**Participants in the Winter School 2016**

| | |
|---|---|
| Ahmad Shah | Masood |
| Ait Kaci | Mazari |
| Baibuz | Ekaterina |
| Benkyi | Isaac |
| Bortoli | Marco |
| Bravic | Ivona |
| Chen | Xiaoyu |
| ChoBuj | Marta |
| Di Luca | Andrea |
| Dimitrova | Maria |
| Dvorak | Marc |
| El Hadki | Hamza |
| Elm | Jonas |
| Ferdoudi | Yassine |
| Fischermeier | David |
| Fliegl | Heike |
| Franzke | Yannick Joel |
| Gamiz-Hernandez | Ana Patricia |
| Ghahremanpour | Mohammad Mehdi |
| Girych | Mykhailo |
| Golze | Dorothea |
| Haapanen | Outi |
| Håkansson | Pär |
| Hänninen | Vesa |
| Hapka | Michal |
| Hatz | Richard |
| Head-Gordon | Martin |
| Herrmann | Nils |
| Holzer | Christof |
| Hyttinen | Noora |
| Iyer | Siddharth |
| Izzaouihda | Safia |
| Johansson | Mikael |
| Joshi | Satya |
| Jussupow | Alexander |
| Kaila | Ville |
| Karttunen | Antti |
| Klumpe | Sven |
| Konschin | Henrik |
| Kussman | Jörg |
| Lehtola | Susi |
| Lembinen | Meeri |
| Li | Jingrui |
| Lowe | Samuel Joseph |
| Mader | Sophie |
| Mares | Jiri |
| Murdachaew | Garold |
| Muuronen | Mikko |
| Myllys | Nanna |

| | |
|---|---|
| Olsen | Jeppe |
| Parkkinen | Pauli |
| Partanen | Lauri |
| Pernal | Katarzyna |
| Ponkkonen | Tuomo |
| Pyykkö | Pekka |
| Rahim | Mohamed |
| Rantala | Tapio |
| Rauhalahti | Markus |
| Reiher | Markus |
| Reiman | Heidi |
| Reiter | Kevin |
| Runeberg | Nino |
| Salminen | Tapio |
| Sandberg | Thomas |
| Sharma | Vivek |
| Solala | Eelis |
| Sundholm | Dage |
| Suomivuori | Carl-Mikael |
| Taubert | Stefan |
| Tiihonen | Juha |
| Vuorio | Joni |
| Wirz | Lukas |
| Zar ba | Jan |
| Zech | Alexander |
| Zgid | Dominika |
| Zhan | Shaoqi |

# On the nature and extent of chalcogen ···$\pi$ interactions

**Authors;** <u>Shah Masood Ahmad</u>, Marco Dalla Tiezza, Marco Bortoli and Laura Orian*

**Affiliation;** *Dipartimento di Scienze Chimiche, Università degli Studi di Padova, Via Marzolo, 1   35131-Padova (PD), Italy*

**Corresponding Email Address;** shahmasood.ahmad@studenti.unipd.it

Weak non-covalent interactions have gained paramount importance in chemistry. They play a crucial role in different phenomena, among which the self-assembly of large molecules, biological pattern recognition and crystal packing. Chalcogen···$\pi$ interactions, which are the focus of the present study, were found in biological active compounds like cysteine, selenocysteine, selenomethionine.[1-2]

In our analysis, calculations were performed to predict, characterize and quantify chalcogen···$\pi$ interactions between $X_2Y$ (X = F, Cl, Br, I and Y = S, Se, Te) and an unsaturated substrate (ethyne, 2-butyne, ethylene and benzene). The density functional BLYP in combination with TZ2P basis set was used and scalar relativistic effects were accounted for through zeroth-order regular approximation (ZORA).[3] MP2/aug-cc-PVTZ (PP) results were included for selected cases. A fragment-based approach (Activation Strain Analysis, ASA) [4] was employed to gain insight on the nature of the interaction established between the chalcogen center and the $\pi$ system, which behave like a Lewis acid-base couple. Trends are shown and discussed and in perspective will be extended to biological sites to investigate chalcogen based redox active enzymes and supramolecular aggregated architectures.

**Keywords:** Activation Strain Analysis, (ASA), chalcogen….$\pi$ interactions, DFT calculations, ZORA, chalcogen centers
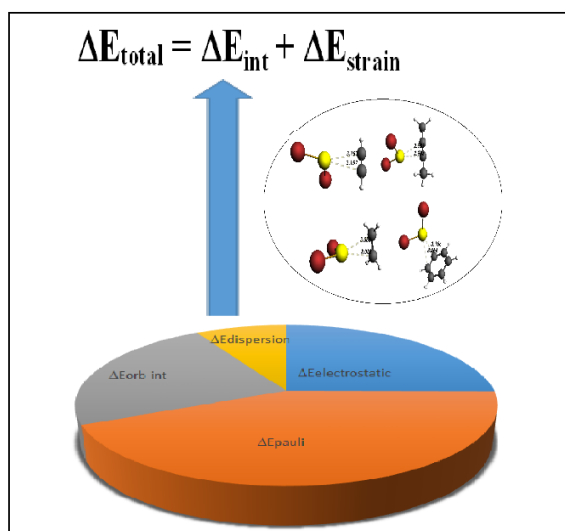
## References

(1) Jacob, C.; Giles, G.I.; Giles, N. M.; Sies. H. *Angew. Chem. Int. Ed*. **2003**, 42, 4742 – 4758.

(2) Nziko, V.P.N.; Scheiner, S.  *J. Phys. Chem. A*. **2015**, 119, 5889−5897.

(3) Esrafili, M. D.; Mohammadian-Sabet, F. *Mol. Phys*. **2015**, 113, 3559-3566.

(4) Zaccaria, F.; Wolters, L.P.; Guerra, C.F.; Orian, L. *J. Comp. Chem*. **2016**, 37, 1672-1680.

# INVESTIGATION OF THE BIOLOGICAL ROLE OF SELENIUM: INSIGHT FROM DFT STUDIES ON MODEL CHALCOGENIDES

Marco Bortoli [a], Laura Orian [a] and F. Matthias Bickelhaupt [b,c].

[a] Dipartimento di Scienze Chimiche, Università degli Studi di Padova, Via Marzolo 1, 35129 Padova, Italy
[b] Department of Theoretical Chemistry and Amsterdam Center for Multiscale Modeling (ACMM), Vrije Universiteit Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands
[c] Institute for Molecules and Materials (IMM), Radboud University, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands

Selenocysteine (Sec), a modified amino acid containing selenium, is found in 25 proteins in the human body. The real reason for the presence of this unusual residue is still not clear, considered that its insertion mechanism is much more complicated than those of the more common amino acids. [1] What is clear, though, is that in glutathione peroxidases (GPx), an important class of proteins, a considerable loss of activity is found if Sec is substituted with Cys. The role of GPx enzymes is to catalyze the reduction of organic hydroperoxides via a three-step mechanism (Scheme 1). [2] The importance of this task in the prevention of many degenerative diseases has led scientists to try to emulate the efficiency of these enzymes through novel, chalcogen based molecules. [3] The main goal is to discover the relevant features of the enzymatic active site and to transfer them to small molecules for an efficient drug design. To achieve this, we are studying the elementary enzymatic reactions in model organic chalcogenides, in cysteine, selenocysteine and tellurocysteine and also in small cluster modelled on the GPx active site with current DFT techniques and activation strain analyses. Focus was centered on Step 3, a nucleophilic attack of a chalcogenolate to a dichalcogenide, which is considered to be rate determining and results on mechanism and energetics of these reactions are presented [4] together with novel findings from the investigation of the oxidation of chalcogenides with $H_2O_2$ (Step 1).
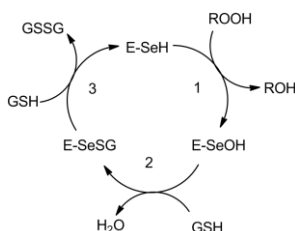


**Scheme 1**. Catalytic mechanism of GPx enzyme (E).

# References

[1] H. J. Reich, R. J. Hondal. ACS Chem.Biol., 11 (2016) 821-841.
[2] L. Flohé, E. Günzler A., H. H. Schock. FEBS Lett., 32 (1973) 132-137.
[3] L. Orian, S. Toppo. Free Radic.Biol.Med., 66 (2014) 65-74.
[4] M. Bortoli, L. P. Wolters, L. Orian, F. M. Bickelhaupt. J.Chem.Theory Comput., 12 (2016) 2752-2761.

# Two-photon absorption of the spatially confined LiH molecule

Justyna Kozłowska, MARTA CHOŁUJ, Robert Zaleśny, Wojciech Bartkowiak

*Department of Physical and Quantum Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, PL – 50370 Wrocław, Poland*

The studies of spatially confined atomic and molecular systems have become a topic of great significance during the past few decades and increasingly attract attention of researchers from many fields of science. It is well-established that spatial restriction can strongly affect various physical and chemical properties [1-4]. In particular, much effort has been devoted to the studies on the electric properties of atoms and molecules in the presence of confining environment. However, it should be pointed out that previous work in this field has almost exclusively focused on the evaluation of the nonresonant electric dipole properties of molecular systems within restricted spaces, neglecting the nonlinear optical processes in the resonant regime. Therefore, our main goal is to investigate the two-photon dipole transitions between the $X^1\Sigma^+$ and $A^1\Sigma^+$ states of the LiH molecule in the presence of the confining environment. In doing so we consider the values of second-order transition moment. Additionally, we analyze the bond-length dependence of the two-photon absorption strength. The external spatial confinement is assumed in the form of cylindrically symmetric harmonic oscillator potential, which mimics a nanotube-like confining cages. The obtained results demonstrate that the spatial confinement can substantially influence the two-photon absorption response of LiH. In order to explain the observed changes in the second-order transition moment the two-level model is employed. The calculations are performed using multiconfiguration self-consistent field (MCSCF) method and response theory.

[1] W. Jaskólski, Phys. Rep., 271 (1996) 1.
[2] J. Lo, M. Klobukowski, Chem. Phys., 328 (2006) 132.
[3] M. Chołuj, W. Bartkowiak, Chem. Phys. Lett., 663 (2016) 84.
[4] R. Zaleśny, R. Góra, J. Kozłowska, J. Luis, H. Ågren, W. Bartkowiak, J. Chem. Theory Comput., 9 (2013) 3463.

# Proton Transfer in the Membrane Domain of Respiratory Complex I

<u>Andrea Di Luca</u>, Ana P. Gamiz-Hernandez, Ville R. I. Kaila

Abstract

Respiratory complex I (NADH:ubiquinone reductase) is the largest enzyme of aerobic respiratory chain and it functions as a redox-driven proton pump, employing the energy from quinone reduction to pump protons across the mitochondrial membrane. Recently resolved crystal structures [1,2] show a long chain of conserved polar and charged residues that span the entire length of the the membrane domain (*ca.* 200 Å), linking the quinone reduction chamber to the other end of the enzyme. Recent molecular dynamics (MD) simulations have clarified the roles of some of these residues [3,4], but the overall molecular mechamism by which it catalyses this long range proton-electron transfer process is still unclear. We perform large-scale classical MD on a microsecond time scale and QM/MM simulations to study hydration effects and proton transfer (pT) in the membrane domain of this gigantic proton pump.

References

1. R. Baradaran, J.M. Berrisford, G.S. Minhas, L.A. Sazanov, Nature 494(2013) 443-450
2. V. Zickermann, C. Wirth, H. Nasiri. K. Siegmund, H. Schwalbe, C. Hunte, U. Brandt, Science 347 (2015) 44-49
3. V.R.I. Kaila, M. Wikström, G. Hummer, PNAS 111 (2014) 6988-6993
4. V. Sharma, G. Belevich, A.P. Gamiz-Hernandez, T. Ròg, I. Vattulainen, M.L. Verkhovskaya, M. Wikström, G. Hummer, V.R.I. Kaila, PNAS 112 (2015) 11571-11576

# Density functional theory studies on 1-butyl-3-methylimidazolium chloride

Maria Dimitrova, Dage Sundholm

University of Helsinki
Helsinki, Finland
maria.dimitrova@helsinki.fi

Ionic liquids are a class of organic compounds which exhibit some peculiar properties including low vapour pressure, no volatility, thermal and chemical stability, electrical conductivity, and catalytic properties. They are also good solvents for polar and non-polar molecules. Ionic liquids are commonly used in laboratory as solvents in organic synthesis, extraction and chromatography. The electric conductivity and the diffusion ability of the ions can be tailored for application in fuel cells and batteries. There are many possible combinations of cations and anions, which makes it possible to fine-tune the chemical and physical properties to the desired application. Due to the rich set of possibilities it is beneficial to do computational studies to help the choice of a suitable molecule.

The properties of ionic liquids have been thoroughly studied both experimentally and computationally. One intriguing experimental technique is the analysing the internal structure of the bulk using the [129]Xe nuclear magnetic resonance (NMR) spectrum. The xenon atom is highly polarizable yet inert probe, which gives rise to large chemical shifts in the NMR spectrum. It was found that the size of the anion in the ionic liquid affects significantly the free volume, which correlates with the solvation ability of the molecule.

The theoretical study involves obtaining the optimized geometries of clusters of the ionic liquid with a xenon atom at DFT level, and calculating the nuclear shieldings to predict the [129]Xe NMR spectrum using ZORA. The first part of the study involves obtaining the geometry of the ionic liquid cluster at the PBEh-3c/def2-mSVP/D3-BJ level of theory. The density functional allows calculations on extended systems within a reasonable time frame. After the structure was obtained, a xenon atom is added to different locations and the structures optimized further. The nuclear shielding calculations require that relativistic effects be taken into account for the xenon atom.

# Theoretical investigation of the Zinc Oxide ZnO: Ground and Excited States

Yassine Ferdoudi [1], Najia Komiha [1], Khadija Marakchi [1]

[1] Laboratory of Spectroscopy Molecular Modeling Materials and Environment, Department of Chemistry, Faculty of Sciences, Mohammed V University of Rabat.

## Abstract:

Zinc is a chemical element known for its applications in many fields (environment, cosmetics, pharmaceuticals, nutritional additives, it is considered important because of the major role it plays in many enzymatic reactions indispensable to the life of living beings, Recent research has shown that zinc oxide also has the same importance except that the complicity of its spectra and electronic structure entangled makes its study by experimenters and theorists difficult.. Solving equations based on the construction of approximate wave functions for ZnO systems, followed by a study of this compound by the Variable Multireference [MRCI] and Coupled Cluster Methods [RCCSD (T)] using augmented bases. Obtained from these calculations will be compared with the experimental results.

# Analysis of magnetically induced current densities in molecules

H. Fliegl[a)] and D. Sundholm[b)]

a) *Centre for Theoretical and Computational Chemistry (CTCC), Department of Chemistry, University of Oslo, P.O.Box 1033 Blindern, N-0315 Oslo, Norway.* b) *Department of Chemistry, P.O. Box 55 (A.I. Virtanens plats 1), FIN-00014 University of Helsinki, Finland.*

An overview of different ways to systematically analyze the magnetically induced current density in molecules is presented using the gauge including magnetically induced current method (GIMIC).[1, 2] GIMIC is a independent program that is used for the calculation of magnetically induced current densities using London orbitals. Numerical integration of the current flow around molecular rings and along selected chemical bonds can be used for determining current pathways and the degree of aromaticity of various molecules according to the magnetic criterion. A new feature of the GIMIC program is the calculation of the anisotropy of the magnetically induced density using gauge including atomic orbitals.[3] As an example for a multiring system the magnetically induced current density of trans porphyrin is presented and discussed.[4]
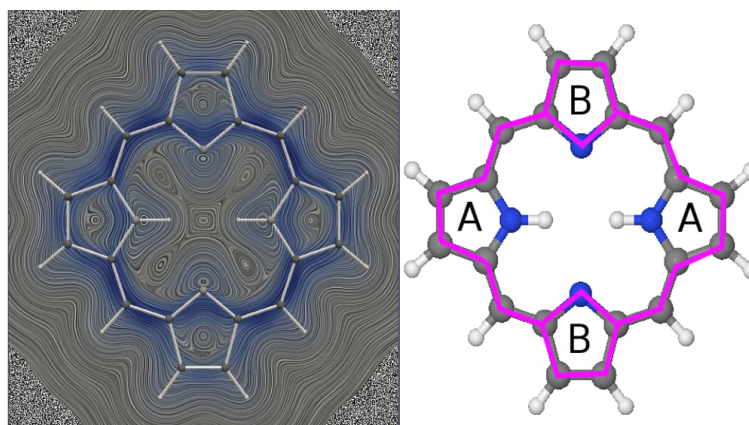
[1]  J. Jusélius, D. Sundholm and J. Gauss, *J. Chem. Phys.*, **121**, 3952 (2004)
[2]  D. Sundholm, H. Fliegl and R. F. Berger, *WIREs*, **6**, 369, (2016)
[3]  H. Fliegl, J. Jusélius and D. Sundholm, *J. Phys. Chem. A*, **120**, 5658, (2016)
[4]  H. Fliegl and D. Sundholm, *J. Org. Chem.*, **77**, 3408, (2012)

# THREE-BODY EFFECTS IN DFT VIA MUTUAL POLARIZATION OF FRAGMENT DENSITIES

M. Hapka, Ł. Rajchel, M. Modrzejewski, M. M. Szczęśniak, G. Chałasiński

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

The Pauli Blockade method allows calculations of noncovalent interactions via mutual polarization of fragment densities. When based on Kohn-Sham description of the monomers [1] Pauli Blockade may be recast into a rigorous dispersion-free DFT approach termed PBdf. We present an extension of the dispersion-free Pauli Blockade method to the three-body case. We compare the performance of PBdf to that of supermolecular DFT and wavefunction methods for a series of trimers ranging from the model $He_3$, $Ar_3$, $Ar_2$-HF and $Ar_2$-HCl complexes to the selected systems from the 3B-69 test set [2]. Both PBdf and supermolecular DFT results are analyzed using the partitioning of the nonadditive three-body energy into the exchange and deformation contributions [3]. The performance of different xc functionals is tested, including range-separated hybrids.

[1] Ł. Rajchel, P. S. Żuchowski, M. M. Szczęśniak, G. Chałasiński, Phys. Rev. Lett., 104 (2010) 163001.
[2] J. Řezáč, Y. Huang, P. Hobza, G. J. Beran, J. Chem. Theory Comput. 11 (2015) 3065.
[3] S.M. Cybulski, C. E. Seversen, J. Chem. Phys. 122 (2005) 014117.

# Physiological autoxidation behaviour of vitamin C

## Nils Herrmann, Norah Heinz, Michael Dolg, Xiaoyan Cao

*Institute for Theoretical Chemistry, University of Cologne, Greinstr. 4, 50939 Cologne, Germany*
*E-mail: N.Herrmann@uni-koeln.de, phone: (+49)(0)221 - 470 - 6885*

The study of vitamin C and its reducing capacity is of great importance for the understanding of the human defense mechanism against radical species and crucial to a wide range of medical applications. Due to the antioxidative effect of vitamin C, aggressive radicals, like reactive oxygen species, that are under suspicion to benefit cancer generation, can be rendered harmless. On the other hand induced autoxidations of vitamin C may actually produce reactive oxygen species and allow a controlled generation of the latter at cancerous cells leading to apoptosis. The development of possible catalysts, triggering this autoxidation, is an ongoing challenge in modern cancer research.

Oxidation and autoxidation reactions of vitamin C have been investigated using quantum chemical first-principle and ab initio methods. Reaction energies and Gibbs energies of the reactions were calculated at the DFT level, applying the gradient-corrected BP and the hybrid B3LYP functionals together with basis sets of triple zeta quality. Based on these calculations adiabatic and vertical ionisation potentials as well as electron affinities were determined for all biologically active vitamin C species. Additionally, single-point CC2, CCSD and CCSD(T) calculations were used for calibration of the DFT data.[1]
Since the investigated reactions take place in a physiological environment, modelling of an aqueous vitamin C solution is mandatory. Several approaches have been accounted for, employing continuum models and explicit water molecules, approximated as effective fragment potentials. These were expressed by Coulomb interactions of multipolar charge distributions, dipole polarizability and empirical repulsive potentials.

[1] Herrmann, N., Heinz, N., Dolg, M., Cao, X, *J. Comput. Chem.* **2016**, 37, 1914.

# Recent advances in describing dispersion / van der Waals interactions

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

*[1]Institut für Physikalische Chemie, Karlsruher Institut für Technologie, Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany*

We aim at developing new variants and methods to improve predictions on binding energies of van der Waals bonded systems. A main working tool for this task is the symmetry-adapted perturbation theory ("SAPT") that has been newly implemented into our working package TURBOMOLE. To improve on existing theory, we enhanced certain aspects of SAPT:

1) Our main goal is to use explicitly correlated functions which help improve the basis set convergence. The dispersion energy is a correlation energy and therefore suffers from slow basis set convergence. We therefore aim at employing the F12 methodology to improve basis set convergence. First tests have shown that the convergence can be improved by up to two cardinal numbers compared to standard basis sets. [1]
2) Heavy elements constitute a challenge for quantum chemical methods. To further investigate the nature of e.g. metal – π or aurophilic interactions we implemented a two-component version of DFT-SAPT into Turbomole.
3) With a combined $G_0W_0$-BSE-SAPT approach we aim at minimizing the influence of the DFT XC kernel on the energy components of the SAPT scheme.

[1] J. A. Frey, C. Holzer, W. Klopper, and Samuel Leutwyler, Chem. Rev., 116, 5614 (2016)

# Catalytic Mechanism of Quinolone Biosynthesis in Dioxygenase AsqJ

Sophie Mader, Alois Bräuer, Ana P. Gamiz-Hernandez, Michael Groll, Ville R. I. Kaila

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

# Photo-oxidation of Water On Small TiO$_2$ Nanoparticles[1]

Mikko Muuronen,[a] Shane Parker,[a] Enrico Berardo,[b,c] Alexander Le,[a] Martijn Zwijnenburg[b] and Filipp Furche[a]

[a]Department of Chemistry, University of California, Irvine
[b]Department of Chemistry, University College London
[c]Department of Chemistry, Imperial College London

Contact: mmuurone@uci.edu

Ever since the ability of TiO$_2$ to split water was discovered in 1972, the use of TiO$_2$ for solar fuel generation has been intensively studied. The high kinetic barrier for photolytic water splitting on TiO$_2$ surfaces is caused by oxygen evolution reaction in which water is oxidized to O$_2$. The first of the four one-electron oxidation steps is likely rate limiting; however, the mechanism of this step is controversial.

We have explored the photoreactivity of small hydrated TiO$_2$ nanoparticles using unconstrained nonadiabatic molecular dynamics simulations (NAMD). Our methodology is based on Tully surface hopping and time-dependent hybrid density functional theory. The results indicate that ultrafast electron-proton transfer from physisorbed water to the photohole initiates the photo-oxidation on the S$_1$ potential energy surface. The new mechanism readily explains the observation of mobile hydroxyl radicals in recent experiments. Two key driving forces for the photo-oxidation reaction are identified: Localization of the electron-hole pair and stabilization of the photohole by hydrogen bonding interaction.

# Is the chemistry of lawrencium peculiar?

Pekka PYYKKÖ[a], Wen-Hua XU[a,b]

[a]Department of Chemistry, University of Helsinki, POB 55 (A. I. Virtasen aukio 1), FIN–00014 Helsinki, Finland. E-mail: *Pekka.Pyykko@helsinki.fi*
[b]Key Laboratory of Synthetic and Natural Functional Chemistry of the Ministry of Education, College of Chemistry and Molecular Science, Northwest University, 710127 Xi'an, China

The Periodic Table (PT) is about chemistry. Lawrencium (Lr, $Z = 103$) is a short-lived man-made element. Its position in the PT had been debated for some time.[1] Recent experimental work [2] confirmed the theoretical predictions of its ground state,[3] which is different from that of its lanthanide counterpart lutetium. Lr is $7s^2(7p_{1/2})^1$, not $7s^26d^1$. In this study, we find that lawrencium atomic ionization potentials and molecular electronic structures are similar to lutetium in various regards. The molecular systems considered include hydrides, trichlorides, monocarbonyls and other organometallic molecules, from zero- to trivalent lawrencium[4].

We conclude that the peculiar atomic ground state of Lr does *not* lead to special chemistry, thus further supporting the current position of lawrencium in the PT.



Periodic Table 1-172

[1]   1 W. B. Jensen, *Found. Chem.*, 2015, 17, 23-31.
[2]   2 T. K. Sato, M. Asai, A. Borschevsky, T. Stora, N. Sato, Y. Kaneya, K. Tsukada, Ch. E. Düllmann, K., Eberhardt, E. Eliav, S. Ichikawa, U. Kaldor, J. V. Kratz, S. Miyashita, Y. Nagame, K. Ooe, A. Osa, D. Renisch, J. Runke, M. Schädel, O. Thörle-Pospiech, A. Toyoshima and N. Trautmann, *Nature*, 2015, **520**, 209-211.
[3]   J. P. Desclaux, B Fricke, *J. Physique*, 1980, **41**, 943-945.
[4]   W.-H. Xu, P. Pyykkö, *Phys. Chem. Chem. Phys*, 2016, **18**, 17351-17355.

# IMPROVING RUTHENIUM-BASED WATER SPLITTING

Markus Rauhalahti[1*], Ville R.I. Kaila[2], and Mikael Johansson[1*]

[1] Department of Chemistry, University of Helsinki, P.O. Box 55, FI-00014 Helsinki, Finland
2 Dept Chemie, Technische Universität München (TUM), Lichtenbergstraße 4, D-85747 Garching, Germany
e-mail: markus.rauhalahti@helsinki.fi, mikael.johansson@iki.fi
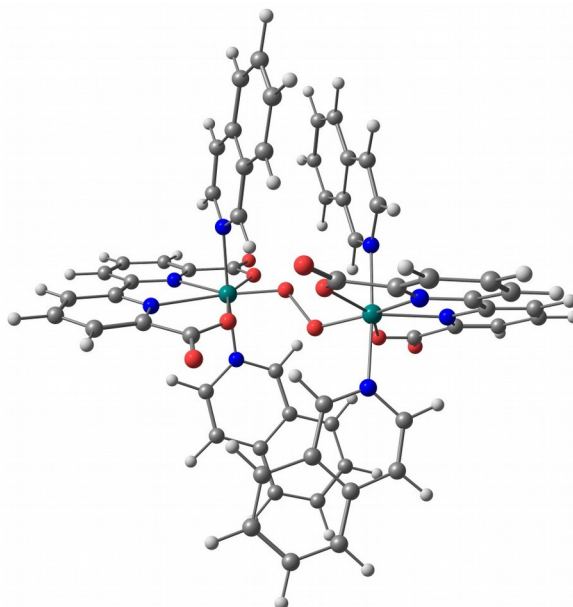
Rational design of artificial water-splitting catalysts is central for developing new sustainable energy technology. The catalytic efficiency of the natural water-splitting enzyme, photosystem II, has been remarkably difficult to achieve artificially; only recently have synthetic, molecular catalysts with comparable activities been presented.[1] Here, using powerful first-principles quantum chemical reaction path calculations and hybrid quantum mechanics/classical mechanics (QM/MM) simulations, we explore the elusive molecular mechanism of a class of ruthenium-based catalysts. We find that the thermodynamic driving force for the water-splitting process is obtained from the free energy released from $\pi$-stacking interactions within the catalytically active dimer core. Understanding the reaction mechanism allows us to design new catalysts that further lower the activation barrier for the water-splitting process by systematically increasing weak interactions within the catalytic dimer.[2]

1)  L. Duan, F. Bozoglian, S. Mandal, B. Stewart, T. Privalov, A. Llobet, L Sun. A molecular ruthenium catalyst with water-oxidation activity comparable to that of photosystem II. *Nat. Chem.* **2012**, *4*, 418–423.
2)  M.P. Johansson, V.R.I. Kaila, *practically submitted manuscript*

# Vibrational circular dichroism spectra
# for large systems and systems with heavy elements

**Kevin Reiter[1], Michael Kühn[2], Florian Weigend[1,2]**

*[1]Institute of Nanotechnology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz Platz 1, 76334 Eggenstein-Leopoldshafen, Germany*
*[2]Institute of Physical Chemistry, Karlsruhe Institute of Technology, Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany*

Vibrational circular dichroism (VCD) intensities are proportional to the rotational strengths which are defined as the imaginary part of the scalar product between the electric and magnetic dipole transition moments for vibrational transitions. We have implemented the calculation of VCD spectra as proposed by Cheeseman [1] in TURBOMOLE by extending the modules mpshift (for the magnetic part) and aoforce (for the vibrational/electric part). Calculation of the VCD spectrum of the icosahedral $C_{420}$ cluster takes 170 hours on a single CPU if symmetry is exploited, the CPU effort being dominated by the vibrational part.

For systems with heavy elements we followed van Wüllen's suggestion [2] to ensure gauge invariance when using effective core potentials (ECPs) in calculations of magnetic properties and employed this also for VCD spectra. We confirmed the gauge invariance for both the chemical shielding tensors and the VCD spectra for e.g. $Co(ppy)_3$, ppy=2-Phenylpyridine, and the heavier homologue $Ir(ppy)_3$.

[1] Cheeseman, J. R., Frisch, M. J., Devlin, F. J., Stephens, P. J., *Chem. Phys. Lett.* **1996**, *252*, 211.
[2] van Wüllen, C., *J. Chem. Phys.* **2012**, *136,* 114110.

# Tuning the protein-induced absorption shifts of retinal in engineered rhodopsin mimics

Carl-Mikael Suomivuori [a, b], Lucas Lang [b], Ana P. Gamiz-Hernandez [b], Dage Sundholm [a], and Ville R. I. Kaila [b]

[a] University of Helsinki
Helsinki, Finland
carl-mikael.suomivuori@helsinki.fi

[b] Technische Universität München
Garching, Germany

**Keywords:** spectral tuning, retinal, quantum chemistry, photobiology, biochemistry

**Abstract:** Rational design of light-capturing properties requires understanding the molecular and electronic structure of chromophores in their native chemical or biological environment. We employ here large-scale quantum chemical calculations to study the light-capturing properties of retinal in recently designed human cellular retinol binding protein II (hCRBPII) variants (Wang *et al. Science*, 2012, **338**, 1340-1343). Our calculations show that these proteins absorb across a large part of the visible spectrum by combined polarization and electrostatic effects. These effects stabilize the ground or excited state energy levels of the retinal by perturbing the Schiff-base or β-ionone moieties of the chromophore, which in turn modulates the amount of charge transfer within the molecule. Based on the predicted tuning principles, we design putative *in silico* mutations that further shift the absorption properties of retinal in hCRBPII towards the ultraviolet and infrared regions of the spectrum.

**References:**

Carl-Mikael Suomivuori, Lucas Lang, Ana P. Gamiz-Hernandez, Dage Sundholm, Ville R. I. Kaila (2016), "Tuning the protein-induced absorption shifts of retinal in engineered rhodopsin mimics", *Chem. Eur. J.* 22(24):8254-8261
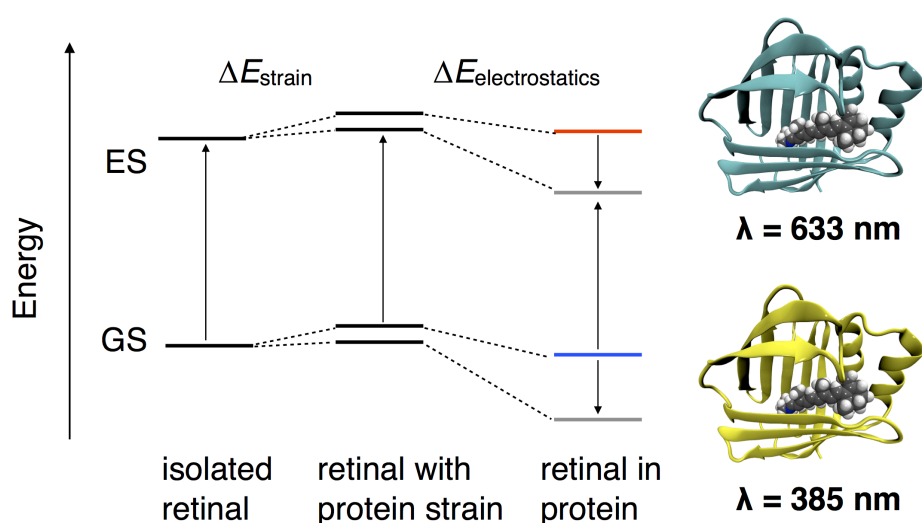
# Quantum Monte Carlo methods from ground state to thermal equilibrium and real-time propagation of electronic structure

J. Tiihonen, I. Ruokosenmäki, I. Kylänpää and T.T. Rantala

Department of Physics, Tampere University of Technology, 33720 Tampere, Finland
email: juha.tiihonen@tut.fi

Electronic correlation is the most challenging part of electronic structure theory and calculations. Conventionally, it is included by corrections on top of Hartree–Fock approach or approximate functionals within Density Functional Theory. However, integration in terms of Quantum Monte Carlo (QMC) yields exact account of correlation, and thus, provides the most accurate description of electronic structure.

Here, we present two novel QMC approaches based on the Feynman path integrals (PI): one in imaginary time and another one in real time. The former leads to the description of electronic structure in finite temperature (PIMC) [1], and the latter to the zero-Kelvin description of eigenstates or quantum dynamics (RTPI) [2]. Curiously, properties of the path-integral approaches meet at the better known Diffusion Monte Carlo (DMC) [3], which yields the exact static ground state at zero-Kelvin.

In all approaches, the many-body effects or correlations are included exactly within the numerical accuracy. Furthermore, the Born–Oppenheimer approximation is not necessarily required, but the nuclei can easily be released to thermal motion and quantum dynamics, if relevant. The biggest challenges are computational burden and description of the exchange interaction of fermions.

We demonstrate these approaches in a few problems, where the effect of correlation is pronounced: computation of molecular polarizabilities (PIMC) [4], Hooke's atom (RTPI) [5] and positron binding atoms (DMC).

[1] D. M. Ceperley. Path integrals in the theory of condensed Helium. *Rev. Mod. Phys*, 67(2):279–355, Apr 1995.
[2] Ilkka Ruokosenmäki and Tapio T. Rantala. Numerical path integral approach to quantum dynamics and stationary quantum states. *Commun. Comput. Phys.*, 18(01):91–103, Jul 2015.
[3] B L Hammond, W A Lester, and P J Reynolds. *Monte Carlo Methods in Ab Initio Quantum Chemistry*. World Scientific, Mar 1994.
[4] Juha Tiihonen, Ilkka Kylänpää, and Tapio T. Rantala. General polarizability and hyperpolarizability estimators for the path-integral Monte Carlo method applied to small atoms, ions, and molecules at finite temperatures. *Phys. Rev. A*, 94(3):032515, September 2016.
[5] Ilkka Ruokosenmäki, Hossein Gholizade, Ilkka Kylänpää, and Tapio T. Rantala. Numerical path integral solution to strong Coulomb correlation in one dimensional Hooke's atom. *Computer Physics Communications*, 210:45–53, Jan 2017.

# FDE-ADC: Multiscale density embedding with an accurate wavefunction method

Alexander Zech[1], Stefan Prager[2], Andreas Dreuw[2], Tomasz. A. Wesolowski[1]

[1]*Department of Physical Chemistry, University of Geneva, 1205 Geneva, Switzerland*
[2]*Interdisciplinary Center for Scientific Computing, University of Heidelberg, 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[3,4]. We present the new multiscale variant FDE-ADC[5] as a combination of FDET and ADC. The current implementation of FDE-ADC uses the Linearized FDET formalism[6], 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.

Three molecular model systems were studied using two different FDE-ADC techniques in which the environment consisted of up to five water molecules. The molecular test systems were chosen to investigate molecule - environment interactions of varying strength from dispersion interaction up to multiple hydrogen bonds. The overall difference between the supermolecular ADC calculations and the FDE-ADC calculations in excitation energies is lower than 0.09 eV (max) and 0.032 eV in average. Also oscillator strengths are reproduced in good agreement with the supermolecular calculation. Initial results show that the FDE-ADC method is a promising approach for considering environmental effects on electronically excited states.

[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] J. Schirmer, A. B. Trofimov, *J. Chem. Phys.* **120**, 11449 (2004).
[5] S. Prager, A. Zech, F. Aquilante, A. Dreuw, T. A. Wesolowski (2016). (submitted to *J. Chem. Phys.*).
[6] A. Zech, F. Aquilante, T. A. Wesolowski, *J. Chem. Phys.* **143**, 164106 (2015).