



# BOOK OF ABSTRACTS

## RSC THEORETICAL CHEMISTRY GROUP CONFERENCE

University of Nottingham, June 20 - 22, 2016

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# High-dimensional quantum dynamics of functional organic polymer materials: Coherence and correlations at the nanoscale

Irene Burghardt<sup>1</sup>, Matthias Polkehn<sup>1</sup>, Robert Binder<sup>1</sup> and Hiroyuki Tamura<sup>2</sup>

<sup>1</sup>Institute for Physical and Theoretical Chemistry, Goethe University Frankfurt, 60438 Frankfurt am Main, Germany

<sup>2</sup>WPI-Advanced Institute for Material Research, *Tohoku University*, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

We present high-dimensional quantum dynamical studies of ultrafast photoinduced exciton migration and dissociation in functional organic materials, in view of understanding the intricate interplay of electronic delocalization, coherent nonadiabatic dynamics, and trapping phenomena. As highlighted by recent experiments, quantum coherence can play a key role in the elementary transfer steps, despite the presence of static and dynamic disorder.

Our approach combines first-principles parametrized Hamiltonians, based on TDDFT and/or high-level electronic structure calculations, with accurate quantum dynamics simulations using the Multi-Configuration Time-Dependent Hartree (MCTDH) method [1] and its multi-layer and Gaussian-based [2] variants, and as well as non-Markovian reduced dynamics techniques [3]. This talk will specifically address (i) exciton dissociation and free carrier generation in donor-acceptor materials, including models for P3HT-PCBM heterojunctions [4,5] and highly ordered thiophene-perylene diimide assemblies [6,7], (ii) exciton multiplication in acene materials [8], and (iii) the elementary mechanism of exciton migration as well as charge-transfer exciton formation in polythiophene and poly-(*p*-phenylene vinylene) type materials [9]. Special emphasis is placed on the specific influence of molecular packing, which can act as determining factor in efficient energy and charge transfer.

The presented case studies illustrate that the hierarchical multiconfigurational approach is ideally tailored to vibronic lattice models in many dimensions. Against the background of these studies, we will comment on the role of temporal and spatial coherence, along with a consistent description of the transition to a classical statistical regime.

[1] M. H. Beck, A. Jäckle, G. A. Worth, H.-D. Meyer, *Phys. Rep.* 324, 1 (2000).

[2] G. W. Richings, I. Polyak, K. E. Spinlove, G. A. Worth, I. Burghardt, B. Lasorne, *Int. Rev. Phys. Chem.*, 34, 265 (2015).

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[4] H. Tamura, I. Burghardt, *J. Am. Chem. Soc.* 135, 16364 (2013).

[5] M. Huix-Rotllant, H. Tamura, I. Burghardt, *J. Phys. Chem. Lett.* 6, 1702 (2015).

[6] M. Polkehn, H. Tamura, P. Eisenbrandt, S. Haacke, S. Méry, I. Burghardt, *J. Phys. Chem. Lett.* 7, 1327 (2016).

[7] L. Li, P. Eisenbrandt, T. Roland, M. Polkehn, P.-O. Schwartz et al., *Phys. Chem. Chem. Phys.* DOI: 10.1039/C6CP00644B (2016).

[8] H. Tamura, M. Huix-Rotllant, I. Burghardt, Y. Olivier, D. Beljonne, *Phys. Rev. Lett.*, 115, 107401 (2015).

[9] J. Wahl, R. Binder, I. Burghardt, *Comput. Theor. Chem.*, 1040, 167 (2014).

# Exploring the activation mechanisms in ligand-gated ion channels by enhanced sampling methods

Carla Molteni

King's College London, London, WC2R 2LS, UK

E-mail: [carla.molteni@kcl.ac.uk](mailto:carla.molteni@kcl.ac.uk)

Pentameric ligand-gated ion channels (pLGICs), embedded in the membrane of nerve cells, are important neuroreceptors that mediate fast synaptic transmission, are involved in several neurological disorders and are target sites for drugs and, in invertebrates, insecticides. However, we have little idea of how they function at the molecular level due to their complexity and limited experimental information. We have investigated the first crucial step of their activation mechanism, which consists in the binding of a neurotransmitter to their extracellular domain, focussing of the prototypical case of the neurotransmitter GABA binding to the insect RDL receptor, which is linked to the resistance to the insecticide dieldrin. Using the "funnel-metadynamics" computational technique, which efficiently enhances the sampling of bound and unbound states using a funnel-shaped restraining potential to limit the exploration in the solvent, we have described the binding free energy landscape, identified the chain of events leading GABA from the solvent into the binding-pocket and estimated the binding affinity. Moreover, we have shown how this landscape is disrupted by mutations which prevent the receptor to function. We have also assessed the potential of trans-cis proline switch for the gating of the ion channel, in the case of the 5-HT<sub>3</sub> receptor, which is activated by serotonin. The RDL and the 5-HT<sub>3</sub> receptors share structural and functional features with other pLGICs, hence our work provides valuable protocols to study the activation mechanisms of pLGICs beyond conventional docking and molecular dynamics techniques.

# Simulating excited-states dynamics using the MCTDH method

Graham Worth

School of Chemistry, University of Birmingham, Edgbaston, B15 2TT, UK

E-mail: g.a.worth@bham.ac.uk

To study the time-evolution of photo-excited molecules it is necessary to solve the time-dependent Schrödinger equation. The easiest way to do this conceptually is to expand the nuclear wavefunction in a basis set and solve the resulting equations of motion. The multi-configurational time-dependent Hartree (MCTDH) method is an efficient way to do this [1,2] and has been used in the study of a variety of fundamental processes. Recent calculations have been used to, e.g. unravel the signal of time-resolved photo-electron spectroscopy of pyrrole [3] and identify a new charge transfer state in pyrrole clusters [4]. Much of the effort for such calculation goes in to calculating the potential energy surfaces. In the talk, recent developments of the direct dynamics variational multi-configurational Gaussian (DD-vMCG) method [5,6] will be presented. In these calculations the potential energy surfaces are calculated on-the-fly, making them more straightforward to run, only limited by the accuracy of the quantum chemistry method used.

[1] M. Beck, A. Jackle, G.A. Worth, and H.-D. Meyer, *Phys. Rep.*, 2000, **324**: 1–106.

[2] G. A. Worth, H.-D. Meyer, H. Koppel, L. S. Cederbaum, and I. Burghardt. *Int. Rev. Phys. Chem.*, 2008, **7**: 569–606.

[3] G. Wu, S. P. Neville, O. Schalk, T. Sekikawa, M. N. R. Ashfold, G. A. Worth, and A. Stolow. *J. Chem. Phys.*, 2015, **142**: 074302.

[4] S. P. Neville, O. Kirkby, N. Kaltsoyannis, G. A. Worth, and H. H. F. Fielding. *Nature Comm.*, 2016, **7**: 11357.

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## Contributed Talks

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# Self-consistent implementation of meta-GGA exchange-correlation functionals within the ONETEP linear-scaling DFT code

James C. Womack and Chris-Kriton Skylaris

Chemistry, Faculty of Natural & Environmental Sciences,  
University of Southampton, Highfield, Southampton, SO17 1BJ, UK  
E-mail: J.C.Womack@soton.ac.uk

In the Kohn-Sham formulation of density functional theory (DFT), the complicated exchange and correlation interactions of many-electron systems are described by the exchange-correlation functional,  $E_{xc}[n]$ , for which the exact form is unknown. Numerous approximate forms for this functional have been developed over the past several decades, and are categorized into broad families by the charge-density-dependent ingredients used in their construction. While the LDA (local density approximation) and GGA (generalized gradient approximation) families use the charge density,  $n$ , and its gradient, to describe exchange and correlation effects, functionals from the meta-GGA family typically also depend upon the kinetic energy density,  $\tau$ . The use of  $\tau$  to construct exchange-correlation functions allows the development of more sophisticated, flexible and accurate functional forms, but also presents new challenges and complexities for their implementation.

In order to extend the theoretical advantages of meta-GGA functionals to large-scale DFT calculations on thousands of atoms, we have implemented support for  $\tau$ -dependent meta-GGA functionals in ONETEP [1], a linear-scaling electronic structure package. The ONETEP code achieves linear-scaling computational cost with near-complete-basis-set accuracy by means of a unique formulation of density-matrix DFT in which the total energy is directly minimized with respect to both the density matrix and a set of strictly localized, self-consistently optimized local orbitals (non-orthogonal generalized Wannier functions, or NGWFs).

The self-consistent implementation of meta-GGA functionals within the linear-scaling formalism of ONETEP presented some significant challenges, requiring detailed consideration of the effect of  $\tau$ -dependence on the gradient of the total electronic energy, and the form of the  $\tau$ -dependent exchange-correlation potential in terms of the NGWFs used in ONETEP. In this work, we present the theoretical innovations necessary to implement  $\tau$ -dependent meta-GGA functionals for use in self-consistent linear-scaling DFT calculations using ONETEP. We also present the validation of the accuracy of the implemented meta-GGA functionals and demonstrate the computational scaling of our approach.

[1] C.-K. Skylaris, P. D. Haynes, A. A. Mostofi, and M. C. Payne, *J. Chem. Phys.*, 2005, 122, 084119.

# DFT-based embedding methods

Fred Manby

Bristol University School of Chemistry, England

E-mail: [fred.manby@bristol.ac.uk](mailto:fred.manby@bristol.ac.uk)

Various quantum embedding techniques, in which one quantum mechanical level of theory is embedded in another, are emerging as powerful tools for extending the domain of applications in quantum chemistry. In this talk I will survey some of the key developments, and describe various efforts in our own group to develop methods that allow embedding of high-accuracy electronic structure methods in density functional theory, and extension of quantum chemistry to condensed-phase problems.



# Artificial nucleic acids: Coupled cluster solvated electronic spectroscopy to 50 $\mu$ s MD simulation of AEGIS helices

Robert Molt<sup>a,b</sup>, Jason Byrd<sup>c</sup>, Millie Georgiadis<sup>d</sup>, and Nigel Richards<sup>a</sup>

<sup>a</sup>School of Chemistry, Cardiff University, Park Place, Cardiff, CF10 4AT, UK

<sup>b</sup>Department of Chemistry and Chemical Biology, Indiana University-Purdue University Indianapolis, IN, 46202, USA

<sup>c</sup>Department of Chemistry, Quantum Theory Project, University of Florida, Gainesville FL32611, USA

<sup>d</sup>Department of Biochemistry & Molecular Biology, Indiana University School of Medicine, Indianapolis, IN, 46202, USA

E-mail: r.molt.chemical.physics@gmail.com

We present the physical chemistry underlying several artificial nucleic acids from *ab initio* fragment coupled cluster calculations to 50  $\mu$ s MD calculations of AEGIS DNA helices. Artificial nucleic acids have been expanding in utility, capable of forming stable DNA helices experimentally, and represent a promising horizon of future genetic manipulation. Our studies range from establishing the properties of individual nucleic acids, quantifying the dispersion of their stacking interactions, establishing the tautomeric equilibria via calculated electronic spectroscopy in solution, and observing the macroscopic DNA helical effects of the unusual dispersion interactions of artificial nucleic acids. This work serves to advance fragmented coupled cluster methodology as well as give insight to the chemistry governing synthetic biology.

# Fast time-dependent Density Functional Theory calculations of X-ray absorption and emission spectroscopy

Nicholas A. Besley

School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK  
E-mail: [nick.besley@nottingham.ac.uk](mailto:nick.besley@nottingham.ac.uk)

Advances in experimental techniques have provided X-ray spectroscopy with a much greater richness in structure and the ability to probe chemical processes on an ultrafast timescale. Quantum chemical calculations often play a key role in the analysis of experimental data and it is important that the computational methodology progresses alongside experiment. In this talk the calculation of X-ray absorption and emission spectroscopy using time-dependent density functional theory will be outlined. Recent progress to improve the efficiency and speed of these calculations and their extension to large systems will be described.

# Molecular dynamics study of self-assembly of aqueous solutions of poly[9,9-bis(4-sulfonylbutoxyphenyl)fluorene-2,7-diyl-2,2'-bithiophene] (PBS-PF2T) in the presence of pentaethylene glycol monododecyl ether ( $C_{12}E_5$ )

Beverly Stewart, Hugh Douglas Burrows

Centro de Química de Coimbra, Chemistry Department, University of Coimbra, 3004-535, Coimbra, Portugal  
E-mail: bstewart@qui.uc.pt

The high efficiencies observed in photosynthetic light harvesting systems are a result of their elegant self-assembled structures. In order to mimic these structures in synthetic systems it is required to both control and understand aggregation.

Here the use of computational techniques is presented as a method by which to observe the behaviour of a small fluorene conjugated polymer structure [1]. Interest lies primarily in the study of anionic PBS-PF2T [2] and its observed aggregation behaviour as well as the significance of surfactant presence upon this aggregation. Dynamic simulations have thus far indicated that aggregation of PBS-PF2T, and related conjugated polyelectrolytes, is inhibited in the presence of non-ionic oxyethylene based surfactants  $C_mE_n$  [3], by way of separating the polymers and encapsulating them in liquid crystalline surfactant phases. Here the effects of pentaethylene glycol monododecyl ether  $C_{12}E_5$ , is investigated as an aggregation inhibitor.

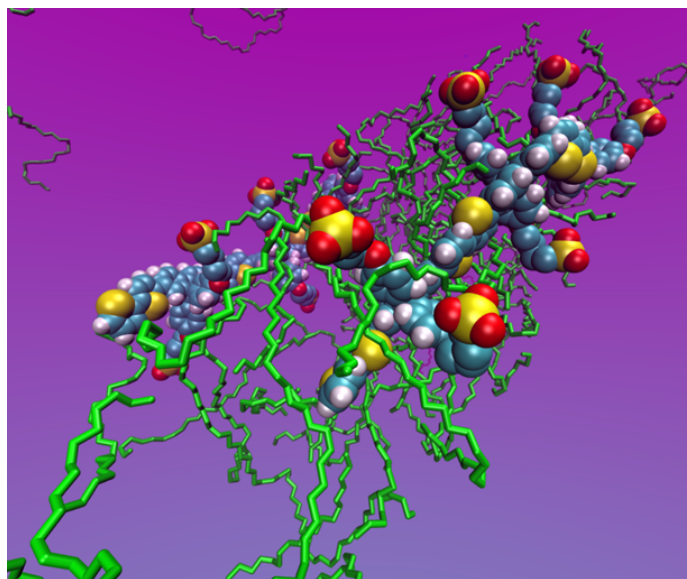


Figure 1. PBS-PF2T encapsulated by  $C_{12}E_5$ .

The importance of various inter- and intra-molecular interactions, as well as solvent temperature, will be discussed as contributing factors in the production of well-defined aggregated structures. By using a computational approach it is possible to develop an understanding of how specific factors affect both the structures and properties of aggregated systems and attempt to produce specific self-assembled

structures which may optimise the efficiency of energy and electron transfer processes in synthetic architectures which mimic the natural photosynthetic light harvesting complex.

[1] Burrows, H. D. Tapia, M. J. Fonseca, S. M. Pradhan, S. Scherf, U. Silva, C.L. Pais, A. C. C. Valente, A. J. M. Schillén. K. Alfredsson, V. Carnerup. M. Tomišič, M. and Jamnik, A. *Langmuir* 2006, 25, 5545-5556.

[2] Knaapila, M. Fonseca, S. M. Stewart, B. Torkkeli, M. Perlich, J. Pradhan, S. Scherf, U. Castro, R. A. E. and Burrows, H. D. *Soft Matter*, 2014, 10, 3103-3111.

[3] Burrows, H. D. Fonseca, S. M. Silva, C. L. Pais, A. C. C. Tapia, M. J. Pradhan. S. and Scherf, U. *Phys. Chem. Chem. Phys*, 2008, 10, 4420-4428.

# Correlation consistent basis sets for the group 1 atoms K–Fr

J. Grant Hill

Department of Chemistry, University of Sheffield, Brook Hill, Sheffield S3 7HF, UK

E-mail: grant.hill@sheffield.ac.uk

The correlation consistent family of basis sets see a lot of use in high-accuracy *ab initio* quantum chemistry [1,2], partly due to their regular energetic convergence characteristics leading to efficient complete basis set limit extrapolation techniques. Developments in ultracold (<1 mK) chemistry means accurate calculations on molecules containing heavy alkali metals, such as RbCs [3] are of interest to both theoretical and experimental groups working in this area, yet there is a limited choice of basis sets for such molecules. With this motivation, the design of correlation consistent basis sets for the group 1 atoms K–Fr will be presented.

Basis sets to be used in conjunction with small-core pseudopotentials of the Stuttgart-Massey variety [4], denoted cc-pVnZ-PP ( $n = D, T, Q, 5$ ), have been optimised along with all-electron Douglas-Kroll sets, cc-pVnZ-DK ( $n = D–Q$ ). These basis sets can also be augmented with diffuse functions for the calculation of long-range interactions, and with additional functions for the description of core-valence correlation. The validation of the resulting basis sets on the diatomics  $M_2$ , MH and MF ( $M = K, Rb, Cs$  and Fr), at the CCSD(T) level of theory, will also be described. It is evident that correlation of the outer core electrons is vital for computed spectroscopic constants to approach existing experimental data.

[1] T. H. Dunning, Jr, *J. Chem. Phys.*, 1989, 90, 1007-1023.

[2] J. G. Hill, *Int. J. Quantum Chem.*, 2013, 113, 21-34.

[3] P. K. Molony, P. D. Gregory, Z. Li et al., *Phys. Rev. Lett.*, 2014, 113, 255301.

[4] I. S. Lim, P. Schwerdtfeger, B. Metz and H. Stoll, *J. Chem. Phys.*, 2005, 122, 104103.

# Radical SAM enzymes – Mechanism, dynamics and radical reaction profiling

Christof M. Jaeger<sup>a</sup>, Damiano Spadoni<sup>a</sup>, Charles Laughton<sup>b</sup> and Anna K. Croft<sup>a</sup>

<sup>a</sup>Department of Chemical and Environmental Engineering, Faculty of Engineering,  
University of Nottingham, University Park, Nottingham, NG7 2RD, UK

<sup>b</sup>Faculty of Science, University of Nottingham, University Park, Nottingham, NG7 2RD, UK  
E-mail: c.jaeger@nottingham.ac.uk

Enzymes capable of controlling radicals present a wide range of radical-dependent mechanisms, with potential for applications in medicinal and synthetic chemistry. The radical SAM enzyme family uses S-adenosyl methionine (SAM) as co-substrate or cofactor to generate radicals directly within the protein. While a general framework for this initial catalytic mechanism has been established over the past years,[1] much less is known about the subsequent chemical rearrangements in most cases. Understanding of these mechanisms can be enhanced through the use of computational approaches. Besides detailed full QM/MM methods, combined molecular dynamics and ‘snapshot’ (e.g. electronic structure) methods can give highly beneficial insights complementing one another.

We present recent results illustrating how such computational approaches can be used to shed light on the radical control mechanisms utilised in radical SAM enzymes, particularly with a view to understanding how these enzymes might both facilitate desired conversions and prevent unwanted side reactions.

We also focus on the problem that the need of this deeper understanding is also the bottleneck for a more rapid access to rational enzyme design. We will show how radical reaction profiling through calculating radical stabilisation energies (RSEs) [2] offers an attractive possibility to assess changes of the overall thermodynamics of radical rearrangements as central steps in radical SAM enzyme catalysis through the example of the recently structurally resolved bacterial 7-carboxy-7-deazaguanine (CDG) synthase (QueE).[3] A combination of molecular dynamics (MD) simulations and quantum mechanical (QM) calculations has provided new insights into the mechanism of how the QueE enzyme controls its radical rearrangement, which involves a very interesting ring-contraction step and additional metal cation binding that influences the catalysis.[4]

[1] J. B. Broderick, *et al.*, *Chem. Rev.*, 2014, 114, 4229.

[2] J. Hioe and H. Zipse, *Faraday Disc.*, 2010, 145, 301.

[3] D. P. Dowling, *et al.*, *Nat. Chem. Biol.*, 2014, 10, 106

[4] R. M. McCarty and V. Bandarian, *Bioorg. Chem.*, 2012, 43, 15.

# Oscillating charge migration between glycine lone pairs silenced by nuclear delocalisation: CASSCF Ehrenfest dynamics study

Iakov Polyak, Andrew Jenkins, Morgane Vacher, Michael J. Bearpark and Michael A. Robb

Faculty of Natural Sciences, Department of Chemistry,  
Imperial College London, South Kensington Campus, London, SW7 2AZ, UK  
E-mail: i.polyak@imperial.ac.uk

Recent advances in attosecond spectroscopy enabled a deeper insight into the electron dynamics following ionisation of molecules. Accordingly, theoretical studies in this field become increasingly important. One of the time-dependent methods of choice is Ehrenfest dynamics, and in our group we developed a second-order Ehrenfest dynamics, using complete active space self-consistent field (CASSCF) to obtain accurate time-dependent electronic wavefunctions and corresponding energies on-the-fly [1], which has been successfully used to study electron dynamics both at frozen molecular geometries and coupled to the dynamics of nuclei. An important issue to investigate is decoherence of electron density oscillations upon ionisation – ability to predict decoherence is vital for designing an experiment. Previously we have shown that charge on glycine lone pairs coherently oscillates without significant interaction with nuclear motion [2]. In the current work our study reveals fast decoherence of charge migration in glycine that happens if appropriate sampling of the initial nuclear wavepacket is taken into account. We investigate the effect of the chosen active space on the final results as well as try to get insight into the way the initial wavepacket should be constructed to provide an accurate description of electron dynamics.

[1] M. Vacher, D. Mendive-Tapia, M. J. Bearpark and M. A. Robb, *Theor. Chem. Acc.*, 2014, 133, 1505.

[2] M. Vacher, M. J. Bearpark and M. A. Robb, *J. Chem. Phys.*, 2014, 140, 201102.

# Uranyl U-O<sub>yl</sub> stretching vibrations as a quantitative measure of equatorial bond covalency: a quantum chemical investigation

Poppy Di Pietro<sup>1</sup>, Andy Kerridge<sup>2</sup>

<sup>1</sup>Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK

<sup>2</sup>Department of Chemistry, Lancaster University, Lancaster, LA1 4YB, UK

e-mail: a.kerridge@lancaster.ac.uk

The concept of covalency can be interpreted in many ways, and different interpretations may lead to contradictory conclusions. Theoretical approaches to understanding covalent contributions to bonding typically employ either i) orbital-based or ii) density-based analysis methods<sup>1-2</sup>. The complicated electron structure of actinide complexes, present due to the combined effects of relativity, strong electron correlation and weak interactions with ligand fields can render orbital-based approaches ambiguous but this in itself isn't justification for the validity of density based approaches.

Here we consider a range of model uranyl complexes and demonstrate that complementary descriptions of covalent contributions to bonding derived from density based analyses are commensurate with variation in binding energies<sup>3</sup>. Furthermore, we demonstrate strong correlations between these measures and calculated U-O<sub>yl</sub> vibrational frequencies indicating that, in these systems at least, such vibrations can be considered a quantitative measure of equatorial bond covalency.

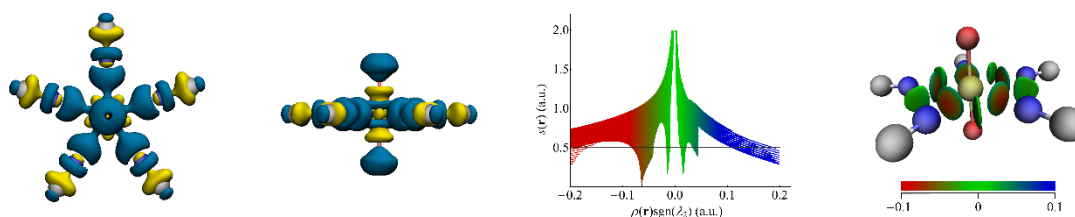


Figure 1. Density difference plots and analysis of the reduced density gradient of  $[\text{UO}_2(\text{NC})_5]^{3-}$

[1] A. Kerridge, *Dalton Trans.*, 2013, 42, 16428

[2] A. Kerridge, *RSC Adv.*, 2014, 4, 12078

[3] P. Di Pietro and A. Kerridge, *Inorg. Chem.*, 2016, 55, 573



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# Explicitly correlated treatment of transition metal containing systems: An ongoing effort

Stella Kritikou and J. Grant Hill

Department of Chemistry, University of Sheffield, Brook Hill, Sheffield S3 7HF, UK

E-mail: skritikou1@sheffield.ac.uk

The explicitly correlated (F12) *ab initio* methods significantly reduce the basis set demands of high-accuracy quantum chemistry, enabling meaningful coupled cluster and multi-reference configuration interaction calculations to be carried out on a much wider range of systems. Advances in basis sets designed specifically for use in F12 calculations have pushed this even further. There are examples in the literature of F12 methods now being used to investigate transition metal complexes, which has typically been the reserve of density functional theory.

The accuracy of explicitly correlated coupled cluster methods for 3d transition metal-containing molecules will be demonstrated through analysis of geometries and atomisation energies of a recently proposed test set [1]. Comparison with experimental and composite thermochemistry derived data reveals accelerated convergence that will translate to significant computational savings. Nonetheless, explicitly correlated calculations using existing basis sets do not always converge smoothly, removing some of the attraction of using wavefunction-based methods. In order to tackle this problem, correlation consistent basis sets for the 4d transition metal elements Y-Pd have been developed and optimised specifically for use with F12 methods. These sets are designed with efficiency and smooth convergence in mind, and they hold the promise of accurate calculations on transition metal-containing complexes of a chemically relevant size.

[1] X. Xu, W. Zhang, M. Tang and D. G. Truhlar, *J. Chem. Theory Comput.*, 2012, 11, 2036-2052.

# Quantum dynamics with adaptive basis sets and short-time trajectories

Maximilian A. C. Saller and Scott Habershon

Department of Chemistry, Warwick University, Coventry, CV4 7AL  
Centre for Scientific Computing, Warwick University, Coventry, CV4 7AL  
E-mail: m.a.c.saller@warwick.ac.uk

The computational study of the quantum dynamics of non-trivial systems heavily relies on efficient expansion of the inherently complex, multidimensional wavefunction to facilitate propagation in time. At present, basis sets employed in quantum dynamics simulations generally fall into one of two classes. Basis sets which, after having initially been distributed in phase space, remain constant thereafter, with time propagation being solely expressed through variation of a set of expansion coefficients, are commonly referred to as being “time-independent”. Conversely, if basis functions are propagated through phase space alongside their coefficients, the resulting basis set is termed “time-dependent”.

While the aforementioned strategies have been employed in numerous, successful quantum dynamics simulations, they both carry with them an inherent set of drawbacks [1]. Due to their static nature, time-independent basis sets must strive to describe the wavefunction across all of phase space at all times, based only on the information available during their initial sampling. In practice, this results in very large basis sets, spanning all of relevant phase space in a grid-like manner, leading to unfortunate exponential scaling. Time-dependent basis sets, while enabled by their dynamic character to remain smaller in size, can violate energy conservation laws unless propagated using variational equations of motion. Furthermore, basis function propagation can suffer greatly from numerical ill-conditioning.

In a recent publication [2], we introduced a novel approach to basis set sampling capitalising on the advantages of both aforementioned strategies, while avoiding their drawbacks. We sample phase space using a set of trajectories to selectively place basis functions in regions relevant to wavefunction propagation. Treating the resulting basis set time-independently yielded very encouraging results for two challenging benchmark problems, namely the relaxation dynamics of photo-excited pyrazine and the Spin-Boson Hamiltonian.

We are currently aiming to address the key assumption of this technique, namely, the validity of classical trajectories as an approximation to quantum dynamics, which is known to only be sound in the short time limit. We submit that short bursts of trajectory sampling will result in a small, highly accurate adaptive basis set, resampled and optimized via the matching pursuit algorithm.

[1] S. Habershon, *J. Chem. Phys.*, 136 014109 (2012)

[2] M. A. C. Saller, S. Habershon, *J. Chem. Theo. Comput.*, 11 8 (2015)

# Properties of bimetallic AuAg nanoparticles for H<sub>2</sub> production

Anna Gould<sup>ab</sup>, Andrew J. Logsdail<sup>b</sup> and C. Richard A. Catlow<sup>b</sup>

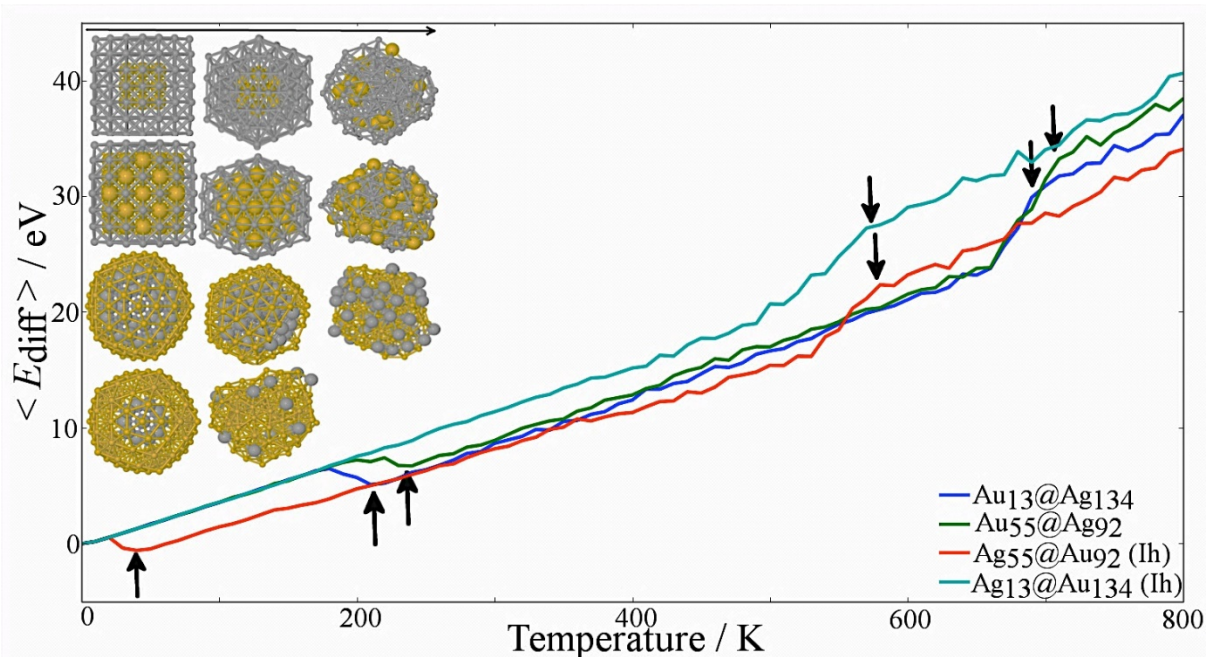
<sup>a</sup>UK Catalysis Hub, Research Complex at Harwell, Oxon, Didcot, OX11 0FA, UK

<sup>b</sup>Kathleen Lonsdale Materials Chemistry, Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK  
E-mail: a.gould@ucl.ac.uk

Bimetallic nanoclusters (“nanoalloys”) are nanometre-sized aggregates that exhibit distinctive properties from those associated with single atoms or bulk matter. A variety of sizes and chemical arrangements are possible for nanoalloys, making them suitable for widespread application in engineering, magnetism, and catalysis; Au–Ag nanoalloys have been shown to improve reaction turnover, in comparison to monometallic alternatives, when used as co-catalysts for photocatalytic H<sub>2</sub> production.

In the presented work, we have investigated the thermodynamic and kinetic stability of 147-atom Au-Ag nanoalloys, as a function of their chemical ordering and composition, using density functional theory (DFT) and interatomic potentials (IPs). We determined the most thermodynamically stable chemical arrangements for differing Au:Ag ratios, and their electronic properties were evaluated with respect to the photocatalytic H<sub>2</sub> evolution reaction [1]. We have also examined the influence of heating processes on the nanoclusters, as calcination procedures are often required in experiment to remove capping agents such as polyvinylpyrrolidone (PVP). The nanoclusters were heated from 0 – 900 K (NVT) using IP molecular dynamics and we observed low temperature diffusion of Ag core atoms to the surface for Ag@Au (core@shell) nanoparticles, resulting in a pseudo-spherical geometry and altered chemical properties (Fig. 1). This low temperature diffusion may explain why there are few successful experimental reports of Ag@Au synthesis, in comparison to Au@Ag, as we illustrate that the stability of this chemical arrangements is highly dependent on shell thickness [2].

Finally, we also study the adsorption of molecular intermediaries on the nanoparticles, determining their binding strength and possible reactivity. The CO molecule is of particular interest, as this can be used as a probe molecule experimentally; IR stretching frequency shifts often reflect changes in the nanoparticle morphology or chemical arrangements. The calculated CO frequencies are compared with in situ experimental data, obtained from combined extended X-ray absorption fine structure and diffuse reflectance infrared spectroscopy (EXAFS/DRIFTS).



**Fig. 1.** Average internal energy relative to  $E_0$  as a function of temperature for core@shell nanoclusters; a key is provided for the differing chemical arrangements.  $T_t$  and  $T_m$  are highlighted by upward and downward arrows, respectively. Inset, left to right: Nanoclusters at 0 K,  $T_t$  (where applicable; the pseudo-spherical arrangement is shown for Ag55@Au92), and  $T_m$ . Inset, top to bottom: Au13@Ag134, Au55@Ag92, Ag55@Au92, Ag13@Au134; core atoms have been enlarged for clarity.

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# Capturing static correlation effects without using multi-reference methods

Joshua Black

School of Chemistry, Cardiff University, Main Building,  
Park Place, Cardiff, CF10 3AT, UK  
E-mail: blackja@cardiff.ac.uk

Coupled cluster theory is now widely used in computational chemistry, with CCSD(T) often being the *de facto* standard for the calculation of various molecular properties. This is due to its success in capturing the dynamic electron correlation effects. However, when static correlation starts to become important within a system, such as in transition states and radical molecules, traditional coupled cluster theory can produce erroneous and unreliable results. We propose a method, Quasi-Variational coupled cluster theory, which is able to capture both dynamic and static effects. With our 'black box' method, we can then investigate these challenging chemical systems without the need to use the expensive and difficult multi-reference methods

# Lattice vibrations in molecular crystals: Polymorphism and phase transitions

Jonas Nyman and Graeme M. Day

School of Chemistry, University of Southampton, University Road, Southampton, SO17 1BJ, UK

E-mail: jn1m12@soton.ac.uk

It is possible to predict how molecules will crystallise by performing an exhaustive search of all possible molecular packing alternatives and identifying the most energetically favourable packings. The development of methods for Crystal Structure Prediction (CSP) is a rapidly growing field within computational chemistry. The most common methods rely on computing the cohesive energy between the molecules, while ignoring effects due to temperature and pressure. Lattice vibrational calculations can be used to account for thermal contributions and hence have the potential of improving the outcome of crystal structure predictions and may reveal the temperature-dependence of the stabilities of alternative crystal forms, see Fig. 1.

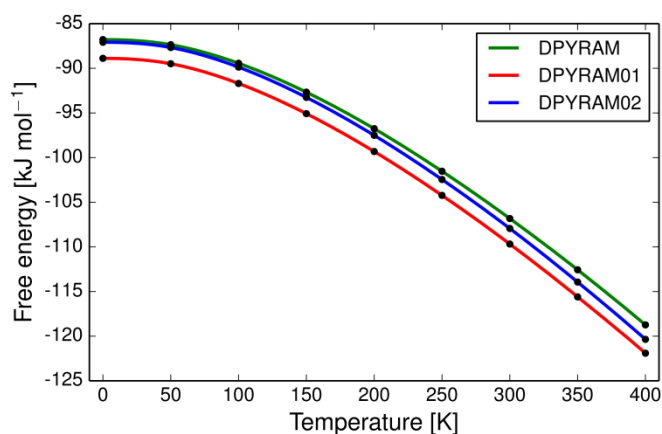


Figure 1. Calculated quasi-harmonic lattice free energy of three polymorphs of 2,2'-dipyridylamine (CSD ref. DPYRAM).

We have implemented computationally very efficient methods that facilitate large scale application of harmonic and quasi-harmonic lattice dynamics to hundreds of polymorph pairs or to entire landscapes of predicted crystal structures [1, 2]. A benchmarked and highly accurate anisotropic force field is used to perform rigid-molecule vibrational calculations to obtain Gibbs free energies of molecular crystals [3]. Special care is taken in dealing with phonon dispersion in a way rarely affordable with electronic structure methods. I present results demonstrating that polymorphs of organic molecular crystals have very small energy- and entropy differences, which has important consequences for the prediction and development of molecular materials. In addition, I discuss the importance of accounting for thermal expansion and the prospects of predicting phase transitions.

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# Single base flipping mechanisms and kinetics in a DNA duplex: an energy landscape perspective

Debayan Chakraborty, Kaushik Sen and David J. Wales

Department of Chemistry, University of Cambridge, Lensfield Road, CB2 1EW, United Kingdom

Email: dc550@cam.ac.uk

Base flipping is an elementary and localized deformation of a DNA fragment, initiated by the rupture of Watson-Crick interactions at a target base-pair, followed by extrusion of one of the bases to an extrahelical position. On extrusion, the genetic information otherwise encoded, becomes accessible to enzymes. In many important cellular processes such as DNA transcription and replication, base flipping constitutes a key step. In addition, there is growing evidence to suggest the importance of base flipping in DNA damage recognition by repair enzymes. Despite a wealth of experimental and theoretical studies, the microscopic details of base flipping mechanisms and kinetics are not clearly understood. In this work, we employ the Discrete Path Sampling method in conjunction with an all-atom potential and an implicit solvent model to investigate the flipping mechanisms and kinetics in a B-DNA duplex, in terms of its underlying energy landscape. We find that base flipping can occur either via the major or minor grooves, in agreement with previous simulations. Furthermore, the flipping time scales are estimated to be in the millisecond regime, consistent with imino-proton exchange experiments. Our results also demonstrate that even for local deformations such as base-flipping, a perfect structural order parameter may not exist, and therefore highlight the pitfalls of using low-dimensional projections of the energy landscape.



# Applying direct quantum dynamics to photo-excited processes: Proton transfer and charge migration

Kaite Eryn Spinlove and Graham Worth

School of Chemistry, College of Engineering and Physical Sciences,  
University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK  
E-mail: kes714@bham.ac.uk

In order to understand photo-excited processes it has been proven to be important to describe significant quantum effects such as tunnelling and conical intersections. A method of direct quantum dynamics for the study of such photo-excited processes has recently been implemented in the Quantics software package. The DD-vMCG (direct dynamics by the variational multi-configurational Gaussian) method promises to be fast, efficient, and with better convergence properties than previous methods based on classical trajectories [1]. As it is in the development phase, testing is required.

The underlying physical processes by which mutagenesis occurs in DNA/RNA, whether by UV radiation or spontaneous occurrence, has been the subject of extensive chemical and biological research. Prototypically the inter- and intra-molecular proton-transfers in excited states of 2-pyridone/2-hydroxypyridine and Formamide/Formamidic acid have been used as analogues to the description of mutagenesis. They present an interesting system to study with the DD-vMCG method as they may demonstrate competition between proton-transfer and non-adiabatic curve crossing [2,3].

Another photo-excited process of interest is the competition between charge-transfer and charge-migration. A new direct dynamics method, based on the Ehrenfest approach, has been used previously to study charge-migration in the Toluene cation [4]. A model Hamiltonian for the Allene ( $C_3H_4$ ) radical cation has been used as a test in previous Quantics studies on charge-transfer [5], and presents an ideal system to test the Ehrenfest approach.

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# An investigation into competition between halogen bonding and hydrogen bonding in microsolvated 1-methyl-5-halouracil

Simon W. L. Hogan and Tanja van Mourik

EaStCHEM School of Chemistry, University of St Andrews, St Andrews, KY16 9ST, UK  
E-mail: sh594@st-andrews.ac.uk

An investigation into halogen bonding and hydrogen bonding interactions between a molecule of 1-methyl-5-halouracil (XU) (X = F, Cl, Br, I, or At) and a water molecule (XU-w) or two water molecules (XU-2w), primarily in the region between the C5-X5 bond and the C4=O4 bond was performed [1]. For all calculations the M06-2X functional was used in conjunction with either the 6-31+G\* basis set (for all elements lighter than iodine) or aug-cc-pVDZ-PP (for iodine and astatine). For XU-w halogen bonds were found to form between X5 and the water oxygen atom (Ow) where X is Br, I or At; while that interaction was found for X = Cl, Br, I or At in the case of XU-2w. In the case of XU-2w the structure with a halogen bond also included water-water and water-O4 hydrogen bonds. For XU-w all of the halogen bonded minima were found to be connected to a hydrogen bonded minimum via a transition state, and the geometry and barrier height of each transition state was computed. All minima and transition states were confirmed by harmonic vibrational frequency analysis. In all cases the strength of the halogen bond, the barrier height and linearity of the C5-X5-Ow angle increases as the halogen group is descended. All of these observations are attributed to the greater polarisability (and hence stronger sigma hole effect) as the halogen becomes heavier. The lack of a halogen bonded ClU-w despite its presence in the case of ClU-2w is ascribed to the stronger competing water – O4 hydrogen bond. The presence of halogen bonds with a C5-X5-Ow angle in the range 150°-160° degrees demonstrates the flexibility of the halogen bond in departing from its ideal angle (linear) when there are secondary factors bearing on the geometry as can be found in the relatively complex chemical environment of the XU-2w systems.

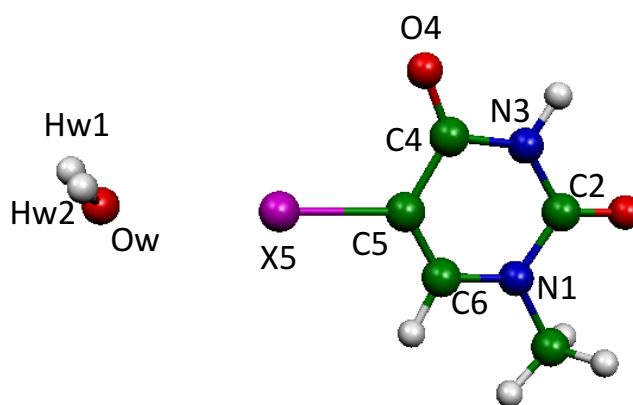


Figure 1: The 1-methyl-5-halouracil plus water system. X=F, Cl, Br, I or At

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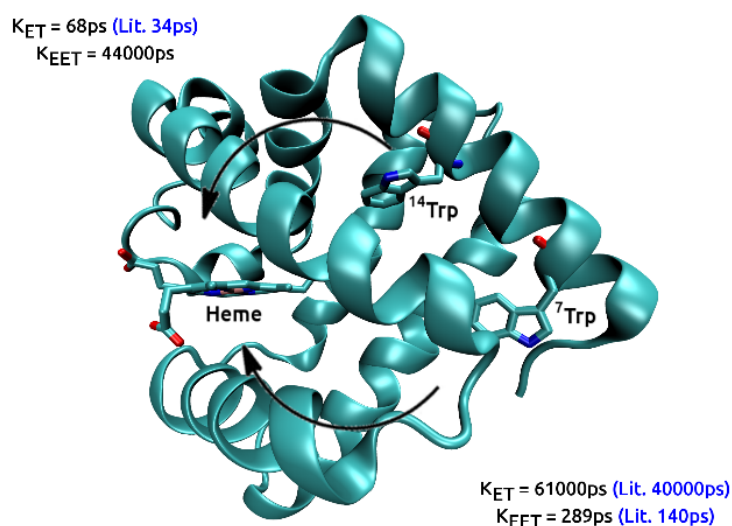
Zhuo Li (University of Nottingham)

# Modelling tryptophan to heme electron transfer and excitation energy transfer in myoglobin

Christian Suess, Nicholas A. Besley and Jonathan D. Hirst

School of Chemistry – University of Nottingham, University Park, Nottingham, NG7 2RD, UK  
E-mail: pcxcs7@nottingham.ac.uk

Electron transfer (ET) is amongst the most important chemical processes, and are ubiquitous throughout nature. This has motivated the development of experimental techniques in order to characterise pathways of electron transfer and energy transfer in proteins in more detail. Recently, Chergui and co-workers used two-dimensional ultraviolet (2D-UV) spectroscopy to study the ultrafast electron transfer in myoglobin [1]. Myoglobin acts as an oxygen carrier in muscle tissue and comprises a single polypeptide chain of 153 amino acids with an iron porphyrin active site. The 2D-UV study focused on the ET and excitation energy transfer (EET) between the two tryptophan residues (7Trp and 14Trp) and the heme. As heme proteins do not fluoresce it is difficult to distinguish between ET or EET hence how electrons decay remains ambiguous. In this poster we describe the modelling of these processes based upon quantum chemical calculations. Single excitation configuration interaction (CIS) and time-dependent density functional theory (TDDFT) are used within the framework of Marcus theory to estimate the rates of tryptophan to heme ET and EET. Key intermediate residues between the donor and acceptor are identified using the pathways tunnelling model, and the inclusion of these residues is critical in TDDFT calculations of the electron coupling matrix elements. Strategies to reduce the cost of the calculations such as using a restricted excitation subspace method [2] are explored. It is shown that  $^{14}\text{Trp}$  excitation decays by electron transfer to the heme on a much faster timescale than the excitation energy transfer process whilst  $^7\text{Trp}$  relaxes by excitation energy transfer to the heme faster than the electron transfer.



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# Tunneling dynamics of HF-H<sub>2</sub>O on an accurate analytic potential

Chuhui Xiao and David P. Tew

School of Chemistry, University of Bristol, Bristol, BS8 1TH, UK

E-mail: cx15078@bristol.ac.uk

The hydrogen bond is important due to its dominant role in natural science. The HF-H<sub>2</sub>O complex, the simplest hydrogen halide-water complex, has received attention from both experimentalists and theoreticians [1]. Experimental spectra, however, are hard to obtain because of the low volatility of water and hydrogen fluoride mixture [2] and hard to assign due to the tunneling dynamics [3]. Ab initio calculation of ro-vibrational energy levels on an accurate electronic potential can provide much needed insight. We built a potential energy surface (PES) by the least absolute shrinkage and selection operator (LASSO) regression and fit to 10000 CCSD(T)-(F12\*) energies at random geometries [4]. LASSO regression is the state-of-the-art linear regression that can minimize overfitting by constrained conditions when adding a massively amount of functions. The geometries and frequencies both at the equilibrium and transition state obtained from PES agree closely with the ab initio results. Additionally, the barrier to inversion is 126.55 cm<sup>-1</sup> for ab initio calculation and 132.39 cm<sup>-1</sup> for PES, both of which are close to the experimental data, 126 cm<sup>-1</sup> [5]. The converged tunneling energy levels are also obtained using full-dimensional vibrational approach – VSCF and VCI, using the Reaction Path Hamiltonian [6].

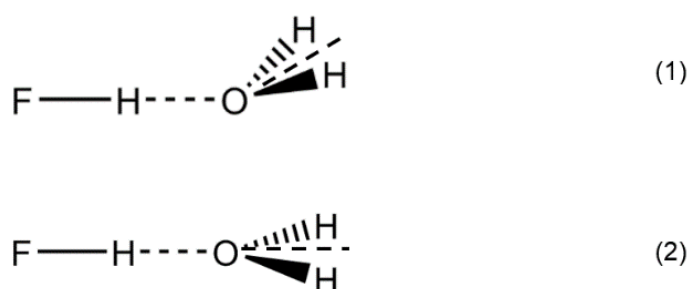


Figure 1. Structures of HF-H<sub>2</sub>O complex. (1) FH-OH<sub>2</sub> with C<sub>s</sub> symmetry, (2) FH-OH<sub>2</sub> with C<sub>2v</sub> symmetry

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# Anomalous properties in network materials

Domagoj Fijan and Mark Wilson

Department of Chemistry, Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road,  
Oxford OX1 3QZ, United Kingdom

E-mail: domagoj.fijan@chem.ox.ac.uk; mark.wilson@chem.ox.ac.uk

Thermodynamic and kinetic anomalies are often encountered in tetrahedral liquids, most famously in water (for example, the density anomaly). The origin of the anomalies is often linked to behaviour of quantities associated to phase transition phenomena which occur in the metastable supercooled regime that is largely inaccessible by conventional experiments. As a result simulations are often used to explore this problem. Several theories and scenarios have been proposed that link behaviour of anomalous properties to the existence of a liquid-liquid critical point [1][2][3]. Stillinger-Weber (SW) potentials are often employed to model tetrahedral liquids. These potentials are composed of a standard pairwise term with exponential decay and a triplet term which penalizes deviations from ideal tetrahedral angles [4]. In recent years the critical point for SW silicon has been uncovered [5] and loci of anomalous properties calculated for constant pressure for different strengths of triplet term in SW potential [6]. However, no systematic study of the SW potential that involves the calculation of critical points and spinodal lines and links them to anomalous properties as a function of the strength of triplet term has yet been reported. In this study we take a systematic approach to explore the parameter space of the triplet term in the SW potential at various temperatures, pressures and densities. This enables us to more thoroughly understand the appearance of thermodynamic and kinetic anomalies in tetrahedral liquids and their connection to the underlying tetrahedrality of the system.

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# A computational study of $\text{Ge}_5\text{O}(\text{PO}_4)_6$

Gregor McInnes, Mark Tham, John Irvine and Herbert Früchtl

Eastchem, School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, KY16 9ST, UK

E-mail: gdm22@st-andrews.ac.uk

Solid Oxide Fuel Cells (SOFCs) are being investigated for use as possible green energy storage devices. This computational study is based on practical work conducted on  $\text{Ge}_5\text{O}(\text{PO}_4)_6$  which is being considered for use as a possible electrolyte material and attempts to find the migration pathway through the structure used by oxygen. The crystal structure of  $\text{Ge}_5\text{O}(\text{PO}_4)_6$  consists of  $\text{GeO}_6$  octahedra and  $\text{GeO}_4$  tetrahedra linked by  $\text{PO}_4$  groups forming a 3 dimensional lattice.

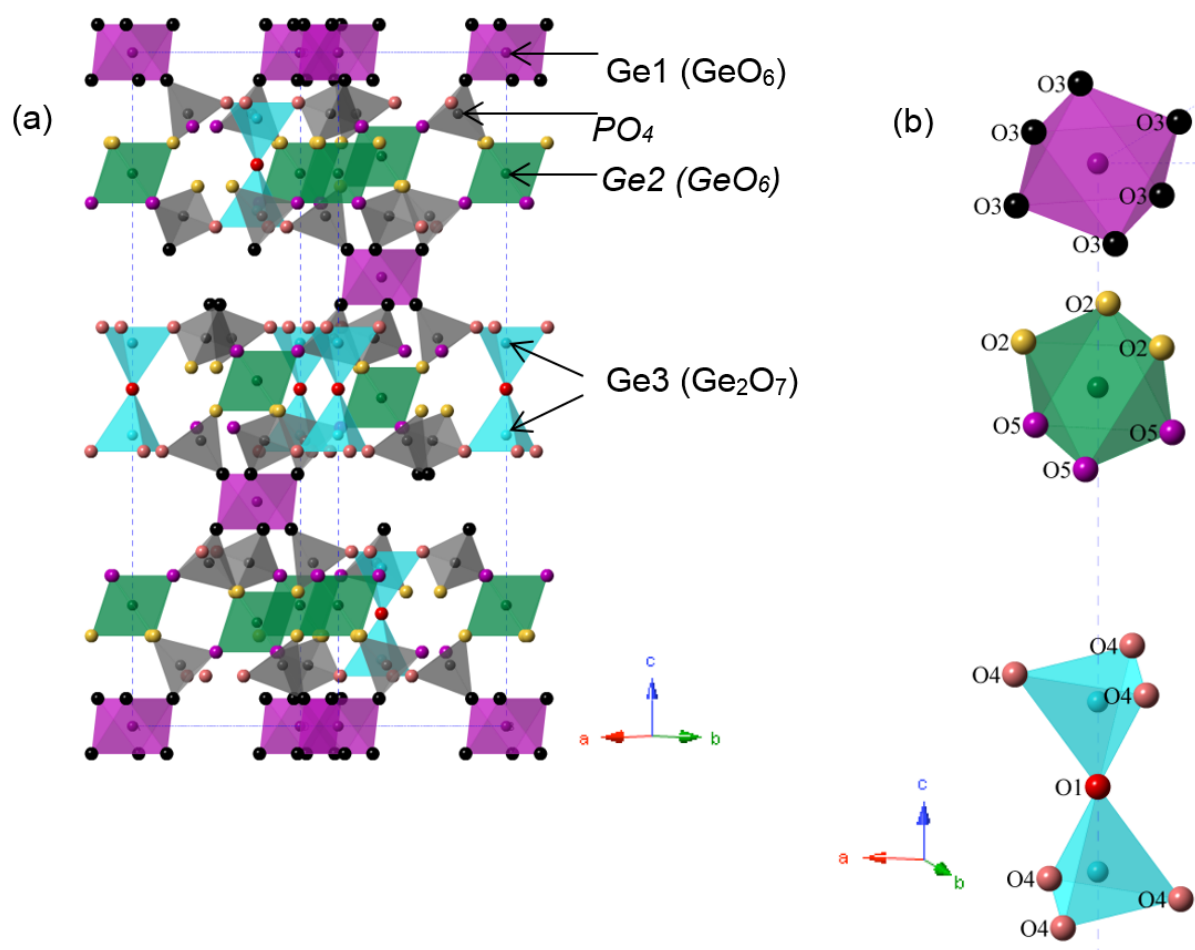


Figure 1. Projection of  $\text{Ge}_5\text{O}(\text{PO}_4)_6$  where a) is the unit cell showing the atoms crystallographically defined as Ge1 (purple), Ge2 (Green), Ge3 (light blue) and phosphorus (grey). b) shows the oxygen atoms crystallographically defined as O1 (red), O2 (yellow), O3 (black), O4 (pink) and O5 (purple)

Practical work has shown that this material has a conductivity of  $1.1 \times 10^{-4} \text{ S cm}^{-1}$  for bulk processes. This corresponds to an activation energy of 0.35 eV for the oxygen migration process. This activation



energy in conjunction with results appearing to show that O1 (shown in figure 1) is mobile, has resulted in the proposal that oxygen migration occurs along the c-axis of the lattice involving the movement of the O1 oxygen along the lattice in an interstitialcy mechanism.

This computational study looks at possible pathways through the lattice in an attempt to find out if the proposed pathway is correct, and if not, then attempt to find a pathway which fits with the observed experimental results. We have so far used Nudged Elastic Band calculations to investigate different vacancy mechanisms through the lattice. The lowest energy pathway we have found so far using a vacancy or interstitialcy mechanism occurs through the a/b-axis and with an activation barrier of 2 eV, with movement along the c-axis showing a much higher barrier, so that the latter can be ruled out. The energy difference between the lowest energy pathway and the experimental results leads us to conclude that yet another pathway must be present. More pathways are now being investigated with a focus on pathways involving an alternative lattice structure that has been shown to be present within the  $\text{Ge}_5\text{O}(\text{PO}_4)_6$  electrolyte (shown in figure 2)

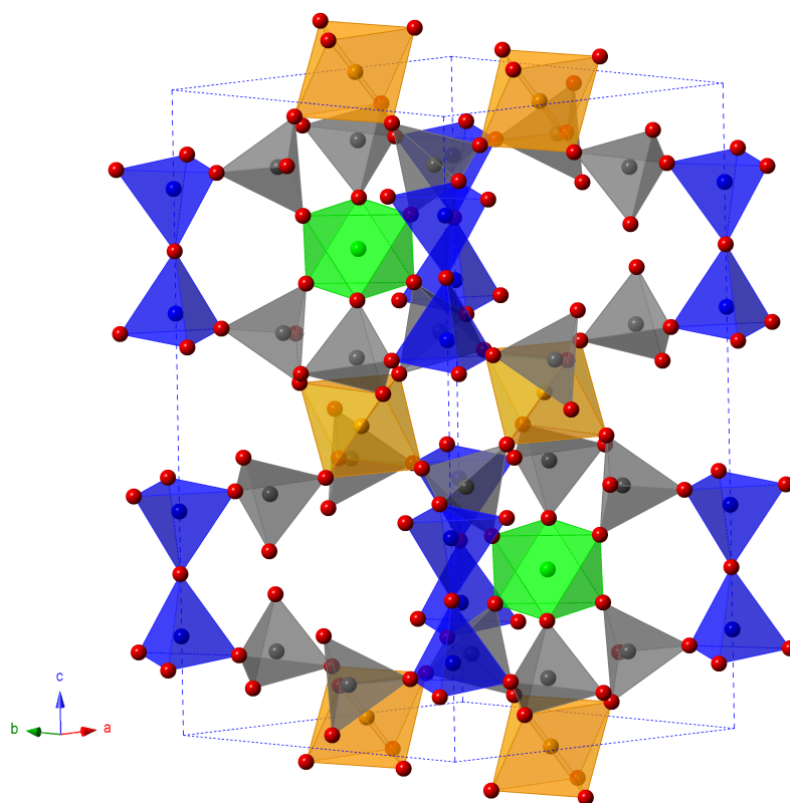


Figure 2. A possible alternative lattice structure for  $\text{Ge}_5\text{O}(\text{PO}_4)_6$

## Gas-phase and MgO(100)-supported Au, Pd, and AuPd sub-nanometre clusters: structures and energetic analysis

Heider A. Hussein,<sup>1,2</sup> Roy L. Johnston<sup>1</sup>

<sup>1</sup>School of Chemistry, University of Birmingham, Birmingham, United Kingdom

<sup>2</sup>Department of Chemistry, College of Science, University of Kufa, Najaf, Iraq

E-mail: r.l.johnston@bham.ac.uk

Sub-nanometre clusters can be defined as groups or aggregates of a few to tens of metal atoms which are below 1.0 nm in size. These clusters may contain the same atoms, giving pure clusters, or two or more different atoms presenting hetero-clusters. In this project, The Birmingham Parallel Genetic Algorithm (BPGA) has been adopted for the global optimization of free and MgO(100)-supported Pd, Au and AuPd nanocluster structures, over the size range 4-10 atoms. Structures were evaluated directly using density functional theory, which has allowed the identification of Pd, Au and AuPd global minima. The energetics, structures, and tendency towards segregation has been evaluated using different stability criteria such as binding energy, excess energies, and second difference in energy. The ability of the searches to find the putative global minimum has been assessed using a homotop search method, which shows a high degree of success.

# Current density-functional theory using meta-generalized gradient exchange-correlation functionals

James W. Furness<sup>1</sup>, Joachim Verbeke<sup>1</sup>, Andrew M. Teale<sup>1</sup>, Erik I. Tellgren<sup>2</sup>, Stella Stopkowicz<sup>2</sup>, Ulf Ekström<sup>2</sup> and Trygve Helgaker<sup>2</sup>

<sup>1</sup> School of Chemistry, University of Nottingham, Nottingham, UK

<sup>2</sup> Centre for Theoretical Computational Chemistry, University of Oslo, Oslo, Norway  
E-mail: pcxf1@nottingham.ac.uk; andrew.teale@nottingham.ac.uk

We present the self-consistent implementation of current-dependent (hybrid) meta generalized gradient approximation (mGGA) density functionals using London atomic orbitals. A previously proposed generalized kinetic energy density[1, 2] arising naturally from consideration of the spherically averaged exchange hole[3], is utilized to implement mGGAs in the framework of Kohn-Sham current density functional theory (KS-CDFT). A unique feature of the non-perturbative implementation of these functionals is the ability to seamlessly explore a wide range of magnetic fields up to 1 a.u. (~ 235000T) in strength. CDFT functionals based on the TPSS[4] and B98[5] forms are investigated and their performance is assessed by comparison with accurate CCSD(T) data[6]. In the weak field regime magnetic properties such as magnetizabilities and NMR shielding constants show modest but systematic improvements over GGA functionals. However, in strong field regime the mGGA based forms lead to a significantly improved description of the recently proposed perpendicular paramagnetic bonding mechanism[7], comparing well with CCSD(T) data[8]. In contrast to functionals based on the vorticity[9] these forms are found to be numerically stable[10] and their accuracy at high field suggests the extension of mGGAs to CDFT via the generalized kinetic energy density should provide a useful starting point for further development of CDFT approximations[11].

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# Structures and energy landscapes of micro-hydrated $\text{ClO}_3^-$ and $\text{ClO}_4^-$ clusters

John C. Hey, Emily J. Doyle and Roy L. Johnston

School of Chemistry, University of Birmingham, Birmingham, B15 2TT, UK

E-mail: jch936@bham.ac.uk

Electrolytic solutions are extremely important in both biology and industry, as the properties of solutions can be drastically altered by the presence of salts.<sup>1</sup> Salts have long been known to affect the solubility and stability of proteins in solution, in 1888, Hofmeister and Lewyth devised an ordering for several common ions, ranking them according to this effect, this ordering is known as the Hofmeister series.<sup>2-5</sup> Perchlorate ( $\text{ClO}_4^-$ ) and Chlorate ( $\text{ClO}_3^-$ ) are both highly chaotropic Hofmeister ions, in that they promote disorder within the hydrogen bonding network and reduce the solubility of proteins.<sup>6,7</sup> Sulfate ( $\text{SO}_4^{2-}$ ) on the other hand is a kosmotropic Hofmeister ion, which increases protein stability and promotes order within the hydrogen bonding framework of water.<sup>8-11</sup>

In this work we find low energy conformations for micro-hydrated perchlorate and chlorate clusters with  $N_{\text{H}_2\text{O}} \leq 12$  waters and present putative global minima. These low energy conformations were found using a basin-hopping search with empirical potentials for the halo-oxyanion and the TIP4P potential for water, using the pele software package on the BlueBEAR HPC cluster. These structures were then locally minimised at the DFT level using the B3LYP exchange-correlation functional and the 6-311++G\*\* basis set.<sup>6,12-16</sup> The energy landscapes of the chlorate and perchlorate clusters are then explored using a doubly-nudged elastic band method and visualised as disconnectivity trees before being compared to one another and to Sulfate to give a comparison of two different chaotropes with a strongly kosmotropic ion.<sup>17</sup>

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# Cyclic breakdown of ring currents using graph theoretical methods

Joseph Clarke and Patrick Fowler

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK

E-mail: jclarke3@sheffield.ac.uk

The graph theoretical model of conjugated-circuit methods<sup>1</sup> gives a qualitatively correct calculation of the ring currents of benzenoids. The model can be approximately compared with the 'gold standard' of Hückel-London<sup>2</sup> and full *ab initio* calculations.<sup>3</sup> However, conjugated-circuit models have fundamental flaws when applied to some simple systems, such as cyclopentadiene. Furthermore, conjugated-circuit models give very simple interpretations for island-like systems, such as perylene, but may be *too* simple for extensions. We describe a cycle-decomposition of the Hückel method that gives analysis of cycle contributions to current and should allow calibration of new conjugated circuit-like models of ring currents that apply much more widely than the present Kekuléan-only models.

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# Network-based analysis of model photosynthetic systems

Lewis A. Baker and Scott Habershon

Department of Chemistry and Centre for Scientific Computing, University of Warwick, Coventry, UK.

E-mail: L.Baker@warwick.ac.uk

Pigment-protein complexes (PPCs) play a central role in facilitating excitation energy transfer (EET) from light-harvesting antenna complexes to reaction centres in photosynthetic systems; understanding molecular organisation in these biological networks is key to developing better artificial light harvesting systems. We combine quantum-mechanical simulations and a network-based picture of transport to investigate how chromophore organisation and protein environment in PPCs impacts on EET efficiency and robustness [1-3]. Focusing on the Fenna-Matthews-Olson (FMO) complex and the light harvesting complex (LHCII), we consider the impact on EET efficiency of both disrupting the chromophore network and changing the influence of (local and global) environmental dephasing. Surprisingly, we find a large degree of resilience to changes in both chromophore network and protein environmental dephasing, the extent of which is greater than previously observed; for example, FMO and LHCII maintain EET when 50% of the constituent chromophores are removed. Overall, these robustness and efficiency characteristics are attributed to the highly connected nature of the chromophore network and the presence of multiple EET pathways, features which might easily be built into artificial photosynthetic systems.

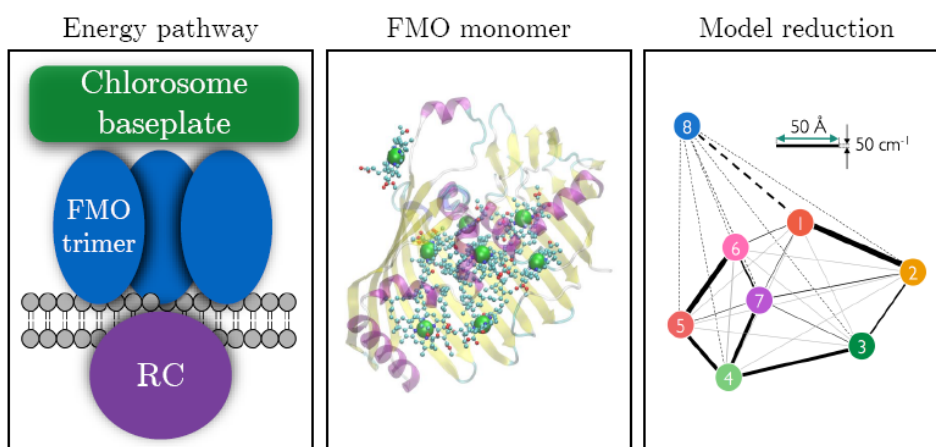


Figure 1. Model reduction of the energy transport pathway in green sulphur bacterium.

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# Effect of graphene support on large Pt nanoparticles

Lucas G. Verga, Andrea Russell, Chris-Kriton Skylaris

Department of Chemistry, University of Southampton, University Road, Southampton, SO17 1BJ, UK

E-mail: lgv1y14@soton.ac.uk

During the last decades, the interest in more powerful and flexible ways to generate energy, such as the fuel cell technology, is constantly increasing. Fuel cells are capable of producing electrical energy with higher efficiency and autonomy and may help to reduce the dependence on fossil fuels and lower the emission of toxic products into the atmosphere. Specifically, the direct methanol and ethanol fuel cells, DMFCs and DEFCs, are emerging technologies with several possible applications due to the easiness of handling these fuels, their high energy density, low pollutant emission, and low working temperatures.

One of the main challenges on DEFCs is the search for efficient catalysts for the ethanol oxidation reaction, EOR [1], and the oxygen reduction reaction, ORR [1]. Nowadays, state-of-the-art catalysts are created via deposition of monolayers or nanoparticles of the catalytic material over supports, increasing the active surface area and decreasing the loading of catalytic material and, consequently, the overall cost of fuel cells [1]–[3]. Therefore, the understanding about the interaction between catalyst and support can be essential to designing efficient DEFCs catalysts.

Here, we employ large-scale DFT simulations for metallic systems [4] as implemented in the ONETEP linear-scaling DFT program [5] to study platinum clusters interacting with a single layer graphene. We compare the stability of platinum monolayers and nanoparticles interacting with the support, and analyse its optimised geometries and electronic properties. Our results show that nanoparticles are more stable than monolayers, and that the difference between their stabilities increases with the system size. Moreover, our optimized platinum structures exhibit inter-atomic expansion in facets close to the graphene sheet, and the electronic analysis shows electron transfer from the platinum clusters to the support. Both effects can change the catalytic behaviour of the Pt nanoparticles, showing the importance of deeper understanding of the support effects.

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# Photo-excited molecular dynamics of molecules associated with the green fluorescent protein

Marcus P. Taylor and Graham A. Worth

School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT

E-mail: mxt404@bham.ac.uk

There has been immense interest in the green fluorescent protein (GFP) due to its plethora of potential applications and, as yet, lack of full detail surrounding its photophysics.[1,2] In particular its broad photoelectron spectrum and relative location of the electronic states for the anion and radical form have attracted significant research both experimentally and theoretically.[3-6] One approach to tackle this problem is a bottom-up approach, starting with analysis of the components comprising the GFP chromophore; hydroxybenzylidene-2,3-dimethylimidazolinone (HBDI). Photodetachment spectra have been obtained for the anion to radical transition of imidazole, bis-imidazoloxo, phenoxide and bisphenoxide. The spectra were calculated from wavepacket propagation using the QUANTICS program[7,8], a pre-requisite of which is the generation of a two-state model Hamiltonian for each molecule. Construction of these Hamiltonians required the fitting of parameters to points calculated along the potential energy surface using *ab initio* methods.

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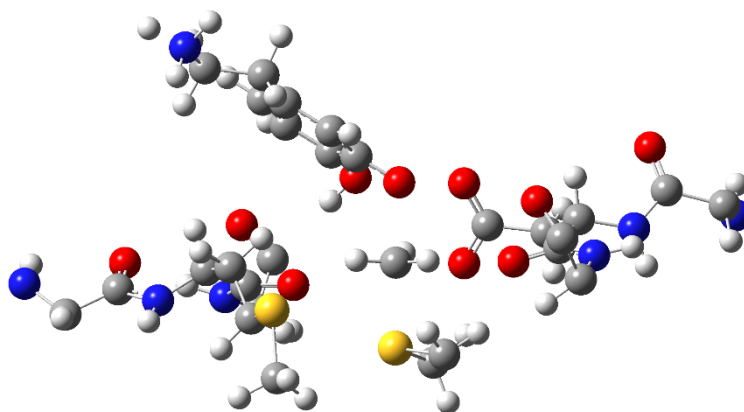


# Isotope effect calculations in the supramolecular age

Philippe B. Wilson and Prof. Ian H. Williams

Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK

E-mail: P.B.Wilson@bath.ac.uk



Kinetic isotope effects are widely used as experimental probes of chemical and biochemical reaction mechanisms, but how they should be interpreted for enzymic reactions remains problematic. Computational simulation using QM/MM methods is capable of providing valuable insight, but robust procedures have not yet been established, and opinion still differs between experimental<sup>(1,2)</sup> and computational<sup>(3,4)</sup> approaches to enzyme-catalyzed methyl transfer.

Our recent studies have indicated that the electrostatic environment around a site of isotopic substitution may have a significant influence that has not previously been taken into account in the interpretation of experimental kinetic isotope effects. We have shown that isotope effects for transfer of a methyl cation from vacuum to a dielectric continuum vary dramatically over the range of dielectric constants normally associated with enzyme active sites,<sup>(5)</sup> and have argued that the corrections for vibrational anharmonicity on isotope effects are best treated by means of scaling of calculated harmonic frequencies.<sup>(6)</sup> We have also shown that hydrogen-bonding interactions between methyl CH bonds and oxygen atoms within a cage environment may have a significant influence upon kinetic isotope effects for methyl transfer between a nucleophile and nucleofuge. This may imply an alternative explanation, at least in part, for observed trends in kinetic isotope effects for enzyme-catalysed methyl transfer.<sup>(1,2)</sup> We suggest that our methodology is applied for the calculation and interpretation of isotope effects, and detail possible alternatives and approximations for future work in the field.

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# A force field for the accurate calculation of the structure and vibrational spectroscopy of carbon materials

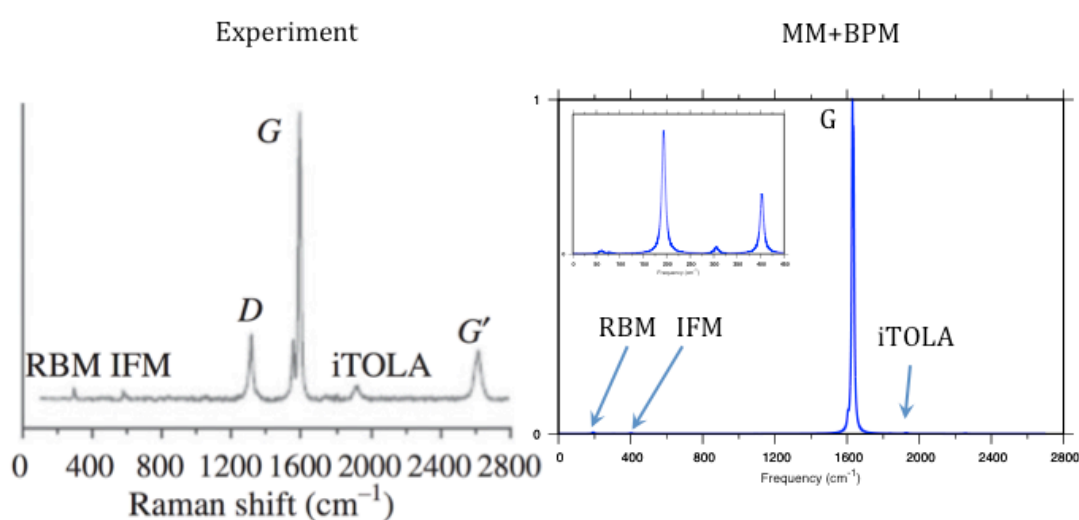
Pritesh Tailor, Richard J. Wheatley and Nicholas A. Besley

School of Chemistry, University of Nottingham, Nottingham, NG7 2RD

Email: pcxpt@nottingham.ac.uk

The accurate prediction of the vibrational spectroscopy of carbon nanomaterials is a problem of fundamental interest and a challenge for computational methods. The capability to compute the vibrational frequencies and associated spectra of these systems accurately can potentially aid the interpretation and classification of carbon nanotubes (CNT) and graphene in experimental measurements and allow the relationship between the molecular structure and the observed features to be explored.

Calculation of the vibrational spectroscopy of these materials using quantum chemistry within a non-periodic framework is computationally too expensive. An alternative approach is to simplify the description of the force-field through the use of an empirical potential. For such methods to be of value then the resulting decrease in computational cost cannot lead to an unacceptable reduction in accuracy. Here we present a fully empirical method for modeling the Raman spectroscopy of CNTs and graphene. The calculations use a purpose built force-field based on the Murrell-Mottram potential [1] in combination with the Empirical Bond Polarizability model. Analytical first and second derivatives of the Murrell-Mottram have been implemented and the potential reparameterized via a Monte-Carlo "hessian matching" approach creating a force-field which accurately models the vibrational behavior and spectroscopy of CNTs and graphene. It is shown that the potential accurately models the Raman spectroscopy of these systems at a fraction of the computational cost allowing for the accurate atomistic vibrational analysis of systems with greater than 10,000 atoms. Subsequently, the Raman spectroscopy of CNTs with defects is explored.



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# A new hybrid functional for Density Functional Theory inspired by the Unsold approximation

Tim Wiles and Fred Manby

Bristol University School of Chemistry, England

E-mail: timothy.wiles@bristol.ac.uk

Density Functional Theory (DFT) is a successful ab-initio method for calculating the electronic structure of molecules. Its success is due to its low scaling in computational complexity with system size. The energy of the molecule is expressed as a functional of  $\rho_{KS}(\mathbf{r})$ , the density of the "Kohn-Sham auxiliary system" at every point in space.

"Hybrid" functionals are a widely-used correction that can be added to the DFT energy to improve its accuracy. These functionals depend on the single-particle reduced-density matrix  $\rho_{KS}(\mathbf{r}, \mathbf{r}')$ , in addition to the density  $\rho_{KS}(\mathbf{r})$ . We present a new hybrid functional inspired by the "Unsold approximation"[1]. We aim to test this new method against Coupled-Cluster Theory calculations of the electronic energy of molecules.

$$E_{UW12} = \langle \Phi_{KS} | \hat{V} \hat{W} | \Phi_{KS} \rangle - \langle \Phi_{KS} | \hat{V} | \Phi_{KS} \rangle \langle \Phi_{KS} | \hat{W} | \Phi_{KS} \rangle \quad (1)$$

$$\hat{V} = \frac{1}{2} \sum_{\sigma_1 \sigma_2} \int d\mathbf{r}_1 d\mathbf{r}_2 r_{12}^{-1} a_{\sigma_1}^\dagger(\mathbf{r}_1) a_{\sigma_2}^\dagger(\mathbf{r}_2) a_{\sigma_2}(\mathbf{r}_2) a_{\sigma_1}(\mathbf{r}_1) \quad (2)$$

$$\hat{W} = \frac{1}{2} \sum_{\sigma_1 \sigma_2} \int d\mathbf{r}_1 d\mathbf{r}_2 w(r_{12}) a_{\sigma_1}^\dagger(\mathbf{r}_1) a_{\sigma_2}^\dagger(\mathbf{r}_2) a_{\sigma_2}(\mathbf{r}_2) a_{\sigma_1}(\mathbf{r}_1). \quad (3)$$

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# Vibrational structures in the near-UV electronic circular dichroism spectra of proteins

Zhuo Li and Jonathan D. Hirst

School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom

E-mail: pcxz11@nottingham.ac.uk

A fully quantitative theory of the relationship between protein conformation and optical spectroscopy would facilitate deeper interpretation and insights into biophysical and simulation studies of protein dynamics and folding. We employ the state-averaged CASSCF method to calculate vibrational structures of toluene, p-cresol and 3-methylindole, which represent the chromophores in the aromatic amino acids phenylalanine, tyrosine and tryptophan, respectively. The results of these calculations are used to incorporate the Franck-Condon effects into matrix method calculations of the electronic circular dichroism (CD) spectra of proteins in the near-ultraviolet. A set of 40 proteins, whose structures are reported in the protein data bank, are calculated to assess the influence of vibrational structures in the accuracy of calculations. Mutants of various proteins are calculated to illustrate the relationship between spectra changes and the structural differences induced by the mutation. Computed spectra of some selected proteins from the dataset are compared with the calculations considering the conformational diversity based on the availability of the NMR-determined protein structures. Our calculations considering vibrational structures of the aromatic chromophores have provided some further insight into the physical origins of the nature of protein CD spectra in the near-UV.