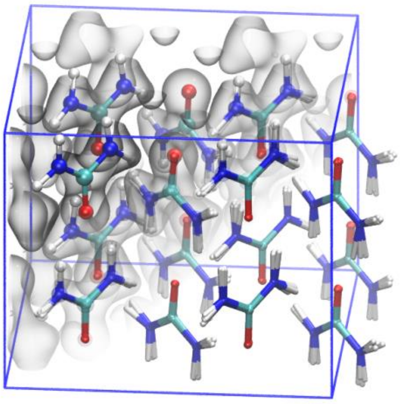
Workshop Report

Addressing Challenges for First-Principles Based Modeling of Molecular Materials



August 25th 2014 to August 29th 2014
CECAM-HQ-EPFL, Lausanne, Switzerland

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Part I – Report on workshop

Description of the workshop:

Molecular materials are of great fundamental and applied importance in science and industry and provide fertile ground for the continuing development of theoretical methods. This workshop aimed at monitoring advances in using first-principles methods to model these materials, particularly from the point of view of the description of weak, non-bonded interactions - both using density functional theory and high-end wavefunction methods. At the same time, it also offered a broader overview of the open challenges in the field, including sampling, crystal-structure prediction, the role of temperature and nuclear quantum effects in determining the relative stability of different polymorphs, multi-scale modelling to predict kinetic and thermodynamic effects on crystal structure and macroscopic shape. The rationale for the relatively broad scope was fostering the creation of a more cohesive community, encouraging an interdisciplinary approach to determine and address the challenges inherent in the modelling of molecular materials.

Summary of discussions:

As can be seen from the programme and abstracts there were a wide variety of excellent talks on modelling molecular materials. The primary aim of the workshop was to encourage dialogue between participants and to maximise this, invited talks were 25 minutes plus 15 minutes for discussion. In addition, the afternoon of the fourth day was devoted to a discussion session and a poster session.

We asked the session chairs to prepare a couple of questions that the speakers should have tried to address. The objective of this was to encourage discussion, and to address the general questions of what are the main challenges, and the problems that hold back the community.

We can summarize the results of the discussion in this list of open challenges:

- Accuracy of the potential energy surface: need better description of intermolecular terms, and a set of more reliable benchmarks
- Beyond minimum energy structures: must include thermal (free-energy) effects, quantum effects such a zero-point motion, possibly beyond a purely harmonic approximation
- Molecular flexibility: a large number of internal degrees of freedom makes it prohibitively expensive to perform systematic crystal-structure prediction
- Including the role of disorder and defects
- Modelling of crystal growth: need multi-scale approach and enhanced sampling techniques to beat the time scale barrier.
- “Beyond classical nucleation” effects. Role of additives and “crystallisation catalysts”

In general, the participants agreed that most of these problems cannot be tackled by brute force, and methodological developments are needed as well as the access to more powerful computational facilities. All these challenges require different kinds of simulations, which in turn demand different levels of computer power. For example:

- Structure search techniques can be applied on relatively loosely-coupled architectures. Large departmental clusters are probably best suited.
- Ab initio simulations, particularly beyond density functional theory, require large computational facilities, at least at the national levels. Treating finite-temperature or quantum effects with (path integral) molecular dynamics and an ab-initio description of the forces requires leading-edge facilities.
- Simulations of nucleation and growth, even when treated at the classical level, require at least national-level HPC facilities.

The numerous challenges and different resources needed to tackle them highlight the scientific and logistical hurdles in modelling these materials.

Given the high interest of many participants and the fast paced developments of methods in the field of molecular materials, we envision having another workshop on a similar subject in 3 years.

Potential for funding and collaborations and relevance to industry:

The broad nature of molecular materials and the workshop's focus on fundamental methods in modelling them makes much of the workshop relevant for funding and collaboration in a number of areas. Advances in first-principles methods (particularly in the form of new techniques and programs) yield very fundamental advances of benefit to various areas. Some particular collaborative or platform aspects are:

- For crystal-structure prediction there are already a series of blind tests where a large number of groups applied their methods to the same molecules. These have been particularly useful and have drawn the interest of the wider scientific community, both academic and industrial. These are arranged in an *ad hoc* fashion though. Formal funding to support the organisation and research carried out in these tests would greatly enhance their use to the wider community.
- In other areas common ground and benchmark systems are needed to compare methodologies and spur their development. This was clear from discussion amongst the participants. Resources are needed to define such common systems and encourage their adoption and study by the wider community.
- Many of the advances and methods discussed in the workshop are heavily reliant on high-performance computational resources. Europe-wide HPC programs such as PRACE are essential for enabling this research.

Aside from research funding the fundamental importance of molecular materials makes much of the progress in this area important to industry. A number of participants already have active collaborations with industry. Fostering inter-disciplinarily research between groups would maximise the benefit of these contacts with industry.

Structure prediction, particularly crystal-structure prediction (CSP), is of great interest to the pharmaceutical industry, which is strong in Europe. Assessing and understanding the risks of polymorphism is a critical part of selecting a solid form for orally administering drugs. A number of pharmaceutical companies are attempting to or considering incorporating CSP into their workflow for developing solid forms. Progress in multiscale modelling and quantum dynamics is also of significant and wide interest, not just to the pharmaceutical industry but also the food, <electronics and energy industries. In general, first-principles understanding of the growth, stability and function of molecular materials is critical to achieving efficient, tailored design of novel materials - a key desire of industry.

Part II – Programme

Day 1 - August, 25 2014

Structure prediction of molecular materials - chair: Greg Beran

- 12:30 to 13:45 - Registration

- 13:45 to 14:00 - Welcome

- 14:00 to 14:40 - **Sally Price**
  Predicting polymorphs of pharmaceuticals – the role of first principles calculations

- 14:40 to 15:20 - **Graeme Day**
  Conformational energy landscapes and molecular geometries in crystal structures

- 15:20 to 15:45 - **Kim Jelfs**
  Molecular prediction of porous organic molecules

- 15:45 to 16:15 - Coffee Break

- 16:15 to 16:55 - **Chick Wilson**
  Setting the experimental challenge: self-assembling extended molecular materials in a solution-mediated environment

- 16:55 to 17:35 - **Berend Smit**
  Computational carbon capture

Day 2 - August, 26 2014

Advanced methods for electronic properties of molecular materials - chair: Robert DiStasio Jr.

- 9:00 to 9:40 - **Stefano Sanvito**
  Charge transport in organic single crystals

- 9:40 to 10:20 - **Leeor Kronik**
  Response properties of molecular crystals from dispersion-corrected density functional theory

- 10:20 to 10:50 - Coffee Break

- 10:50 to 11:30 - **Noa Marom**
  Accurate description of the electronic structure of organic semiconductors by gw

methods

- 11:30 to 12:10 - **Feliciano Giustino**
  Quantum nuclear effects in the photophysics of diamondoids

- 12:10 to 13:30 - Lunch

Non-covalent interactions in molecular materials - chair: David Sherrill

- 13:30 to 14:10 - **Erin Johnson**
  Density-functional theory predicts the relative solubilities of racemic and enantiopure crystals

- 14:10 to 14:50 - **Stefan Grimme**
  Automatic generation of a general inter- and intramolecular force-field from dispersion corrected DFT

- 14:50 to 15:30 - **Alberto Ambrosetti**
  From dispersion interactions to farsighted electron correlation -- a unified approach based on atomic response functions

- 15:30 to 16:00 - Coffee Break

- 16:00 to 16:40 - **Andrew Rohl**
  Accuracy of dispersion corrected van der Waals functionals in calculating structures of molecular crystals

- 16:40 to 17:20 - **Clemence Corminboeuf**
  A walk through electronic structure challenges in the land of thiophene

- 19:30 to 22:30 - Social Dinner

Day 3 - August, 27 2014

Correlated approaches to molecular condensed phases - chair: Stefan Grimme

- 9:00 to 9:40 - **Gregory Beran**
  Low-cost electronic structure approaches for intermolecular interactions: from dimers to crystals

- 9:40 to 10:20 - **Fred Manby**
  Better many-body expansions through better embedding

- 10:20 to 10:50 - Coffee Break

- 10:50 to 11:30 - **Juerg Hutter**
  Mp2 and rpa calculations of liquid water and ice

- 11:30 to 12:10 - **David Sherrill**
  Analysis of intermolecular interactions using symmetry-adapted perturbation theory

- 12:10 to 13:30 - Lunch

Multiscale simulation of molecular materials - chair: Sally Price

- 13:30 to 14:10 - **Matteo Salvalaglio**
  Predicting steady state crystal morphologies from molecular simulations

- 14:10 to 14:50 - **Joerg Behler**
  High-dimensional neural network potentials for large-scale simulations of materials

- 14:50 to 15:30 - **Gareth Tribello**
  Dimensionality reduction and molecular order

- 15:30 to 16:00 - Coffee Break

- 16:00 to 16:40 - **Harald Oberhofer**
  Stability and function of organic molecular crystals

- 16:40 to 17:05 - **Alexander Bagaturyants**
  Multiscale atomistic modeling of amorphous organic functional materials for optical chemical sensing and OLED applications

- 17:05 to 17:45 - **Angelo Gavezzotti**
  From liquid to solid by biased Monte Carlo simulation

Day 4 - August, 28 2014

Quantum dynamics of molecular materials - chair: Leeor Kronik

- 9:00 to 9:40 - **Mariana Rossi**
  Structure and dynamics of biomolecules and water: challenges for first-principles

methods and nuclear quantum effects

- 9:40 to 10:20 - **Tom Markland**
  Nuclear quantum effects in hydrogen bonded networks

- 10:20 to 10:50 - Coffee Break

- 10:50 to 11:30 - **Angelos Michaelides**
  Structure and dynamics of water at surfaces

- 11:30 to 12:10 - **Mark E. Tuckerman**
  The path to first principles modeling with nuclear quantum effects: techniques, applications, and future directions

- 12:10 to 12:35 - **Igor Poltavskyi**
  Towards efficient description of nuclear quantum effects

- 12:35 to 14:30 - Lunch

Open discussion

- 14:30 to 16:00 - Round Table Discussion: Future Directions

- 16:00 to 18:30 - Poster Session

Day 5 - August, 29 2014

Combining theory and experiment for molecular materials - chair: Angelo Gavezzotti

- 9:00 to 9:40 - **Berend Smit**
  Computational carbon capture

- 9:00 to 9:40 - **Carole Morrison**
  Breathe freely: simulating flexible behaviour of metal organic frameworks to solve troublesome x-ray powder diffraction data; response to temperature and co2 loading

- 09:40 to 10:05 - **Martijn A. Zwijnenburg**
  Modelling the optical properties of the organic solid state

- 10:05 to 10:45 - **Robert Distasio**
  The microscopic structure, equilibrium density, and local environment of liquid water

- 10:45 to 10:55 - Closing Word

Part III – Abstracts

Invited and contributed talks

Predicting polymorphs of pharmaceuticals – the role of first principles calculations

Sally Price[1]
University College London

There was a breakthrough in the 4th international blind test of organic crystal structure prediction [1] when all the target crystal structures were predicted using periodic ab initio calculations with a specifically derived empirical dispersion correction. Since then, there has been considerable interest in using dispersion corrected DFT method for predicting the relative energies of known organic polymorphs and the energetically competitive structures generated by crystal structure prediction methods. Progress towards being able to rank the thermodynamic stability of polymorphs is being made [2,3] but this still represents a challenge to theory. The more fundamental question as to how we can interpret the calculated relative energies to predict potential polymorphs for pharmaceuticals, and use the calculations as an aid to pharmaceutical development, will be discussed.[4]

1. G.M.Day, et al. Acta Crystallogr., Sect.B 65 107 (2009)
2. T. Gelbrich, D.E. Braun, A. Ellern, U.J. Griesser, Cryst.Growth Des. 13, 1206 (2013).
3. D. E. Braun, J.A. McMahon, L.H. Koztecki, S.L. Price, S.M. Reutzel-Edens, Cryst.Growth Des. 14, 2056 (2014)
4.S.L. Price, Acta Crystallogr., Sect.B. 69, 313 (2013)

Conformational energy landscapes and molecular geometries in crystal structures

Graeme Day[1], Hugh P. G. Thompson
University of Southampton, Southampton, United Kingdom
University of Cambridge, Cambridge, United Kingdom

One of the challenges in the development of generally applicable structure prediction methods for molecular crystals is the application of global lattice energy searching methods to large, flexible molecules. Two aspects of molecular flexibility that must be considered in crystal structure prediction are: i) the diversity of possible conformers that could be adopted in a crystal and ii) the extent of distortion away from gas phase conformer geometries due to intermolecular forces. We present the results of a density functional theory based study of the relationship between isolated molecules' conformational energy landscapes and the molecular geometries observed in their crystal structures [1]. The results quantify the limits of molecular strain that should be considered in structure prediction and suggest rules for selecting the most likely observable conformers.

[1] H. P. G. Thompson and G. M. Day, Chem. Sci. in press (2014)

Molecular prediction of porous organic molecules

Kim Jelfs[1]
Department of Chemistry, Imperial College London, London, UK

The modular assembly of discrete, intrinsically porous organic molecules is an alternative to forming porous materials through extended networks that are chemically bonded in 3-dimensions.[1] These modular materials can have advantages, such as being easily processable,[2] co-crystallisation allowing property tuning[3] and their greater mobility facilitating stimuli-response behaviour, such as “on”/“off” porosity switching.[4] From a computational perspective, it has been shown that crystal structure prediction techniques can rationalise the observed polymorphs[3] and we have used molecular dynamics simulations to explain observed sorbate selectivity.[4,5] More recently, we have been developing an approach towards in silico design of new porous molecular materials with desired structures and properties. This automates the assembly and screening of hypothetical molecules from a library of precursors. The first goal is to predict the conformation of the molecule that will be formed. It is crucial to test whether the molecule will be “shape persistent”, keeping an internal void in the absence of solvent, as we have previously spent months synthesising large molecules that collapse upon desolvation. The second goal is to correctly predict which molecule will form from a pair of precursors – e.g. will a [2+3], [4+6], [6+9] or [8+12] reaction occur? We have demonstrated the successful prediction of an odd-even effect for a series of alkane diamines.[6] Further, we can predict how post-synthetic modification can engineer shape-persistence and acid and base-resistance[7], as well as using computational predictions to engineer novel shaped molecules and to perform rapid computational screening to predict properties for hypothetical molecules.

[1] T. Tozawa, J. T. A. Jones, S. I. Swamy, S. Jiang, A. I. Cooper et al. Nature Materials, 8 973 (2009).
[2] T. Hasell, S. Y. Chong, K. E. Jelfs, D. J. Adams and A. I. Cooper J. Am. Chem. Soc. 134 588 (2012).
[3] J. T. A. Jones, T. Hasell, X. Wu, J. Bacsa, K. E. Jelfs, A. I. Cooper et al. Nature 367 474 (2011).
[4] J. T. A. Jones, D. Holden, T. Mitra, T. Hasell, K. E. Jelfs, A. I. Cooper et al. Angew. Chem. Int. Ed. 50 (3) 749 (2010).
[5] T. Mitra, K. E. Jelfs, M. Schmidtmannm A. Ahmed, A. I. Cooper et al. Nature Chem. 5 276 (2013).
[6] K. E. Jelfs, E. G. B. Eden, J. L. Culshaw, S. Shakespeare, A. I. Cooper et al. J. Am. Chem. Soc. 135 9307 (2013).
[7] M. Liu, M. A. Little, K. E. Jelfs, J. T. A. Jones, M. Schmidtmann, S. Y. Chong, T. Hasell, A. I. Cooper, J. Am. Chem. Soc. 136 (21) 7583 (2014).

Setting the experimental challenge: self-assembling extended molecular materials in a solution-mediated environment

Chick Wilson[1]
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Much of our recent experimental work has focused on the use of the principles of crystal engineering in attempting to direct the assembly of favourable molecular solid-state architectures with optimised properties. Target properties for these molecular materials include optical properties including tuneable colour [1] and refractive index and solubility [2], and the materials being assembled are frequently produced in a multi-component environment. This can be manifest either in deliberate attempts to make molecular complexes or multi-component molecules crystals (co-crystals) with optimised or novel properties, or by introducing a second component into the assembly process with a view to templating favourable solid forms of a single component product [3]. In either case, the use of a co-former molecule (in either stoichiometric or trace amounts) is a vital component in guiding the process towards the assembly of the desired solid form. These methods are aimed at two distinct areas: discovery of novel solid-state molecular systems as potential functional materials and in optimising favourable solid form production, for example in controlling polymorphism and particle attributes in manufacturing molecular materials for practical applications. One key target area is that of crystallisation and its applications in production processes. The common feature in these efforts is the complexity of the environment in which the materials are assembled, often containing two molecular components and at least one solvent component, as molecular self-assembly is frequently undertaken in the solution-mediated environment, using the techniques of crystallisation. One of the immediate goals of this work is to apply these principles in the industrial applied environment, for example by implementing crystallisation in continuous flow environments within industrial processes to manufacture fine chemicals and pharmaceuticals. Much of our current experimental work in this domain is framed within the context of the EPSRC Centre for Innovative Manufacturing in Continuous Manufacturing and Crystallisation (CMAC, [4]) in the UK, in which underpinning research is tackling all elements of the continuous manufacturing process for molecular materials from initial solid-form assembly to formulation of optimised particles for production processes. The experimental challenges in investigating this area are huge and are tackled in both designed and empirical ways, each of which offers a degree of success. The challenges for modelling are arguably more severe, given the complexity of the multi-component environment, the dynamic nature of this environment and the extended nature of the periodic solid materials being formed. This talk will explore some of the target systems and offer some thoughts as to the requirements of experimentalists and modellers in trying to tackle this area.

[1] C L Jones, C C Wilson & L H Thomas, CrystEngComm, 2014, 16, 5849-5858
[2] L H Thomas, A R Klapwijk, C Wales & C C Wilson, CrystEngComm, 2014, 16, 5924-5932
[3] L H Thomas, C Wales, L Zhao & C C Wilson (2011). Cryst Growth Design, 11, 1450-1452
[4] www.cmac.ac.uk

Structural transformation in polymeric liquid sulfur by ab initio md simulations

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Bratislava, Slovakia

Recently, a structural transformation in liquid sulfur has beenexperimentally observed at pressures below 10 GPa and temperaturesaround 1000 K [1]. The transformation was identified through a smallchange in the character of radial distribution function andcoordination number and was interpreted as abrupt breaking of longchains into shorter ones in the high-temperature liquid. We studiedthis chain-breakage phenomenon by means of ab initio moleculardynamics using a sample with 512 atoms in the temperature intervalfrom 800 to 2000 K. We calculate and discuss several structural andphysical properties related to this liquid-liquid transition. Weconfirm that it is a transformation between long and short polymericchains with some amount of branched chains. The properties thatexhibit substantial changes include quantities such as chain length,diffusion coefficient, electronic properties (semiconductor-metaltransition), etc.

[1] Lei Liu, Yoshio Kono, Curtis Kenney-Benson, Wenge Yang, Yan Bi, and Guoyin Shen, Phys. Rev. B 89, 174201 (2014)

Charge transport in organic single crystals

Stefano Sanvito[1], Carlo Motta
School of Physics, AMBER and CRANN, Trinity College, Dublin 2, Ireland
School of Physics, AMBER and CRANN, Trinity College, Dublin 2, Ireland

Charge transport in organic single crystals is a complex problem, where the computation of accurate structural and vibrational properties needs to be coupled to ways of determining the charge mobility. Here we will present a rigorous computational scheme for evaluating the charge carrier mobility of pure organic crystals at finite temperature, which is material-specific, it accounts for van der Waals interactions and it includes vibrational contributions from the entire phonon spectrum of the crystal. Such an approach is based on the ab initio framework provided by density functional theory and the construction of a tight-binding effective model via Wannier transformation. The final Hamiltonian includes coupling of the electrons to the crystals phonons, which are also calculated from density functional theory. We apply this methodology to the case of durene, a small pi-conjugated molecule, which forms a high-mobility herringbone-stacked crystal. We show that accounting correctly for dispersive forces is fundamental for obtaining a high-quality phonon spectrum, in agreement with experiments. Then the mobility as a function of temperature is calculated along different crystallographic directions and the phonons most responsible for the scattering are identified.

Response properties of molecular crystals from dispersion-corrected density functional theory

Leeor Kronik[1]
Weizmann Institute of Science, Rehovoth, Israel

In this talk, I will show that there are many cases where simple, minimally-empirical pair-wise correction schemes allow for useful determination of molecular crystal response properties, such as elastic constants and vibrational properties. I will show how this allows us to achieve unique insights into selected properties of (mostly) biogenic and bio-inspired molecular crystals. I will further show how the approach can be combined with modern density functionals to achieve a quantitatively accurate electronic structure, allowing for predictive power in the study of organic electronic and photovoltaic materials.

Accurate description of the electronic structure of organic semiconductors by gw methods

Noa Marom[1]
Tulane University, New Orleans, LA, USA

Organic photovoltaics are attractive for large area, low cost applications and for flexible modules. However, their relatively low efficiency leaves much to be desired. Insight from computation may help improve device performance by designing new organic semiconductors and ordered nanostructured interfaces. It is important to obtain an accurate description of the electronic structure of organic semiconductors, including the fundamental gaps and absolute positions of the donor HOMO and the LUMO at the interface. This requires going beyond ground state density functional theory (DFT). Many-body perturbation theory is often used for this purpose within the GW approximation, where G is the one particle Green function and W is the dynamically screened Coulomb interaction. Typically, GW calculations are performed as a non-self-consistent perturbative correction to DFT eigenvalues, known as G0W0. The predictive power of G0W0 is limited by a strong dependence of the results on the DFT starting point. Self-interaction errors (SIE), spurious charge transfer, and incorrect ordering and hybridization of molecular orbitals may propagate from the DFT level to G0W0. These issues may be addressed by judiciously choosing a hybrid DFT starting point or by going beyond G0W0 to a higher level of self-consistency. Here, this is demonstrated for prototypical organic semiconductors.

[1] T. Körzdörfer and N. Marom, PRB 86, 041110(R) (2012)
[2] N. Marom, F. Caruso, X. Ren, O. Hofmann, T. Körzdörfer, J. R. Chelikowsky, A. Rubio, M. Scheffler, and P. Rinke, PRB 86 245127 (2012)
[3] N. Marom, X. Ren, J. E. Moussa, J. R. Chelikowsky, and L. Kronik, Phys. Rev. B 84, 195143 (2011)
[4] E. Salomon, P. Amsalem, N. Marom, M. Vondracek, L. Kronik, N. Koch, and T. Angot, Phys. Rev. B 87 075407 (2013)
[5] N. Marom, J. E. Moussa, X. Ren, A. Tkatchenko, and J. R. Chelikowsky, Phys. Rev. B 84, 245115

(2011)
[6] N. Marom, T. Körzdörfer, X. Ren, A. Tkatchenko, and J.R. Chelikowsky, to be published
[7] X. Ren, N. Marom, F. Caruso, M. Scheffl_er, and P. Rinke, to be published

Quantum nuclear effects in the photophysics of diamondoids

Feliciano Giustino[1]
Department of Materials, University of Oxford

Diamondoids are nanoscale carbon molecules and nanoparticles where the atomic connectivity is essentially identical to that of bulk diamond. The simplest diamondoid, called adamantane, is a small cycloalkane with ten carbon atoms defining a cage as in the diamond lattice. The entire diamondoids family can be thought of as if generated by fusing together adamantane building blocks in a molecular lego. While adamantane was known since the 1930s, the discovery of larger diamondoids in crude oil took place only ten years ago [1], and triggered a wave of research into the technological application of these materials. Among their many potential applications, diamondoids are particularly interesting as monochromatic electron emitters, fluorescent markers, and single-photon sources. All these applications require a detailed understanding of the electronic and optical properties of diamondoids.An intriguing aspect of previous electronic structure calculations on diamondoids is that they report a significant overestimation of the optical gap with respect to experiment (even the most accurate QMC approaches), as well as a disagreement in the qualitative shape of the optical absorption spectrum (within TDDFT).In this talk I will show how these discrepancies can be resolved altogether by incorporating electron-phonon physics in the theoretical description of the optical spectra of diamondoids [2]. In particular I will show how quantum nuclear dynamics induces a significant broadening of the optical absorption lineshape, and the zero-point motion induces a large redshift of the absorption onset. The computational method that we employed in these calculations is based on Importance Sampling Monte Carlo integration. I will discuss the theory underlying this method, recent developments, and future possible applications to molecules and solids.

[1] J. Dahl, S. G. Liu, and R. M. K. Carlson, R. M. K., Science 299, 96 (2003).
[2] C. E. Patrick and F. Giustino, Nat. Commun. 4, 2006 (2013).

Density-functional theory predicts the relative solubilities of racemic and enantiopure crystals

Erin Johnson[1], Alberto Otero-de-la-Roza
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National Institute for Nanotechnology, Edmonton, Canada

Isolation of chiral molecules as pure enantiomers remains a fundamental challenge in chemical research. Enantioselective enrichment through preferential crystallization is an efficient method to achieve enantiopure compounds, but its applicability depends on the relative stability of the enantiopure and racemic crystal forms. Using a simple thermodynamic model and density-functional theory calculations with the exchange-hole dipole moment (XDM) dispersion model [1,2], it is possible to predict the difference in solubility between the enantiopure and racemic solid phases. The calculation of the enantiomeric excess at the chiral eutectic point is shown to be an exquisitely sensitive test of theoretical methods for intermolecular interactions in the solid phase [3].

[1] A. Otero de la Roza and E. R. Johnson. J. Chem. Phys. 136, 174109 (2012).
[2] A. Otero de la Roza and E. R. Johnson. J. Chem. Phys. 137, 054103 (2012).
[3] A. Otero de la Roza, B. Huynh Cao, I. K. Price, J. E. Hein, and E. R. Johnson. Angew. Chem. 10.1002/anie.201403541R2

Automatic generation of a general inter- and intramolecular force-field from dispersion corrected DFT

Stefan Grimme[1]
Mulliken Center for Theoretical Chemistry, University of Bonn, Germany

From equilbrium molecular properties of a DFT-D3 calculation an intramolecularforce-field (FF) is automatically generated. It is coupled with an intermolecular potential including the D3 dispersion correction and Hirshfeld based atomic charges to yield a consistent model which can be applied in pure FF based molecular dynamics simulations of condensed phase systems or for QM/MM treatments of explicit solvation. The method can be applied without specific fitting to any molecular system (including metal complexes) for which the necessary DFT information can be computed. In addition to standard GGA methods, the semi-empirical DFTB3-D3 approach is used as a basis for large systems (mostly proteins) with up to 1000 atoms. The potential allows smooth dissociation of a molecule into atoms or fragments. A new estimate for the covalent dissociation limit is proposed which on average yields FF atomization energies accurate to about 10%. Similar accuracy is achieved for typical non-covalent interaction energy benchmarks (e.g. S22, S66, S12L, L7). For standard conformational tests from the GMTKN30 data base, the approach yields much better relativeenergies than conventional FFs.

From dispersion interactions to farsighted electron correlation -- a unified approach based on atomic response functions

Alberto Ambrosetti[1], Alexandre Tkatchenko
Università di Padova
Fritz-Haber Institut der MPG, Berlin

The Coulomb interaction between electrons leads to ubiquitous many-body correlation effects, which influence the structure, stability, and response properties of molecules and solids. In this respect, a reliable (accurate and efficient) determination of the long-range correlation energy is the main challenge, and requires a seamless modeling of hybridization and many-body electrodynamic effects. Here we show that these requirements can be met by mapping the system susceptibility onto a set of coupled atomic response functions (ARF). We build upon the recent MBD method [1], and introduce a rigorous range-separation of the inter-ARF interaction, allowing for a unified treatment of weakly and strongly polarizable systems [2]. The resulting method is efficiently applied to molecular databases including small molecules (S66x8), molecular crystals (X23), and strongly anisotropic supramolecular complexes (S12L), achieving uniform performance for this wide variety of systems (overall agreement with high-level reference data within ~6\%). A detailed analysis of long-range correlation effects demonstrates that many-body terms are an essential ingredient for a unified treatment of heterogeneous systems: many-body contributions go beyond conventional renormalization effects, varying depending on the dimensionality and topology of the system, and can give rise to strongly delocalized collective fluctuation modes. Notably, such modes can induce a relative "farsightedness" of the correlation energy in polarizable nanostructures, causing marked modifications of the "conventional" interaction power laws.

[1] A. Tkatchenko, R.A. DiStasio Jr., R. Car, and M. Scheffler, Phys. Rev. Lett. 108, 236402 (2012).
[2] A. Ambrosetti, A.M. Reilly, R.A. DiStasio Jr., and A. Tkatchenko, J. Chem. Phys. 140, 18A508 (2014).

Accuracy of dispersion corrected van der Waals functionals in calculating structures of molecular crystals

Andrew Rohl[1], Damien Carter
Curtin University, Bentley, Australia

The development of new functionals and methods to describe van der Waals forces in density functional theory (DFT) has become prevalent in recent years [1], with most studies focussing on the reliability of the calculated energies of assemblies of molecules, and to a lesser extent molecular crystalline systems. Very few have tackled the question of how well these functionals reproduce crystal structures. We will demonstrate the accuracy of some common dispersion corrected van der Waals functionals on the crystal structures comprising the C21 reference set [2], a data set of structures determined at room temperature and a series of monosaccharide structures. The impact of basis set type and quality will be assessed and the best strategy for calculating the most accurate structures and associated energies will be elucidated. Finally how this knowledge can be used to greatly increase the quality of a set of interatomic potentials will be demonstrated.

[1] S. Grimme, WIREs Comput. Mol. Sci. 1 211 (2011)
[2] A. Otero-de-la-Roza, E.R. Johnson, J. Chem. Phys., 137 054103 (2012)

A walk through electronic structure challenges in the land of thiophene

Clemence Corminboeuf[1], Riccardo Petraglia, Eric Bremond, Peter Tentscher, Antonio Prjl, Basile Curchod,
Ecole Polytechnique Fédérale de Lausanne

Our research focuses on the realization of efficient and accurate computational methods capable of simulating Ï€-conjugated systems relevant to the field of organic electronics. Among the most versatile p-type organic semiconductors, oligothiophenes display considerable potential as low-cost materials for solution-processed field-effect transistors with good air stability. The apparent simplicity of thiophene derivatives contrasts the complexity of their electronic structure, where commonly used electronic structure frameworks suffer from obvious failures. The talk provides an overview of our recent activity, which includes addressing lingering difficulties in describing energies and geometries of (oligo)thiophene derivatives.[1] Emphasis will be placed on improved DFT and SCC-DFTB-based treatments of charged radical oligomers (i.e., charge carrier precursor), organic charge-transfer complexes as well as on the proper description of large-scale stacks of oligomers,[2] exciton coupling between oligomeric chains[3] and excited state dynamics. We will also describe strategies to fine-tune the specific intermolecular interactions and orientations between Ï€-conjugated moiety to achieve better charge transport.[2,4]

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Low-cost electronic structure approaches for intermolecular interactions: from dimers to crystals

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Intermolecular interactions play a critical role in molecular materials, but modeling them accurately is a long-standing challenge. Fragment methods provide an effective strategy for decomposing materials like molecular crystals into smaller, more tractable electronic structure problems, but the question remains how best to model these smaller fragments. In this talk, we will examine recent developments in obtaining pairwise intermolecular interaction energies that approach complete-basis-set CCSD(T) quality with cost comparable to only MP2 in a modest basis set. Starting from the dispersion corrected MP2C model, we have been exploring strategies that allow one to simultaneously improve the treatment of electron-electron correlation and compensate for finite basis set effects.

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Better many-body expansions through better embedding

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The many-body expansion provides an important framework for high-accuracy energetics of molecular crystals. There are two primary ways to systematically improve accuracy: first, one can include higher-order many-body terms; and second, one can embed lower-order terms in increasingly accurate models of the environment provided by the other monomers. We have focused our attention on the latter. A sequence of embedding theories will be discussed, based on point charges, smoothed charges, simple models of Pauli repulsion effects and full wavefunction-in-DFT embedding.

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MP2 and RPA calculations of liquid water and ice

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We have developed a novel algorithm for the calculation of MP2 and RPA correlation energies of extended systems based on a hybrid Gaussian and Plane Waves (GPW) approach with the resolution-of-identity approximation (RI).The method relies on the dual representation of the RI fitting densities in terms of Gaussian and Plane Waves auxiliary functions, leading to a simplified treatment of the Coulomb interactions that is particularly efficient in the condensed phase. The RI approximation allows to speed up the MP2 energy calculations by a factor 10 to 15 compared to the canonical implementation, but still requiring O(N^5) operations, and in the RPA case, reduces the computational effort to O(N^4 log N). The implementation has low memory requirements and displays excellent parallel scalability up to tens thousands of processes. Furthermore, the computationally most demanding parts can be accelerated by employing graphics processing units (GPU).In this way, RI-MP2 and RI-RPA calculations for condensed phase systems containing hundreds of atoms and thousands of basis functions can be performed within minutes employing few hundreds hybrid nodes. This has allowed us to use these high level electronic structure methods for performing first principles simulations of bulk liquid water under ambient conditions and to study properties of ice.

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Analysis of intermolecular interactions using symmetry-adapted perturbation theory

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Symmetry-Adapted Perturbation Theory (SAPT) [1] provides valuable insight into intermolecular interactions by quantifying the various components of the interaction energy: electrostatics, induction/polarization, dispersion, and exchange-repulsion. Our group has introduced density-fitting and natural orbital techniques to obtain much more efficient algorithms for wavefunction-based SAPT [2,3]. With these algorithms, we have recently completed a systematic study of the accuracy of various truncations of SAPT with different basis sets [4]. High-order SAPT methods provide interaction energies in very good agreement with supermolecular CCSD(T) computations, and even low-order SAPT provides fairly accurate results when paired with appropriate basis sets. Given the good reliability of SAPT, we have recently introduced a more fine-grained approach that yields energy components partitioned into pairwise contributions from atoms or functional groups [5]. This approach will be described and illustrated by several examples, such as host-guest complexes and substitutent effects in pi-pi interactions.

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Predicting steady state crystal morphologies from molecular simulations

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Crystal nucleation and growth from solution are physicochemical phenomena playing a key role in a wide variety of processes, ranging from biomineralization to pharmaceutical manufacturing [1].Understanding crystal growth at the molecular level is of great importance in order to enhance our current understanding of crystallization processes. Molecular dynamics simulations of crystal growth are however limited due to the rare nature of the events occurring at the molecular scale. In this talk the use of metadynamics [2-4] to explore urea crystal growth from solution will be discussed. Urea crystal growth from solution represents a paradigmatic example of a crystallization process that leads to a wide variety of solvent-dependent steady state crystal morphologies.

Experimental evidences [5,6] as well as computational results [7] highlight that both solvent and additives play a major effect on urea crystal habits. Computational predictions of the crystal shapes obtained from metadynamics will be commented and compared to experimental results [8].

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High-dimensional neural network potentials for large-scale simulations of materials

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In recent years artificial neural networks (NNs) have become a powerful new approach to construct potential-energy surfaces of nearly first-principles quality for many systems [1-4]. In most practical applications, however, NN potentials have been restricted to small molecules in the gas phase or diatomic molecules interacting with frozen metal surfaces. This limitation has been overcome by the introduction of high-dimensional NN potentials [5,6], which allow performing molecular dynamics simulations of very large systems containing thousands of atoms. Like conventional low-dimensional NN potentials, this approach is numerically very accurate and can in principle be combined with any electronic structure method. An important advantage of NN potentials is their ability to describe all types of atomic interactions at the same level irrespective of their physical origin, from covalent bonds via metallic bonding to non-bonded interactions. Often density-functional theory (DFT) is used as reference method for constructing NN potentials, which has well-known limitations, e.g. concerning the description of van der Waals (vdW) interactions. Using water as a model system, we show that vdW corrections can be included in NN potentials based on plain GGA DFT data in the same way as in DFT calculations. Further, the general scope and current limitations of the NN potential method will be discussed employing a number of illustrative example systems using different types of materials.

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Dimensionality reduction and molecular order

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Collective variables and order parameters are important tools for understanding the results obtained from atomistic simulations and, in some cases, for ensuring that a sufficient volume of configuration space is sampled. Such variables allow us to construct low dimensional representations of the information contained in the trajectories output by our simulations and to thus generate a better understanding of the phenomena under examination. The problem is that many of the processes that we wish to study are often quite complex, which makes it difficult to think of appropriate order parameters. Our approach has thus been to use dimensionality reduction algorithms to automate this process of finding collective variables. In particular, we have developed an algorithm called sketch-map that can be used to analyse the results of molecular dynamics simulations. I will present results showing what we have achieved using this algorithm thus far and will also discuss ways that it might be used in the future.

Stability and function of organic molecular crystals

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Molecular crystals play an ever increasing role in our daily lives in many different forms. In Medicine they are among the main drug delivery vehicles in the form of pills, while technologically they become more and more interesting–for example in the form of organic solar cells–due to their abundance and their diverse, highly controllable properties. From a theoretical viewpoint the development of computational approaches to determine stability and function of such molecular crystals is therefore of great importance. Concerning the stability, we demonstrate our techniques by calculating dissolution free energies, and thus rates of an acetylsalicylic acid (Aspirin) crystal in water. Using rare event sampling methods and a classical force field we can not only account for the inter-molecular dispersion forces stabilising the crystal, but also determine entropic effects playing a role in the dissolution process. With respect to the function of molecular crystals, we study the charge transport properties of organic solar cell components using density functional theory. We illustrate our approach on the example of fullerene nano-crystals, where we determine experimentally observable electron mobilities from an analytically solvable hopping model parametrised from first-principles calculations.

Multiscale atomistic modeling of amorphous organic functional materials for optical chemical sensing and oled applications

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Atomistic multiscale simulation is applied to modeling amorphous organic functional materials with specific optical or electronic properties. Materials for optical chemical gas sensors and for organic light-emitting devices (OLED's) are considered as examples. The functionality of such materials is provided by constituting molecules that determine their specific functional properties. In the case of sensing devices, these are so-called indicator molecules (IMs) changing their optical response (mostly, luminescence) upon interaction with a target molecule (detected or analyte molecule, AM). The goal of simulation in this case is to predict the optical properties of the entire structure (sensing material) and its response to various AMs. In the case of OLED's, these are light-emitting and electron- or hole-transporting molecules. The goal of simulation here is to predict the main electronic parameters of these molecules that determine the efficiency of a particular OLED. In both cases, the properties of functional molecules strongly depend on their local supramolecular environment, that is, on the microstructure of the amorphous material. Therefore, a multiscale atomistic approach is used, in which molecular dynamics simulations are used to describe the microstructure of the material, and quantum chemical methods are used to calculate the required electronic properties of the functional molecules in the material. Commonly, a statistical treatment is required to obtain the distribution of wanted molecular properties or their averaged values in the real amorphous material. Problems arising at each step of modeling are analyzed, and current approaches to their solution are discussed. The possibilities of modern atomistic simulation methods are considered using specific examples. [1–5]

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From liquid to solid by biased monte carlo simulation

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This contribution describes the principles of a biased Monte Carlo simulation used to model the transition from a liquid phase towards a solid of variable symmetry-periodicity for organic compounds. The method [1-3] requires the decrease of an "asymmetry" parameter before the usual MC-Metropolis procedure is enforced. Compounds of variable functionality are considered, from hydrocarbons to alcohols and acids. The quality of the answer goes from rather poor, when only a liquid-crystal like phase is obtained, to rather good, when the observed crystal structure is reproduced almost perfectly. The whole machinery has many limitations, both practical - only inversion symmetry is considered - and theoretical, with respect to lack of compliance to thermodynamic equilibrium conditions. Nevertheless, the results provide some insight on the proceedings at a molecular level, e.g. a description of the progressive breaking of general hydrogen bonding in multi-functional liquid materials and the simultaneous formation of the specialized hydrogen bond which is observed in the solid. Such information is not, and will not be in the near future, available experimentally, so the results have the flavor of real prediction. The method can also be applied to investigate the preferential crystallization of racemic crystals from racemic liquids, against spontaneous resolution, or crystallization of separate enantiomers in a conglomerate of homochiral crystals.The issue of reproducibility of molecular simulation protocols will be briefly discussed. Computer package, source codes and full documentation are available at http://users.unimi.it/gavezzot.

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Structure and dynamics of biomolecules and water: challenges for first-principles methods and nuclear quantum effects

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The function and stability of biomolecules rely on a delicate balance of all interactions involved. An accurate theoretical description of these interactions can only be attained by an explicit quantum mechanical treatment of the electronic structure, and often also of the nuclei. In this talk, it will be shown how accurately state-of-the-art first principles electronic structure methods (including van der Waals corrections) can describe the structure and dynamics of polypeptides in isolation and microsolvated [1, 2]. At the level of accuracy we can now achieve in first-principles calculations (errors of ~7 meV per amino-acid), the inclusion of more subtle nuclear quantum effects become more relevant - especially in challenging anharmonic and dynamical frameworks. We introduce a new method based on path integral molecular dynamics, which we call thermostated ring polymer molecular dynamics (TRPMD), for the evaluation of dynamical observables [3]. This method is immune to the pathological problems of both ring polymer molecular dynamics (RPMD) and centroid molecular dynamics (CMD), while being analytically just as well defined as RPMD. We show applications to vibrational spectra of model systems, and proton diffusion in water wires.

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Nuclear quantum effects in hydrogen bonded networks

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Over the past decades molecular simulation has become an increasingly important tool in predicting and interpreting chemical processes. Inherent in these simulations is the assumption that the nuclei behave classically. However, for processes involving light particles such as hydrogen the quantum mechanical nature of the particles can dramatically alter their structure and dynamics. In this talk I will discuss our results on systems ranging from liquid water to proton delocalization in enzyme active sites where we have shown that the inclusion of such effects is essential to obtain the correct behavior.

Structure and dynamics of water at surfaces

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Water/solid interfaces are relevant to a broad range of physicochemical phenomena and technological processes such as corrosion, lubrication, heterogeneous catalysis and electrochemistry (Nature Mater 11, 667 (2012)). In this talk some of our recent work in this area will be discussed. Specifically results on water droplet diffusion on the surfaces of layered materials will be presented and a novel “surfing” mechanism for droplet diffusion discussed. Time permitting, some recent ab initio molecular dynamics results at wet interfaces in which rapid proton transfer is observed will also be discussed and explained.

The path to first principles modeling with nuclear quantum effects: techniques, applications, and future directions

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Nuclear quantum effects influence substantially the physical properties of many systems, especially those containing lighter nuclei. The terms zero point energy and quantum tunnelling are often mentioned in this context, although they are just specific manifestations of a more complex phenomenon. While nuclear quantum effects increase with decreasing temperature, they can be substantial even at ambient conditions for many systems. Potentials and forces generated from electronic structure calculations do not inherently contain these effects, and hence, in principle, they should always be added. Obviously, it is not always necessary to include these effects, however, when it is necessary, it is also necessary to have techniques that are efficient and robust. At present, the method of choice for incorporating nuclear quantum effects into first-principles calculations is via the Feynman path integral formulation of quantum statistical mechanics. Within the discrete version of this formulation, quantum particles are represented as cyclic polymer chains with a harmonic coupling between the pseudo-particles of these chains, the stiffness of which increases as the system becomes increasingly quantum in nature. In this talk, I will discuss a number of issues relating to first-principles path integral calculations, including efficient sampling methods, estimators for physical quantities, calculation of isotope effects, and approximating dynamics. I will discuss several application areas in which first principles path integral calculations have proven invaluable in providing important insights. Finally, I will discuss efforts int he direction of developing community codes for path integral calculations.

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Towards efficient description of nuclear quantum effects

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The increasing accuracy of modern electronic structure calculations requires accurate methods for the inclusion of quantum nature of (light) nuclei for correct prediction of structure, stability, and dynamical properties of many systems, including water, ice, as well as most biological molecules. A standard approach to take nuclear quantum effects into account is the imaginary-time path integrals (PI) simulations, which unfortunately converge very slowly. Recently developed quantum thermostats [1] significantly increase the applicability of PI techniques to larger systems. However, these methods contain a number of adjustable parameters, which is not optimal for application of PI simulations to realistic inhomogeneous systems characterized by a complex spectra of relevant frequencies. We propose two ways to improve PI simulations by using either high-order decompositions for the exponential of the Hamiltonian or mapping of the quantum system into a set of non equilibrium classical subsystems following works of E. Wigner [2], G. E. Uhlenbeck, and L. Gropper [3]. The developed methods decrease the required number of replicas by more than a factor of two comparing to the standard PI simulations based on the primitive approximation, while at the same time visibly increasing the accuracy for a wide range of temperatures. Results are shown for model systems and an accurate quantum-mechanical model of the water molecule and its dimer.

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Computational carbon capture

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The separation of mixtures of volatile molecules presents a critical issue in the clean use of existing fuels and in the generation of alternative fuels. In particular separation of CO2 is at present one of the mayor barriers for large scale CO2 sequestration. For example, the conventional technology for capturing CO2 from the effluent stream of a power plant may require as much as 25% of the electricity being produced. In this presentation an overview will be given on the activities on carbon capture the Energy Frontier Research Center (EFRC) in Berkeley. In this presentation we describe how computational techniques can be used to screen novel materials for carbon capture. Our starting point is the question how to define the optimal material. We introduce the concept of parasitic energy as a metric to compare different materials; the best material is the material that minimizes the loss of efficiency of a power plant. To compute this parasitic energy one need information on the mixture isotherms of the various components of flue gasses. We show how quantum chemical calculations can be used to predict the adsorption energies. In addition, we show how these calculations can be used to develop a force field that allows us to predict the adsorption properties. We will apply these methods for materials for which experimental data is lacking, or for materials that have not yet been synthesized.

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Breathe freely: simulating flexible behaviour of metal organic frameworks to solve troublesome x-ray powder diffraction data; response to temperature and co2 loading

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Ab initio (NPT) molecular dynamics simulations have been used for the first time to successfully predict structural transitions of the flexible metal organic framework MIL-53(Sc) system, in response to changes in temperature and adsorption of CO2 into the framework pores. The resulting time-averaged structures enabled the structure determination of two separate CO2-loaded phases, as observed by synchrotron X-ray power diffraction studies with increasing CO2 pressure. One of these structures was impossible to solve by conventional means due to diffraction peak broadening; the simulations showed this was due to dynamic fluctuations in the framework structure, and a convincing fit to the experimental data set was subsequently obtained. This work will highlight the crucial role that DFT dispersion corrections play in obtaining stable NPT MD simulations of framework materials.

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Modelling the optical properties of the organic solid state

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The organic solid state is, in terms of applications, most commonly associated with pharmaceuticals. However, molecular materials, polymers and organic networks have a long history of use for their optoelectronic properties. Their earliest application in this context was as (synthetic) dyes but more recently they have been found use in solar cells, in light emitting diodes, as photoconductors and even as photocatalysts. The unrivalled synthetic versatility of organic chemistry coupled with the fact that the optical properties of organic materials does not only depend on the molecular structure but also the supramolecular organisation means that there is a wealth of opportunities to maximise material performance in these applications. In my contribution I will illustrate with concrete examples from my group and our experimental collaborators [1-4], how computational chemistry calculations on extended cluster models can give powerful insight into the link between (supra)molecular architecture and optical/excited state properties. I will specifically focus on the effect of intramolecular interactions on spectra and other optical properties and how this can both be a burden, when using spectroscopic data to rationalise amorphous or poorly crystallised structures, but also a clear advantage, when aiming to tune optoelectronic properties. I, finally, will show that the biggest computational challenge is to treat bound excited states – excitons - and free charge carriers - free electrons and holes – in an equal fashion, and to qualitatively predict important material properties such as the exciton binding energy and the standard reduction potential of excitons.

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The microscopic structure, equilibrium density, and local environment of liquid water

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In this work, we have performed extensive density functional theory (DFT) based ab initio molecular dynamics (AIMD) simulations of liquid water at ambient conditions in both the canonical (NVT) and isothermal-isobaric (NpT) ensembles to investigate the individual and collective importance of exact exchange, non-local van der Waals (dispersion) interactions, and nuclear quantum effects on the structural properties of liquid water. AIMD simulations which systematically account for these effects result in structural properties which are in excellent agreement with experiment and a liquid water having an equilibrium density within a few percent of the experimental value of approximately 1 g/cm^3. A detailed analysis of the local environment in ambient liquid water has revealed that individual water molecules naturally fluctuate between spatially high- and low-density environments and the corresponding inherent potential energy surface (IPES) is bimodal, consistent with the existence of polymorphism in the amorphous phases of water. With these findings, the methodology presented herein overcomes the well-known limitations of semi-local DFT and provides a detailed and accurate microscopic description of ambient liquid water.

Poster presentations

Controlling channel interference in two photon absorption: a chemical perspective

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The two-photon absorption (TPA) process is the most widely studied nonlinear optical phenomenon, and various aspects of this process have already been investigated, experimentally as well as theoretically. Erstwhile investigations have shown that the performance-tailored TP active materials are easy to develop by monitoring factors such as length of conjugation, dimensionality of charge-transfer network, strength of donor-acceptor groups, polarity of solvents, self-aggregation, H-bonding, etc. One of the most fascinating phenomena affecting the TP activity of a molecule is channel interference. The term “channel interference” entails that if the TP transition from one electronic state to the other involves more than one optical channel, characterized by the corresponding transition dipole moment (TDM) vectors, the channels may interfere with each other depending upon the angles between the TDM vectors and hence can either increase (constructive interference) or decrease (destructive interference) the overall TP activity of a system to a considerable extent. This phenomenon was first pointed out by Hans Ågren and co-workers in 2D systems. For 3D molecules, an extended version of this idea is crucial. To fill this gap, we developed a generalized model for elucidating and exploring channel interference, valid for systems of any dimensionality. In particular, we have applied it to through-bond (TB) and through-space (TS) charge-transfer systems both in gas phase and in solvents with different polarities. In my presentation, I will first shed light on the concept of channel interference and then discuss the two key findings of our recent works, namely, 1) how simple structurally induced changes in certain dihedral angles of the well-known betaine dye (TB type) will help fine-tune the constructive interference and hence increase the overall TP transition probability of the modified system and 2) abnormal solvent dependence of TP transition probability of a molecular tweezer-trinitrofluorinone complex (TS type). In brief, this presentation will highlight the usefulness of the channel interference effect in designing novel two-photon active materials.

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Ions at silica/liquid water interfaces by dft-md simulations

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We characterize structural properties, acidities and vibrational spectroscopy of (0001) alpha-quartz/liquid water interfaces with singly-charged ions and ion pairs (NaCl, KCl, NaI) via DFT-based molecular dynamics simulations. The main points consist in localizing ions at the interface and induced changes due to their vicinity on the structure of the surface like new orientations of silanols and on interfacial water and subsequent layers. The addressed questions are how/why interfacial water can be disordered or not due to ionic adsorption and until which layer such modifications can be non-negligible. A vibrational analysis of signatures at these ionic interfaces is proposed and compared to the neat interface to assign bands to interfacial structures. Surface pKa's are also calculated on surface sites to investigate the possible ionic strength effects. All these properties are used to rationalize Sum-Frequency Generation (SFG) spectra. This work follows up recent DFT-MD studies at the (0001) alpha-quartz/liquid water interface [1,2] and amorphous silica/liquid water [3] for which interfacial structures (water and solid parts) and vibrational signatures have already been characterized and interpreted.

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Discovery of organic conductors and small band-gap semiconductors via dispersion inclusive dft

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Consistent, accurate prediction of molecular crystalline properties has been a coveted goal of the computational physics and chemistry communities for decades. With recent developments of several dispersion correction schemes within the density functional theory (DFT) framework, reliable calculation of weakly interacting systems is quickly becoming a reality. Presently, prediction of morphology [1-7], band structure [8], band gap [9-11], surface absorption and reactivity [12], thermo-dynamic quantities [5, 13-24], and solubility properties [23, 24] of molecular crystals remains cutting edge, but is quickly becoming common place. With the advancements in methodology and hardware comes the next evolutionary step, the development of a high-throughput DFT derived molecular crystal properties database for the discovery of useful new materials and chemical trends. We plan to bring about a paradigm shift in soft-solid materials research and development by establishing an organic molecular crystal (OMC) properties database.

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Recognizing molecular patterns by machine learning: an agnostic structural definition of the hydrogen bond.

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Recognizing and predicting structural patterns is a fundamental step in understanding the stability and the reactivity of matter. Nowadays, using atomistic simulation methods, it is possible to predict with great accuracy the structural properties of a material. By a purely heuristic point of view, one could interpret the recurrence of structural patterns, as a sign of an underlying chemical bond. This assumption is based on the idea that atomic configurations observed in a computer simulation are consistent with their energetic stability and the thermodynamic conditions, thus the (free) energetic stability of different molecular patterns is implicit in the frequency with which they appear in the simulation. The aim of the work we are presenting, is to use a machine-learning approach (PAMM: Probabilistic Analysis of Molecular Motifs) to rationalize and assist the interpretation and the analysis of the recurrent structural patterns in a quantitative, deterministic and unbiased way. Starting from a high-dimensional description of groups of atoms, PAMM naturally builds an out-of-sample probabilistic definition of the different patterns and associates to each motif an adaptive and system-dependent descriptor. Such a descriptor can then be used subsequently to identify the same patterns in new configurations of the system. As an example of the possible applications of this algorithm we discuss how PAMM can be used to provide a definition of the hydrogen bond in different environments (solvated alanine dipeptide, classical and quantum water, liquid ammonia), spanning the broad energy scale that characterizes different kinds of HBs. In all the cases PAMM correctly identifies a range of structural parameters corresponding to hydrogen-bonded configurations and proposes an order parameter that can easily be used to count the hydrogen bonds surrounding a given atom and to characterize their dynamical behavior.

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Interaction of water with boron nitride doped carbonaceous systems: a hard test for exchange-correlation functionals

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The interaction of water with the pure surfaces, graphene and hexagonal boron nitride (h-BN), has received a lot of attention because of interesting phenomena exhibited by these systems and their promising potential applications in clean energy, water purification, hydrogen storage, and bio-sensing [1-5]. BN doped graphene can also now be made [6-8], opening the way to carefully designed hybrid materials. However, much of the fundamental mechanisms regarding the interaction between these surfaces and water is still not well understood. Using smaller model systems for graphene, h-BN and BN doped graphene (i.e. benzene, borazine and 1,2-azaborine, respectively) we assess the performance of different exchange-correlation functionals within density functional theory by comparing with coupled cluster benchmarks, taking insight from quantum Monte Carlo also. We find that a high fraction of exact exchange is needed in exchange-correlation (xc) functionals in order to predict the correct lowest energy binding orientation of water with the BN doped system, whilst dispersion inclusive xc functionals perform well for predicting interaction energies. The description of exchange in xc functionals is thereby shown to have a noticeable impact on the configuration of a weakly interacting system. Furthermore, we find that BN doping strengthens the adsorption energy of a water monomer compared to adsorption on the pure systems, such that isoelectronic doping may be used to tune the interaction of water with 2-dimensional materials.

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Towards an accurate description of condensed systems

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Accurate theoretical description of cohesive properties of condensed systems is difficult. For example, both strong intermolecular bonds s well as weaker intermolecular bonds need to be described accurately when reliable values of lattice energies of molecular solids are sought. From the range of methods being studied we will present developments and applications of the so-called random phase approximation (RPA) and van der Waals density functionals (vdW-DFs). RPA describes well both strong and weak forces and thus represents a promising tool for the treatment of a large number of systems, including molecular solids and liquids. For example, it yields very good cohesive properties of different water ice phases, being surpassed only by much more expensive quantum Monte Carlo methods.[1] However, computational cost is still an issue and we present an algorithm which scales cubically with the system size, unlike the original O(N^4) scheme. The new implementation allows systems with hundreds of atoms to be studied using modest resources.[2,3] Simpler methods are also of great interest and we will also present an assessment of several vdW-DFs, including VV10, on standard benchmark tests, such as the C21 test set.

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Reliable modelling of stabilities, polymorphism, and response properties in organic materials

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Organic materials are of great fundamental and applied importance in science and industry, with numerous applications in pharmaceuticals, food science, electronics, sensing, and catalysis. A key challenge for theory has been the prediction of their stabilities, polymorphism, and response to external perturbations. In recent years, there has been substantial progress in the modelling of organic materials with semi-local approximations to density functional theory (DFT) coupled with pairwise descriptions of dispersion interactions [1]. However, the majority of studies neglect the contribution of many-body dispersion and also the self-interaction error (SIE) present in widely used density functionals. To categorically understand the importance of these two contributions we have studied two databases of gas-phase and solid-state inter-molecular interactions [2,3]. While pairwise dispersion methods perform remarkably well for simple dimers, they substantially overestimate molecular-crystal lattice energies. Correctly accounting for electrodynamic response and many-body energy contributions using the many-body dispersion (MBD) method [4, 5] yields substantial improvements. The application of a hybrid functional (PBE0) also gives noticeable improvements, particularly for hydrogen-bonded solids. Overall, the PBE0+MBD method is capable of reaching accuracies of a few kJ/mol for both crystalline and gaseous phases compared to high-level theoretical and experimental stabilities [2,3], giving a systematic and seamless method for modelling both gas-phase and condensed molecular materials. The accuracy achieved by PBE0+MBD enables us to account for the correct polymorphic ordering of a number of challenging systems, such as glycine, for the first time [6]. However, the role of many-body dispersion goes beyond lattice energies. Aspirin has two known polymorphs. While they are degenerate in terms of lattice energy [7], form I is clearly more abundant. PBE+MBD reveals that this originates from coupling between subtle coupling between quantum-mechanical lattice vibrations and electronic many-body fluctuations, which entropically stabilises form I over form II. An analysis of the elastic properties of aspirin also shows many-body dispersion contributions of the order of 25% to the elastic constants and bulk and shear moduli.

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Understanding the wetting of nanostructured surfaces

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Understanding the structure, stability and dynamics of nanostructured materials is important for fundamental science as well as for wide range of applications. In particular, considerable attention has been paid to studying the wetting behavior of nanostructured materials. Three recent landmark experiments demonstrated conflicting results for the wetting of graphene [1,2], making the understanding of wetting a hotly debated issue. Rafiee et al. [3] found that graphene is completely transparent to wetting. Shih et al. [4] observed that graphene is not completely, but only partially transparent to wetting. Finally, Raj et al. [5] have re-investigated the same problem [3,4] and obtained certain results that agree with previous observations but disagree with others. Qualitative explanations for the different experimental results have been put forward mainly by using simplified Lennard-Jones potentials. Here, we intend to address this question using density-functional theory (DFT) with many-body dispersion (MBD) interactions. Recently, it has been demonstrated that MBD interactions play a significant role in describing the structure and stability of nanostructured materials [6,7]. The accurate inclusion of MBD interactions will help us to better understand the wetting behavior of nanostructured materials.

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Non-local density functionals meet many-body dispersion: a hybrid approach for van der waals interactions

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There are different approaches to treating van der Waals (vdW) interactions in density-functional theory, which can be loosely divided into the atom-based and the ones based on non-local functionals. The first type consists of a range of methods from atom-pairwise additive schemes by Grimme [1,2] to many-body dispersion (MBD) approach of Tkatchenko et al. [3,4]. These methods typically make use of some precalculated atomic parameters and hence rely on information that is not explicitly contained in the electron density. The other category of vdW methods consists of nonlocal functionals either of the Langreth and Lundquist [5] or the Vydrov and van Voorhis (VV) [6] type. In these approaches, the vdW energy is obtained as a functional of the electron density and only a few tuning parameters are needed. Here, we show that these two contrasting approaches can be synergistically combined. We use the polarizability from the nonlocal functional of VV [7] within the MBD method of Tkatchenko et al. Such a combination is worthy for several reasons. First, it is an atom-centered approach with no atomic parameters. Second, it largely puts aside the problem of partitioning electron density between atoms, which can be problematic in cases such as metals (delocalization) or ionic compounds (charge transfer). Third, it enables more direct comparison of so far unrelated methods. Fourth, it highlights the idea of combining working elements from different approaches.

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Part IV – List of Attendees

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Reilly, Anthony - Cambridge Crystallographic Data Centre (CCDC), United Kingdom
Tkatchenko, Alexandre - Fritz Haber Institute of the Max Planck Society (FHI), Berlin, Germany

Attendees

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Ambrosetti, Alberto - University of Padova, Italy
Bagaturyants, Alexander - Russian Academy of Sciences and National Research Nuclear University, Moscow, Russian Federation
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Martonak, Roman - Comenius University Bratislava, Slovakia, Slovakia
Morrison, Carole - University of Edinburgh, United Kingdom
Oberhofer, Harald - Technical University of Munich, Germany
Pfeiffer-Laplaud, Morgane - University of Evry Val d'Essonne , France
Poltavskyi, Igor - Fritz Haber Institut of the Max Planck Society, Germany
Price, Sally - University College London, United Kingdom
Rohl, Andrew - Curtin University, Australia
Rossi , Mariana - Oxford University, United Kingdom
Salvalaglio, Matteo - Swiss Federal Institute of Technology of Zurich (ETHZ), Lugano, Switzerland
Sanvito, Stefano - Trinity College Dublin, Ireland

Schatschneider, Bohdan - Penn State University, USA
Sherrill, David - Georgia Institute of Technology, Atlanta, USA
Smit, Berend - University of California at Berkeley, USA
Tribello, Gareth - Queen's University Belfast, United Kingdom
Tuckerman, Mark E. - New York University, USA
Wilson, Chick - University of Bath, United Kingdom
Yang, Jianliang Jack - University of Southampton, United Kingdom
Zwijnenburg, Martijn A. - University College London, United Kingdom

Part V – Financial Report

Psi-k Network : Towards Atomistic Materials Design

Psi-k
Daresbury Science & Innovation Campus
Daresbury, Warrington
WA4 4AD
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PSI-K WORKSHOP FINANCE REPORT

Title of the Workshop	Addressing Challenges for First-Principles Based Modeling of Molecular Materials
Workshop Organisers	Anthony Reilly - Alexandre Tkatchenko - Michele Ceriotti
Location of the Workshop	CECAM - EPLF, Lausanne, Switzerland
Dates of the Workshop	25 - 29 August 2014
Total Grant from Psi-k	€ 8 000

EXPENDITURE

(Please complete the tables using numbers ONLY in the amounts fields - the spreadsheet will calculate the totals for you)

WORKSHOP DELEGATES / SPEAKERS			
Name and Country of Claimant	**Travel**	**Accommodation**	**Total (€'s)**
SANVITO Stefano (4 nights Tulipp Innl)		€ 435.00	€ 435.00
SHERRILL David (4 nights Tulipp Inn)		€ 435.00	€ 435.00
PRICE Sally (4 nights Tulipp Inn)		€ 435.00	€ 435.00
MORRISON Carole (4 nights Tulipp Inn)		€ 435.00	€ 435.00
TKATCHENKO Alexandre (4 nights Tulipp Inn)		€ 435.00	€ 435.00
WILSON Chick (4 nights Tulipp Inn)		€ 435.00	€ 435.00
MARTONAK Tom (4 nights Tulipp Inn)		€ 435.00	€ 435.00
BEHLER Joerg (4 nights Tulipp Inn)		€ 435.00	€ 435.00
GIUSTINO Feliciano (4 nights Tulipp Inn)		€ 435.00	€ 435.00
AMBROSETTI Alberto (4 nights Tulipp Inn)		€ 435.00	€ 435.00
MANGY Fred (4 nights Tulipp Inn)		€ 435.00	€ 435.00
HUTTER Juerg (4 nights Tulipp Inn)		€ 435.00	€ 435.00
		Total Travel & Accommodation	**€ 5,220.00**

WORKSHOP REFRESHMENTS / CONFERENCE DINNERS			
Date	**Tea / Coffee**	**Lunch / Dinner**	**Total (€'s)**
Dinner at the Restaurant Le Carrousel		€ 2,780.00	€ 2,780.00
			€ -
			€ -
			€ -
			€ -
		Total Refreshments	**€ 2,780.00**

MISCELLANEOUS EXPENDITURE	
Details	**Total (€'s)**
Total Miscellaneous	**€ -**

Total Travel & Accommodation	**€ 5,220.00**
Total Refreshments	**€ 2,780.00**
Total Miscellaneous	**€ -**

TOTAL EXPENDITURE	**€ 8,000.00**

Psi-k:
A company limited by guarantee:
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Registered as a charity number 1126308