the calculated NMR chemical shifts with their corresponding intermolecular hydrogen bond length, strong linear correlations can be found. This will allow experimentalists to predict exact geometrical distances from their measured NMR spectra in the future.

[1] P. A. Limacher, W. Klopper, *Soft Matter*, **submitted**.

Recent developments in domain local pair natural orbital electron correlation approaches.

Christoph Riplinger[1,2], **Frank Neese**[1]

[1] *Department of Molecular Theory and Spectroscopy, Max Planck Institute for Chemical Energy Conversion, Stiftstr. 34 – 36, D-45470 Mülheim an der Ruhr, Germany*
[2] *FAccTs GmbH, Rolandstr. 67, D-50677 Köln, Germany*

An overview on recent advances in method development employing the domain local pair natural orbital (DLPNO) framework is given. The DLPNO framework, first published in 2013, has been used to implement methods for open and closed shell CCSD(T) energy calculations and for closed shell CCSD(T) electron density calculations for the calculation of first-order molecular properties.[1-5] A multilevel implementation (DLPNO-CCSD(T), DLPNO-MP2, HF) has been established to treat different parts of a chemical system at different accuracy.[6] E.g. one part of a system can be treated at DLPNO-CCSD(T) level, while being embedded in an environment treated at DLPNO-MP2 or HF level.

A very efficient implementation of DLPNO-NEVPT2 yields accurate results for multi-reference cases.[7]

Overall, systems consisting of hundreds of atoms have been modeled in a routine fashion using the various DLPNO implementations. Chemical accuracy compared to the results obtained with the parent methodologies or compared to experimental data is achieved.

[1] C. Riplinger, F. Neese, *J. Chem. Phys.* **138**, 034106 (2013).

[2] C. Riplinger, B. Sandhöfer, A. Hansen, F. Neese, *J. Chem. Phys.* **139**, 134101 (2013).

[3] M. Saitow, U. Becker, C. Riplinger, E. F. Valeev, F. Neese, *J. Chem. Phys.* **146**, 164105 (2017).

[4] C. Riplinger, P. Pinski, U. Becker, E. F. Valeev, F. Neese, *J. Chem. Phys.* **144**, 024109 (2016).

[5] D. Datta, S. Kossmann, F. Neese, *J. Chem. Phys.* **145**, 114101 (2016).

[6] M. Sparta, M. Retegan, P. Pinski, C. Riplinger, U. Becker, F. Neese, *J. Chem. Theory Comput.* Just Accepted Manuscript.

[7] Y. Guo, K. Sivalingam, E. F. Valeev, F. Neese, *J. Chem. Phys.* **144**, 094111 (2016).

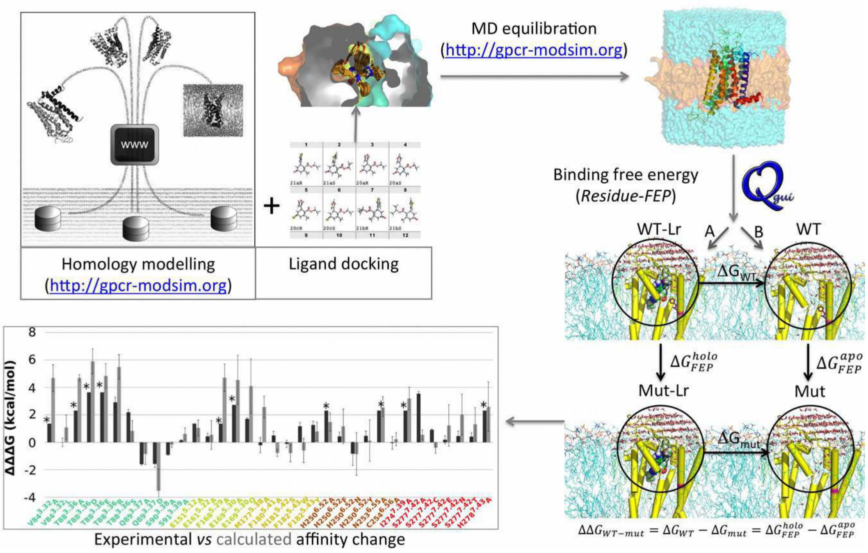
Res-FEP: A tool for in silico site-directed mutagenesis in ligand-binding

Hugo Gutiérrez de Terán, Willem Jespers, Silvana Vasile, Johan Åqvist.

Department of Cell and Molecular Biology, Uppsala University, Biomedical Center, Box 596, SE-751 24 Uppsala, Sweden. E-mail: hugo.gutierrez@icm.uu.se

Site-directed mutagenesis (SDM) is a powerful and widely used tool to characterize ligand-binding at the structural and molecular level. The characterization of ligand binding affinities against a set of mutant proteins, interpreted by computational modeling, is a process that has been used in the hit-to-lead optimization of many drug targets, with GPCRs being a paradigmatic example due to the traditional lack of structural information.

In this poster, I will outline our recently developed computational scheme, based on free energy perturbation (FEP) simulations, to quantitatively and routinely assess the effects of point-mutations on ligand binding as well as the structure-activity relationships (SAR) of congeneric series of ligands [1-2] (Fig 1). The procedure is based on an MD sampling of the protein-ligand binding site, using spherical boundary conditions centred on the binding site, which makes it computationally efficient. This method, which we call Res-FEP is now automated and will be soon released as part of the Q-gui graphical interface of our MD software Q. I will present recent results from three biological systems belonging to the GPCR superfamily of membrane receptors: agonist design for the type 2 (Y2) neuropeptide Y receptor; antagonist design on the A_{2A} and A_3 adenosine receptors, and deorphanization of receptor GPR139 [3]. In some cases, we have complemented our simulations with classical FEP simulations on the ligands, providing a full picture of the energetics of ligand binding in the scope of SDM data or ligand-SAR from the literature or from collaborators. Indeed, all the three examples presented are framed into collaborative projects with medicinal chemists and pharmacologists, both from the academia or from the pharmaceutical industry.



References

[1] Keranen, H.; Aqvist, J.; Gutierrez-de-Teran, H. ChemComm (2015), 51:3522
[2] Boukharta, L.; Gutierrez-de-Teran, H.; Aqvist, J. PlOS Comp. Biol (2014) 10:e1003585 and Xu, Vasile et al, Manuscript in preparation
[3] Nøhr AC, Jespers W, Shehata MA, et al. *Sci Rep*. (2017) 7:1128.

Virtual-reality view on chemistry and materials science

Rubén Jesús García-Hernández[1], **Claudia Draxl**[2,3], **Matthias Scheffler**[3], **Dieter Kranzlmüller**[1]

[1]Leibniz Supercomputing Centre, Boltzmannstr 1, Garching by Munich, Germany
[2]Humboldt-Universität zu Berlin, Zum Großen Windkanal 6, 12489 Berlin
[3]Fritz-Haber-Institut Berlin, Faradayweg 4-6, 14195 Berlin

We present a multi-platform tool that allows us to explore materials in Virtual Reality (VR) which has been developed within the Novel Materials Discovery (NOMAD) Laboratory, a European Centre of Excellence (https://nomad-coe.eu). The so far implemented functionality covers (Fig. 1) crystal structures, Femi surfaces, molecular-dynamics trajectories, and electron-hole pairs (excitons). The latter are 6-dimensional objects where VR can show its potential to visualize effects that otherwise are hard to capture. We demonstrate the power of our implementation on the large variety of data from the *NOMAD Repository*, *Archive*, and *Encyclopedia* which host several millions of calculated materials properties. We will give a life demonstration of molecular adsorption on surfaces and excitons in an organic-inorganic hybrid material.

Our platform can be utilized to view various types of datasets commonly used in chemistry and materials science. The tools run on various state-of-the-art VR setups – from extremely low cost to extremely high cost, adjusting the rendering quality according to the equipment. Our goal is to offer the system that suits the users' budget and needs best. This may range from Google Cardboard (a few Euro) to smartphone-based Samsung GearVR (order 200 Euro) and PC-based HTC-Vive (order 1000 Euro) to room-sized CAVE-like[i] equipment (order Mio. of Euro).

The project received funding from the European Union's Horizon 2020 research and innovation program under grant agreement no. 676580 with The Novel Materials Discovery (NOMAD) Laboratory, a European Center of Excellence.

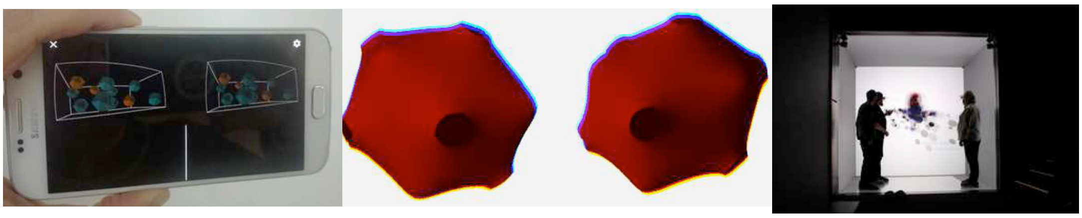


Fig. 1: Crystal structure of Nb_8As_4 (as visualized in Cardboard glasses); Fermi surface of Ag in a Vive system, and adsorption of CO_2 in CaO, as explored in a CAVE system.

---

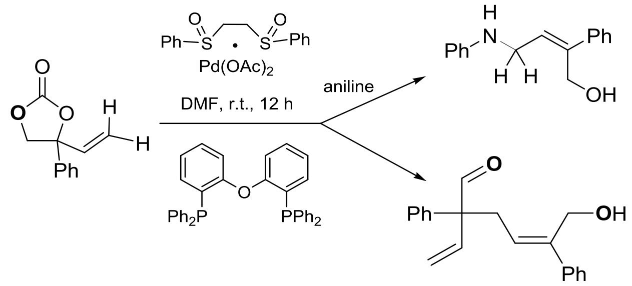
[i] CAVE™ is a trademark of the University of Illinois Board of Trustees. We use the term CAVE to denote both the original system at Illinois and the variants developed by multiple organizations.

Selective Transformation of Cyclic Vinyl Carbonates to Allylic Amines and Aldehydes - A DFT Study

Rositha Kuniyil,[a] Feliu Maseras,[a,b]

[a]*Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology , Av. Països Catalans, 16, Tarragona (Spain)*
[b]*Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra (Spain)*

Cyclic vinyl carbonates are one of the most promising initial products from CO_2 activation. Several applications are being developed for the transformation of cyclic carbonates to various kinds of useful compounds. Allylic amines and allylic aldehydes represents a class of functional olefins which are of greater importance in organic chemistry . Even though significant progress has been observed in recent years for their synthesis, stereoselective synthesis of multi-substituted allylic amines and aldehydes remains a challenging target. Palladium catalyzed decarboxylative approaches from cyclic vinyl carbonates enables the construction of them which are characterized by excellent stereoselectivity, operational simplicity, mild reaction conditions, and wide scope in reaction partners (Scheme 1) [1]. DFT studies were performed to rationalize the stereocontrol in these reactions, and evidence is provided that the formation of a six-membered palladacyclic intermediate has a great role in controlling the stereoselectivity of reaction.



Scheme1. Conversion of cyclic vinyl carbonates to allylic amines and allylic aldehydes

[1] (a) W. Guo, L. Martínez-Rodríguez, R. Kuniyil, E. Martin, E. C. Escudero-Adán, F. Maseras, A. W. Kleij, J. Am. Chem. Soc. **138** 11970 (2016) (b) W. Guo, R. Kuniyil, J. E. Gomez, F. Maseras, A. W. Kleij (manuscript in preparation)