CHIMIA
CHIMIA 2014, Volume 68
ISSN 0009-4293
www. chimia.ch

SCS
Swiss Chemical
Society

Supplementa to Issue 7-8/2014

SCS Fall Meeting 2014
Oral Presentation Abstracts
Session of Computational Chemistry

September 11, 2014
University of Zurich, Irchel Campus
http://scg.ch/fallmeeting2014

Swiss Chemical Society
Schwarztorstrasse 9
3007 Bern
Switzerland
info@scg.ch
www.scg.ch

Light Matter Interaction: The role of quantum coherence in energy transfer

Sabre Kais[1]

[1]Qatar Environment and Energy Research Institute, Doha, Qatar

Sunlight is the most abundant energy source available on earth, and therefore to design systems that can effectively gather, transfer or store solar energy has been a great continuing challenge for researchers.

To achieve this, a very intuitive approach is to learn from Mother Nature.

In light harvesting organisms, the major mechanism that converts light energy into chemical energy is photosynthesis.

I will discuss the role of quantum coherence in the energy transport in photosynthesis and solar cells.

About the Qatar Environment and Energy Research Institute (QEERI):

Vision: To ensure sustainable development and management of Qatar's energy and natural resources, preserving the quality of life of future generations and making Qatar a leader in cutting edge research.

Mission: Build and Develop World Class, State-of-the-Art, Multi-Disciplinary Research Capabilities in Support of QF's Mission and the QNRS Grand Challenges Research.

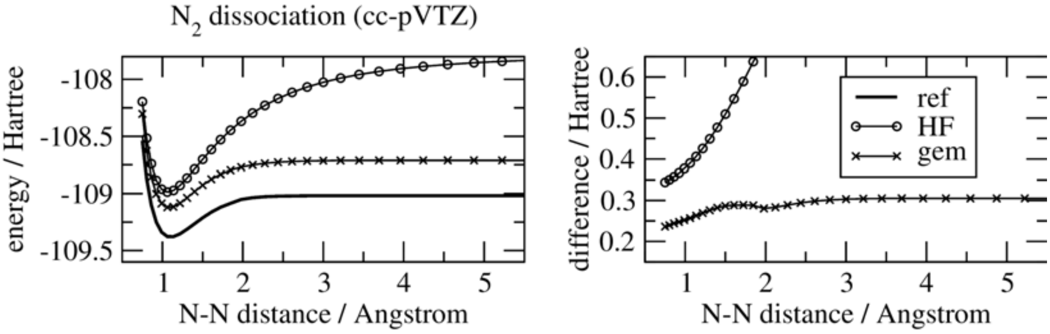
QEERI's Mission is carried out using 3 interconnected strategies:
http://www.qeeri.org.qa

Reviving geminal wavefunction theory: Accurate description of strong electron correlation at mean-field computational cost

Peter Limacher[1], Dimitri Van Neck[2], Paul W. Ayers[1] *

[1]McMaster University, [2]Ghent University

Antisymmetrized product of electron pairs (geminals) have been recognized as conceptually interesting and highly accurate wavefunctions since the early days of quantum chemistry.[1] In contrast to the conventional orbital approach, geminals make explicit use of the two-particle nature of the Hamiltonian. Although very appealing from a fundamental point of view, until recently there were no computationally tractable approaches that did not impose severe restrictions on the geminals (e.g. strong orthogonality).[2] Applying a different, milder set of approximations, it was possible to surmount these bounds and use *non*-orthogonal geminals without sacrificing the mean-field like computational cost.[3]



Our current research interests focus on inexpensive approaches for the mandatory orbital optimization as well as on the adaption of various methods that can account for the remaining dynamical electron correlation.[4][5]

[1] P.R. Surjan, In *Correlation and Localization*; Springer: Berlin **1999**, 203, 63.
[2] P.R. Surjan, A. Szabados, P. Jeszenszki, T. Zoboki, *J. Math. Chem.* **2012**, 50, 534.
[3] P.A. Limacher, P.W. Ayers, P.A. Johnson, S. De Baerdemacker, D. Van Neck, P. Bultinck, *J. Chem. Theory Comput.* **2013**, 9, 1394.
[4] P. Tecmer, K. Boguslawski, P.A. Johnson, P.A. Limacher, M. Chan, T. Verstraelen, P.W. Ayers, *J. Phys. Chem. A*, (in press).
[5] P.A. Limacher, P.W. Ayers, P.A. Johnson, S. De Baerdemacker, D. Van Neck, P. Bultinck, *Phys. Chem. Chem. Phys.* **2014**, 16, 5061.

Four-Component Density Matrix Renormalization Group

Stefan Knecht[1], Örs Legeza[2], Markus Reiher[1] *

[1]ETH Zurich, [2]Wigner Research Center for Physics, Budapest, Hungary

In the past decades relativistic quantum chemistry has significantly improved the understanding of structure, bonding characteristics, and reactivity of heavy element compounds. A reliable study of the chemistry of heavy-elements calls in general for a rigorous treatment of **relativity** and **electron correlation** -- static and dynamic -- on an equal footing. For meeting the latter requirement, the density matrix renormalization group (DMRG) method [1,2] has emerged in recent years in non-relativistic quantum chemistry as a valuable alternative [3-6] to conventional multiconfiguration wave function approaches such as, for example, complete-active-space SCF (CASSCF) as well as multireference configuration interaction (MRCI) and coupled cluster (MRCC).

In this contribution we outline the formulation and implementation of the first relativistic two- and four-component DMRG approach [7] which includes spin-orbit coupling variationally from the onset. The performance of our new relativistic DMRG module is discussed in a pilot application on the TlH molecule.

[1] S. R. White, *Phys. Rev. Lett.*, **1992**, 69, 2863–2866.
[2] S. R. White, R. L. Martin, *J. Chem. Phys.*, **1999**, 110, 4127–4130.
[3] Ö. Legeza, R. Noack, J. Solyom, L. Tincani, in *Computational Many-Particle Physics*, eds. H. Fehske, R. Schneider, A. Weisse, **2008**, 739, 653–664.
[4] K. H. Marti, M. Reiher, *Z. Phys. Chem.*, **2010**, 224, 583-599.
[5] K. H. Marti, M. Reiher, *Phys. Chem. Chem. Phys.*, **2011**, 13, 6750–6759.
[6] G. K.-L. Chan, S. Sharma, *Annu. Rev. Phys. Chem.*, **2011**, 62, 465–481.
[7] S. Knecht, Ö. Legeza, M. Reiher, *J. Chem. Phys.,* **2014**, 140, 041101.

Implementation of exact and approximate methods for nonadiabatic quantum molecular dynamics induced by the interaction with the electromagnetic field

Aurélien Patoz[1], Jiri Vanicek[1] *

[1]EPFL Lausanne

We have implemented a general split-operator/Magnus integrator algorithm of arbitrary order in accuracy for exact nonadiabatic quantum dynamics of a molecule interacting with a time-dependent electromagnetic field. Then, we have derived and implemented analogous geometric integrators of arbitrary order of accuracy for several approximations of treating the molecule-field interaction: the time-dependent perturbation theory, separation of time scales, Condon, rotating-wave, and ultrashort, ``extreme ultrashort'', and ``extremely extreme ultrashort'' pulse approximations. Our general and efficient implementation permits every possible combination of these basic approximations, allowing testing the validity of each approximation under the experimental conditions independently. The algorithms are applied to a one-dimensional three-state harmonic test system and to the four-dimensional vibronic coupling model of pyrazine in order to compare the exact and approximate descriptions of the photoexcitation process with a single laser pulse of finite length as well as nonadiabatic quantum dynamics induced by pump and probe laser pulses.

Towards Intramolecular SAPT

Antonio Prlj[1], Jérôme Gonthier[1], Clemence Corminboeuf[1] *

[1]EPFL Lausanne

Symmetry adapted perturbation theory (SAPT) is certainly the most succesful approach to describe intermolecular interactions[1]. The development of an intramolecular version of SAPT remains theoretically challenging.

Here we present a scheme, which enables the decomposition of intramolecular interactions into physically meaningful energy components: electrostatics, exchange, induction and dispersion. Our approach includes two major steps that are: (1) the construction of a zeroth-order wavefunction for the non-interacting case[2], and (2) the reintroduction of the interaction through biorthogonal perturbation theory. Despite the technical difficulties affecting both the derivation of the wavefunction and the perturbation expansion, our methodology is suitable for providing physically justified energy partitioning.

[1] K. Szalewicz, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.***2012**, 2, 254-272.
[2] J. F. Gonthier and C. Corminboeuf, *J. Chem. Phys.* **2014**, 140, 154107.

Full-dimensional quantum dynamics and spectroscopy of ammonia isotopomers

Csaba Fábri[1], Roberto Marquardt[1], Martin Quack[1] *

[1]Laboratory of Physical Chemistry, ETH Zurich, 8093 Zurich, Switzerland

Ammonia has been a prototype molecule for spectroscopy and quantum tunnelling dynamics for a long time ([1,2] and references cited therein). Recently, accurate full-dimensional potential energy hypersurfaces have become available ([2,3] and references cited therein).

In the present work we have applied and further developed the program GENIUSH ([4] and references therein) for the variational solution of the nuclear Schrödinger equation and the computation and interpretation of vibrational and rotational-vibrational energy levels and wave functions of ammonia isotopomers $^{14}NH_3$, $^{14}NHD_2$, $^{14}NH_2D$, $^{14}ND_3$, $^{14}NHDT$, $^{14}NH_2Mu$, $^{14}ND_2Mu$ and $^{14}NHDMu$. The numerical construction of the general and exact kinetic energy operator allows the application of arbitrarily chosen internal coordinates and body-fixed frame embeddings (including the Eckart frame). Our up-to-date version of GENIUSH is able to employ a contracted vibrational basis set containing products of reduced-dimensional vibrational eigenfunctions, which facilitates the computation of highly-excited rovibrational eigenstates. Besides the computation of accurate rotational-vibrational energy levels and wave functions GENIUSH has been extended to include dynamics under coherent infrared multiphoton excitation [5].

Our work is supported by ETHZ, SNF and ERC.

[1] M. Snels, V. Horká-Zelenková, H. Hollenstein, M. Quack, High Resolution FTIR and Diode Laser Spectroscopy of Supersonic Jets in Handbook of High Resolution Spectroscopy, Vol. 2, pages 1021-1067, M. Quack, and F. Merkt, Eds. Wiley Chichester, 2011
[2] R. Marquardt and M. Quack, Global Analytical Potential Energy Surfaces for High Resolution Molecular Spectroscopy and Reaction Dynamics in Handbook of High Resolution Spectroscopy, Vol. 1, pages 511-549, M. Quack, and F. Merkt, Eds. Wiley Chichester, 2011
[3] R. Marquardt, K. Sagui, J. Zheng, W. Thiel, D. Luckhaus, S. Yurchenko, F. Mariotti, M. Quack, *J. Phys. Chem. A*, **2013**, 117 (32), 7502-7522.
[4] A. G. Császár, C. Fábri, T. Szidarovszky, E. Mátyus, T. Furtenbacher, G. Czakó, *Phys. Chem. Chem. Phys.*, **2012**, 14 (3), 1085-1106.
[5] M. Quack, Multiphoton Excitation, in Encyclopedia of Computational Chemistry, Vol. 3, pages 1775-1791, P. v. R. Schleyer et al, Eds. Wiley Chichester, 1998

Learning the error: Augmenting legacy quantum chemistry with machine learning

Raghunathan Ramakrishnan[1], Pavlo O. Dral [2], Matthias Rupp[1], O. Anatole von Lilienfeld[1] *

[1]University of Basel, [2]Max-Planck-Institut für Kohlenforschung

Chemically accurate, large-scale exploration of molecular space is limited by the computational cost of quantum chemistry methods. We introduce a composite machine learning (ML) strategy for rapid prediction of corrections to routinely employed approximate quantum mechanical (QM) methods. After training, chemically accurate predictions of molecular thermochemical properties of new molecules are possible — with speed-ups of several orders of magnitude. We demonstrate the validity of this QM/ML approach by reproducing enthalpies and free energies of atomization calculated with density functional theory and quantum composite methods for over 130,000 organic molecules and for 6,095 constitutional isomers of $C_7H_{10}O_2$, respectively. QM/ML also predicts electron correlation energies in post Hartree-Fock methods with similar speed-ups and accuracies. We have successfully applied QM/ML to the high-throughput screening of over 10,000 stable diastereomers of $C_7H_{10}O_2$ to identify the molecular pairs with maximal predicted enthalpy, entropy, and free energy of reaction at G4MP2 level of theory.

Unravelling the stabilization mechanism of Al-doped Li-ion conducting Garnets by first-principle simulations.

Teodoro Laino[1], Katharina Meier[1], Alessandro Curioni[1]

[1]IBM Research GmbH

Solid-state lithium batteries are considered the next generation energy storage devices, because of the significant advantages in battery safety due to the lack of any flammable liquid organic electrolyte. Despite the importance of such a concept, a major challenge yet to overcome is the design of a solid-state electrolyte with an high lithium ion conductivity and with optimal mechanical properties. Among the different classes of solid-state electrolytes, Li-stuffed garnets $Li_7La_3Zr_2O_{12}$ (LLZ) [1] are widely studied as excellent lithium ion conductors because LLZ exhibit a ionic conductivity greater than 10^{-4} S/cm at room temperature with chemical and electrochemical stability compared with metallic lithium.

Interestingly enough, LLZ has been characterized in two major crystallographic phases: a high temperature, highly conductive, cubic phase with disordered lithium ion occupancy [1], and a low temperature, lowly conductive, tetragonal phase whose Li sites are completely ordered with 100% occupancy [2]. Because of its high ionic conductivity the cubic phase is the most popular one.

Since the discovery of these materials, most efforts have been directed towards the discovery of possible strategies to stabilize the highly conductive cubic phase at room temperature. The first successful approach was the Aluminum doping [3]. However, it is not well understood yet how the substituted Al works for the stabilization of the cubic phase. Two possible explanation have been proposed to explain the destabilization of the tetragonal phase: 1) the insertion of Al into the Li sites creates some sort of local strain that destabilizes the completely ordered structures; 2) the formed Li vacancies, to maintain charge neutrality upon Al insertion, destabilize the completely ordered Li sites structure. In both cases, as a consequence of the decreased stability of the tetragonal phase, the garnet framework transforms to the cubic structure with disordered Li sites partially occupied by Al.

In this talk, using first principle simulations, we univocally identify the reasons leading to the stabilization of the cubic phase upon Aluminum doping, providing at the same time, a rationale behind the different doping effects of the different doping elements.

[1] R. Murugan, V. Thangadurai and W. Weppner, Angew. Chem., Int. Ed., 2007, 46, 7778–7781.
[2] J. Awaka, N. Kijima, H. Hayakawa and J. Akimoto, J. Solid State Chem., 2009, 182, 2046–2052.
[3] C. A. Geiger, E. Alekseev, B. Lazic, M. Fisch, T. Armbruster, R. Langner, M. Fechtelkord, N. Kim, T. Pettke and W. Weppner, Inorg. Chem., 2011, 50, 1089–1097.

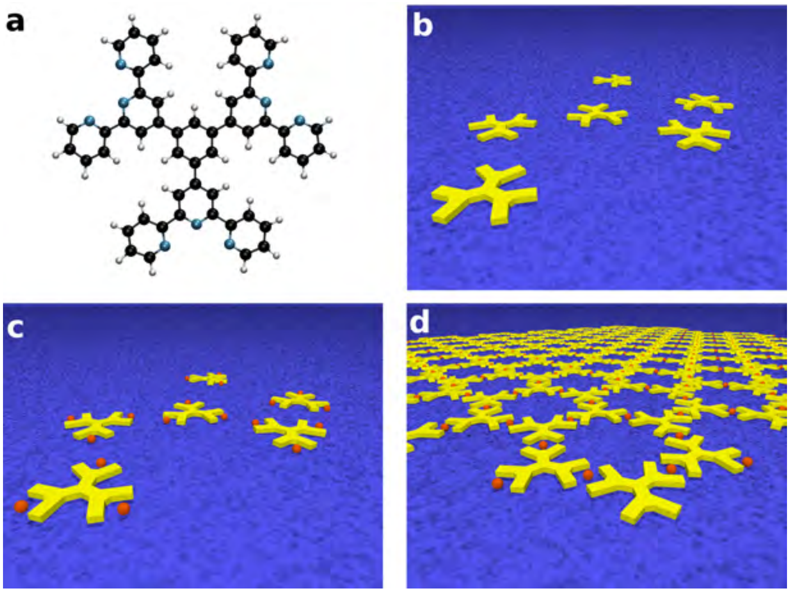
Ab-initio Simulation of two-dimensional Networks on the Surface of Water

Ralph Koitz[1], Marcella Iannuzzi[1], Jürg Hutter[1] *

[1]Department of Chemistry, University of Zurich

Extended two-dimensional networks adsorbed on surfaces have attracted attention for applications in catalysis and nanotechnology. Traditionally, research has focused on sheet-like polymers such as graphene and boron nitride atop metals and metal oxides using computational and surface science techniques. More recently, however, it was demonstrated that ordered networks of monolayer thickness can also be formed on the surface of liquid water by using metal ions, e.g. Zn^{2+}, to bind together multidentate ligand molecules [1, 2]. This presents a promising route towards producing atomically defined free-standing monolayers with chemical functionality. As such networks are challenging to characterize, computational methods can provide valuable insight into their formation and structure.

In this contribution we present large-scale *ab-initio* molecular dynamics (MD) simulations of the formation of a network of *tris*-terpyridine-derived molecules (TTPB, Fig. 1a) on a water surface. In particular, we focus on the structure and dynamics of the molecule on the surface, the mechanism of Zn^{2+} ion insertion from the solution and the subsequent linking of molecules into aggregates (Fig. 1b-d). We employ advanced MD methods to quantify the free energy surface of the involved processes. Our results provide detailed insight into on-surface and subsurface diffusion in this system and chemical reactions of TTPB on the surface of water.



[1] Thomas Bauer, Zhikun Zheng, Alois Renn, Raoul Enning, Andreas Stemmer, Junji Sakamoto, A. Dieter Schlüter, *Angew. Chem. Int. Ed.*, **2011**, 50, 7879-7884.
[2] Rie Makiura, Kohei Tsuchiyama, Osami Sakata, *CrystEngComm*, **2011**, 13, 5538-5541.

Re-Engineering the B1 Domain of Streptococcal Protein G (GB1): Teaching an Old Dog New Tricks

Esra Bozkurt[1], Florence Pojer[1], Giulia Palermo[1], Thereza A. Soares[2], Ursula Röthlisberger[1] *

[1]EPFL Lausanne, [2]Federal University of Pernambuco Recife

Recent advances in molecular modeling and experimental methods have contributed to the area of protein engineering by predicting and generating new proteins, especially, in order to introduce catalytic properties. Here, the previously engineered GB1 domain,[1] which contains a tetrahedral zinc binding site has been revisited to create an efficient biocatalyst. We anticipate that the metallo-GB1 domain might be a new alternative to mimic carbonic anhydrase activity and at the same time to perform a mild (3 + 2) cycloaddition for unactivated nitriles. The main reason for the choice of this system is twofold, the zinc ion acts as a Lewis acid in all catalytic enzymatic sites and the selected scaffold has an unusual thermostability. With the aim to explore potential catalytic roles of the GB1 domain and to understand the reaction mechanisms of these transformations, we perform classical molecular dynamics (MD), quantum mechanics/molecular mechanics (QM/MM) simulations and model calculations by utilizing density functional theory methods. Preliminary computations indicated that (3 + 2) cycloadditions proceed via a concerted mechanism and the nature of the azide group is also important for the activation mechanism of tetrazole formation. Theoretical calculations for zinc finger like models show that activation barriers are lower than the ones previously reported for zinc salt catalysts, $(ZnBr_2)$[2]. Experimental verification of the crystal structure of GB1 domain including the zinc binding site is underway.

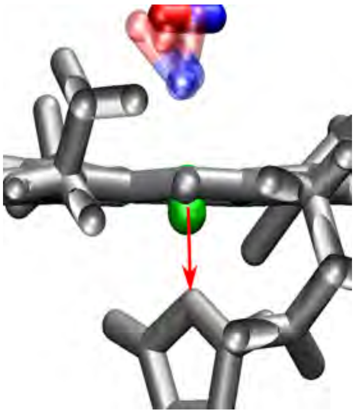
[1] Michael Klemba, Kevin H. Gardner, Stephan Marino, Neil D. Clarke, Lynne Regan, *Nature Structural Biology,* **1995**, 2, 368-373.
[2] Fahmi Himo, Zachary P. Demko, Louis Noodleman, K. Barry Sharpless, *Journal of the American Chemical Society*, **2003**, 125, 9983-9987.

Reactive Processes onto the Multidimensional Potential Energy Surface: Molecular Dynamics of the MbNO system

Maksym Soloviov[1], Markus Meuwly[1] *

[1]University of Basel

Myoglobin is one of the most well-studied heme-containing proteins. The heme Fe in the active site of the protein can bind small diatomic molecules (in particular, NO), this makes the system a good candidate for ligand binding and photodissociation studies. After photoexcitation of the porphyrin system, the bond between the heme Fe and the small diatomic molecule breaks, then NO can either rebind to the heme Fe after the relaxation or leave the active site.[1]



We investigate the effects of the structural changes in the heme group on the dynamics of the NO rebinding after photoexcitation and the possible escape of NO to the other pockets in the protein. The standard force fields based on the harmonic approximation do not allow to describe the reactive processes. In this study we use the DFT parametrized potential energy surfaces (PES) for the doublet and quartet states based on the reproducing kernel Hilbert space approach, combined with the Legendre polynomials. The global effective PES is obtained by smooth mixing of the individual PESs using an approach described by Nagy et al [2]. The dynamics of myoglobin is analyzed in detail.

[1] S. Kim, G. Jin, and M. Lim, *J. Phys. Chem. B,* **2004**, 108, 20366
[2] T. Nagy, J. Yosa, M. Meuwly, *J. Chem. Theo. Comp.,* **2014**, 10, 1366

Anion-π and cation-π interactions on the same aromatic surface

Marie Humbert-Droz[1], Kaori Fujisawa[1], Cesar Beuchat[1], Adam Wilson[1], Tomasz Adam Wesolowski[1], Naomi Sakai[1], Stefan Matile[1] *

[1]University of Geneva School of Chemistry and Biochemistry

The well known cation-π interactions take place on electron-rich aromatic surfaces and are part of the fundamental interactions between and within molecules [1]. Anion-π interactions are, on the contrary, less known and were discovered not long ago [2]. The counter-ion in such ion-π interactions is usually ignored. In this work, we show theoretical and experimental evidence that anion-π and cation-π interactions can occur on the same aromatic surface, leading to ion-pair-π interaction. Push-pull chromophores such as naphtalimides (NMIs) [3] are particularly suited to accommodate such interactions. We present more specifically a full study of the excited state properties of NMIs where positive and negative charges were added in a parallel and antiparallel orientation with respect to the dipole moment. The excited state calculations allowed us to identify the origin of the significant difference observed between the spectra of both compounds[4].

[1] D. A. Dougherty, *Acc. Chem. Res*. **2013**, 46, 885-893.
[2] D. Quinonero *et al., Andew. Chem. Int. Ed*. **2002**, 41, 3389-3392.
[3] R. M. Duke, E. B. Veale, F. M. Pfeffer, P. E. Kruger, T. Gunnlaugsson, *Chem. Soc. Rev.,* **2010**, 39, 3936-3953
[4] K. Fujisawa, C. Beuchat, M. Humbert-Droz, A.Wilson, T. A.Wesolowski, J. Mareda, N. Sakai, S. Matile, *To be submitted*