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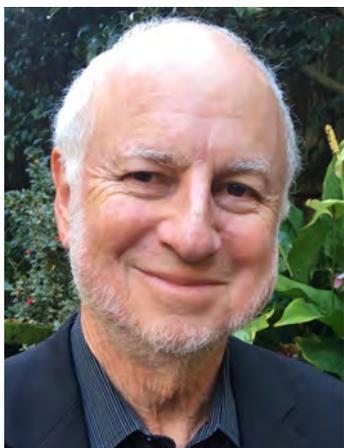
Contact (anytime)

Dr. Amir Karton

+61 4 5122 0944

amir.karton@uwa.edu.au

<http://chemtheorist.com>



Leo Radom was born in Shanghai in 1944. His family moved to Sydney, Australia in 1947. Following his BSc in Chemistry at the University of Sydney, he obtained his PhD degree in experimental physical organic chemistry in 1969 with Raymond Le Fèvre. Leo then turned to theory

during a postdoctoral period with John Pople at Carnegie-Mellon University in Pittsburgh. He returned to Australia in 1972 to the Research School of Chemistry of the Australian National University, and moved to the University of Sydney in 2003 where he is now an Emeritus Professor of Chemistry. Leo's main research interests are concerned with the study of the structures and stabilities of molecules and the mechanisms of reactions in which they are involved, by use of highly accurate computational quantum chemistry procedures. He has published over 500 papers, which have been cited over 35,000 times in the scientific literature. Leo's achievements have been recognized through the award of numerous prizes, including the Rennie Medal (1977), the H.G. Smith Medal (1988) and the Archibald Olle Prize (1992) of the Royal Australian Chemical Institute (RACI), the Schrödinger Medal of the World Association of Theoretical and Computational Chemists (WATOC) (1994), the BBV Foundation Chair at the Autonoma University of Madrid (1998), the 2006 Fukui Medal of the Asia-Pacific Association of Theoretical and Computational Chemists (APATCC), the David Craig Medal of the Australian Academy of Science (2008), the inaugural medal of the Association of Molecular Modellers of Australia (2010), and the Division of Physical Chemistry Medal (2010) of the RACI. Leo is a Fellow of the Royal Australian Chemical Institute and the Royal Society of Chemistry, and has been elected to the Australian Academy of Science and the International Academy of Quantum Molecular Science. His Hirsch Index of 87 is the highest of an Australian chemist. He is the immediate past-president of the World Association of Theoretical and Computational Chemists (WATOC) and is the current president of the Asia-Pacific Association of Theoretical and Computational Chemists (APATCC). Leo is married to Faye Radom, they have two daughters (Jackie and Naomi) and four grandkids aged from three to eight.

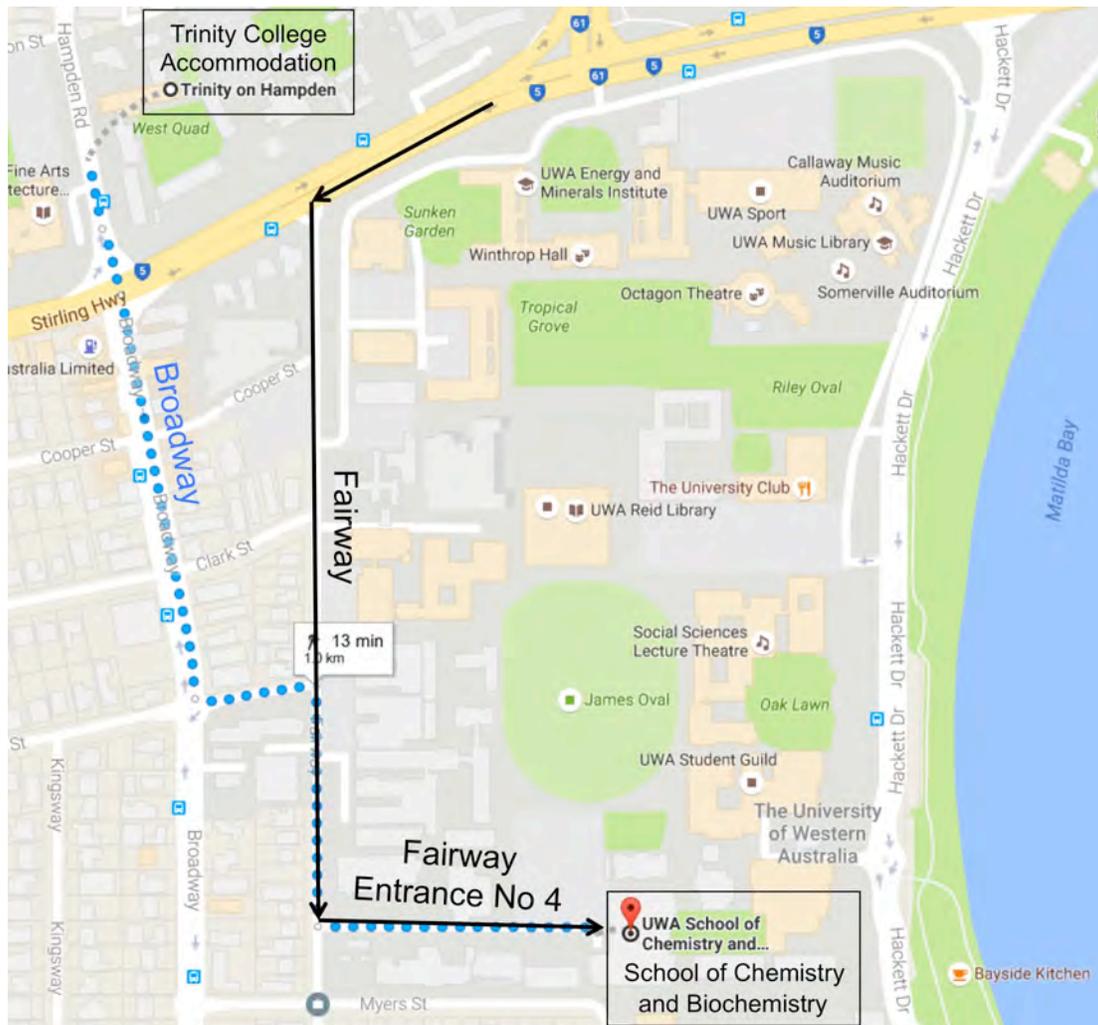


Gershom (Jan M. L.) Martin was born in Belgium in 1964. He obtained his PhD in Chemistry from the University of Antwerp in 1991 with Renaat Gijbels and Jean-Pierre Francois, and his Habilitation (D.Sc.) from the same university in 1994, both on fellowships from the National Fund for Scientific Research (NFWO) of Belgium.

During 1992-3, he was a postdoctoral fellow with Timothy Lee and Peter Taylor at NASA Ames Research Center and subsequently moved with Peter Taylor to the University of California, San Diego. In 1995 Gershom obtained tenure with the NFWO. Following a brief sabbatical with the late Chava Lifshitz at the Hebrew University of Jerusalem, Gershom accepted a faculty position at the Weizmann Institute of Science in 1996, where he is now the incumbent of the Baroness Thatcher Professorial Chair of Chemistry. Gershom's principal research interests are the development and validation of high-level ab initio and density functional theory methods, and the application of these procedures to problems in organic, inorganic, and organometallic chemistry. Gershom developed the popular Weizmann-*n* thermochemical protocols, the SDB-cc-pVnZ basis sets, and a number of density functional theory methods (most notably, BMK and DSD-PBEP86). He has published over 270 papers. His publications have over 15,000 citations and generate an h-index of 67. Gershom's achievements have been recognized through a number of prestigious awards, including the Dirac Medal of WATOC for "the outstanding computational chemist in the world under the age of 40" (2004), the Wolgin Prize for Scientific Excellence (2008), the Outstanding Young Scientist Award of the Israel Chemical Society (2000), and the 1997 Alumni Award of the Belgian-American Educational Foundation. He is a foreign member of the Belgian Royal Academy of Arts and Sciences (KVAB) and a IUPAC Fellow. Gershom's professional interests outside Chemistry include information technology and ESL/EFL teaching. His avocations include the science of music (about which he occasionally lectures), all aspects of history, and Jewish studies. Gershom is married to Wendy Gardner; they and their daughter Aviva are all 'owned' by a native Israeli 'rat terrier' named Lily.

Conference Venue

Lecture Hall G33
School of Chemistry and Biochemistry (Bayliss building)
The University of Western Australia (UWA)
35 Stirling Highway, Crawley 6009
Perth, WA, Australia



Directions:

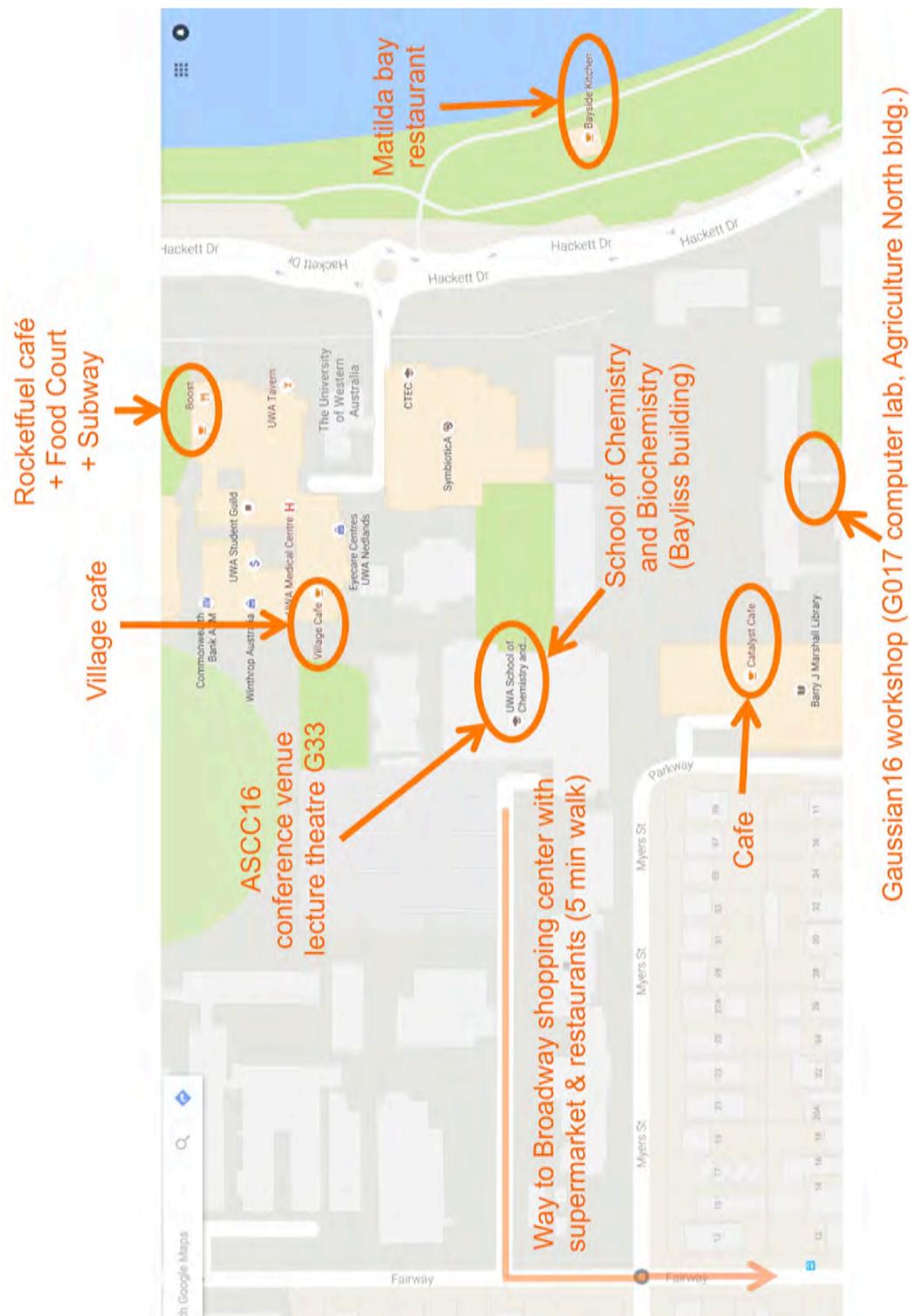
From Trinity College:

Follow the dotted blue line. Walk south on Hampden Rd (100m); cross Stirling Hwy; continue onto Broadway (350 m); at the roundabout turn left onto Edward St (100 m); turn right onto Fairway (200 m); turn left onto Fairway Entrance 4 (220 m); the back entrance of the School of Chemistry (Bayliss bldg.) is located at the end of the driveway.

By Taxi:

Ask the taxi driver to take you to "Fairway" in Crawley. It is simply Fairway, not Fairway street, avenue, or road... you need to enter the campus at Fairway Entrance 4 (black arrows on the map).

Coffee Shops and Restaurants Near the Conference



Gaussian16 Workshop, December 3–7, 2016

A five-day Gaussian workshop "Introduction to Gaussian 16: Theory and Practice" will be held after the ASCC16 conference. The workshop is hosted by Gaussian, Inc. in cooperation with the University of Western Australia. The workshop will be held at the computer lab on the ground floor of the Agriculture North building (Rm. G017, across the Science Library, 2 minute walk from the School of Chemistry and Biochemistry). Full details are available on the Gaussian website at: www.gaussian.com/g_ws/perth_16.htm.

Don't miss MM2017, Sep 27–29, Margaret River, Perth

The Association of Molecular Modellers of Australasia (AMMA) is pleased to announce that the next conference in the MM series (MM2017) will be held in Margaret River in Western Australia from the 27th to 29th of September 2017. A joint bio/materials workshop will be held on the 25th and 26th of September. The AMMA is an organization for molecular modellers, computational and theoretical chemists, cheminformaticians and other persons interested in the simulation of molecular structure, dynamics and properties and are an incorporated branch of the Molecular Graphics and Modelling Society (MGMS). For more details see <http://www.mgms.org.au/>.



ASCC16 Program, Day 1

Thursday, December 1, 2016

Time	Chair	Speaker	Title
8:50 – 9:00			Welcome to ASCC 2016
9:00 – 9:45	Peter Schwerdtfeger	Krishnan Raghavachari <i>[UWA LECTURE]</i>	Connectivity-based hierarchy to eliminate systematic errors: CCSD(T)-quality reaction enthalpies at MP2 or DFT-cost
9:45 – 10:05		Brian Yates	Gold-catalysed hydrofurylation of C–C multiple bonds
10:05 – 10:25		Michelle Coote	Directionality and the role of polarization in electrostatic catalysis
10:25 – 10:55			Coffee break
10:55 – 11:40	Brian Yates	Leo Radom	Personal reflections on 47 years in computational quantum chemistry
11:40 – 12:00		Peter Gill	How single are your doubles?
12:00 – 12:20		Richard Wong	Application of halogen bonding to organocatalysis
12:20 – 13:50			Lunch break
13:50 – 14:35		Jeff Hammond <i>[PAWSEY LECTURE]</i>	Hardware and software technology for coupled-cluster theory
14:35 – 14:55	Dylan Jayatilaka	Michael Collins	Fragmentation and direct <i>ab initio</i> molecular dynamics – Early days
14:55 – 15:15		Meredith Jordan	Walking in the Footsteps...
15:15 – 15:35		David Wilson	Carbon fragments stabilized by donor ligands
15:35 – 16:05			Coffee break
16:05 – 16:25		Brian Smith	To acidity and beyond
16:25 – 16:45	Michelle Coote	Shuhua Li	Homolytic cleavage of B–B bond via the cooperative catalysis of two Lewis bases: Computational design and experimental verification
16:45 – 17:05		Rika Kobayashi	Big chemistry
17:05 – 17:25		Joseph Lane	Quantifying the strength of intramolecular hydrogen bonds
17:25 – 17:45		David Henry	Soil water repellence at a molecular level: Molecular dynamics of amphiphilic compounds on mineral surfaces
17:45 – 19:00			Poster session and drinks

ASCC16 Program, Day 2

Friday, December 2, 2016

Time	Chair	Speaker	Title
9:00 – 9:45		Henry Schaefer <i>[NCI LECTURE]</i>	Leo Radom: Great scientist, great friend
9:45 – 10:05	Peter Gill	Peter Schwerdtfeger	The Lennard-Jones potential revised: Analytical solutions for the solid state from lattice sums and Epstein zeta functions
10:05 – 10:25		Jeffrey Reimers	The dispersion force: what is it, and how it can compete with covalent bonding
10:25 – 10:55	Coffee break		
10:55 – 11:40		Jan Martin	Double hybrids: The third way of quantum chemistry
11:40 – 12:00	Krishnan Raghavachari	Lars Goerigk	Double-hybrid density functionals: An old hat or is there anything new to tell?
12:00 – 12:20		Bun Chan	Double-hybrid density functional theory: Development and application to fullerene chemistry
12:20 – 12:40		Deborah Crittenden	The right tool for the right job: Adventures around the Pople table
12:40 – 14:00	Lunch break		
14:00 – 14:20		Mark Iron	Factors impacting the accuracy of ¹³ C NMR chemical shift predictions using density functional theory – The advantage of long-range corrected functionals
14:20 – 14:40	Jeffrey Reimers	Roger Amos	NMR shieldings using a fragment approach
14:40 – 15:00		Dylan Jayatilaka	Hydrogen atom positions and other derived properties in molecular crystals from combined X-ray diffraction and quantum chemistry refinements
15:00 – 15:20		Andrew Rohl	Simulating the physical performance of molecular crystals
15:20 – 15:40		Pierre-Francois Loos	Excited states of Wigner crystals
15:40 – 16:10	Coffee break		
16:10 – 16:30		Julian Gale	Exploring precursors to biomineral nucleation
16:30 – 16:50		Jing Ma	Polarization effects in the stimuli-responsive molecular monolayers under external electric field
16:50 – 17:10	Richard Wong	Alister Page	Extended timescale simulations – Combining global reaction route mapping with kinetic Monte Carlo theory
17:10 – 17:30		Irene Suarez-Martinez	Generation of nanoporous carbon-derived carbons by molecular dynamics
17:30 – 17:50		Paolo Raiteri	Entropy driven ion association
17:50 – 18:00	Poster prizes and closing remarks		
18:30 – 21:00	Banquet at the university club (pre-registration required)		

Abstracts:

Oral Presentations

Connectivity-Based Hierarchy to Eliminate Systematic Errors: CCSD(T)-Quality Reaction Enthalpies at MP2 or DFT-Cost

K. Raghavachari and A. Sengupta

Department of Chemistry, Indiana University, Bloomington, Indiana, United States

The generalized Connectivity-based hierarchy (CBH) developed in our group, comprises of well-defined and reliable error cancellation schemes to derive accurate enthalpies of formation of both *open* and *closed* shell organic molecules at modest computational cost [1-4]. Herein, we demonstrate the application of the CBH schemes to calculate accurate reaction enthalpies of a broad variety of organic reactions using inexpensive computational methods such as MP2 or DFT. A benchmark set of 25 organic reactions of medium and large molecules (consisting of 17 to 81 atoms) has been composed to evaluate the performance of a range of quantum chemical methods. The isoatomic CBH-2 corrections results in dramatic improvement for all the DFT and wavefunction methods, and thus offer a unique protocol consistent with different methods and different reaction types to obtain accurate reaction enthalpies. The performance of a range of ab initio and DFT methods will be described and assessed in this seminar.

[1] Raghavachari, K.; Saha, A. *Acc. Chem. Res.*, **2014**, *47*, 3596.

[2] Sengupta, A.; Ramabhadran, R. O.; Raghavachari, K., *J. Phys. Chem. B*, **2014**, *118*, 9631.

[3] Sengupta, A.; Raghavachari, K. *J. Chem. Theory Comput.*, **2014**, *10*, 4342.

[4] Sengupta, A.; Ramabhadran, R. O.; Raghavachari, K. *J. Comput. Chem.*, **2016**, *37*, 286.

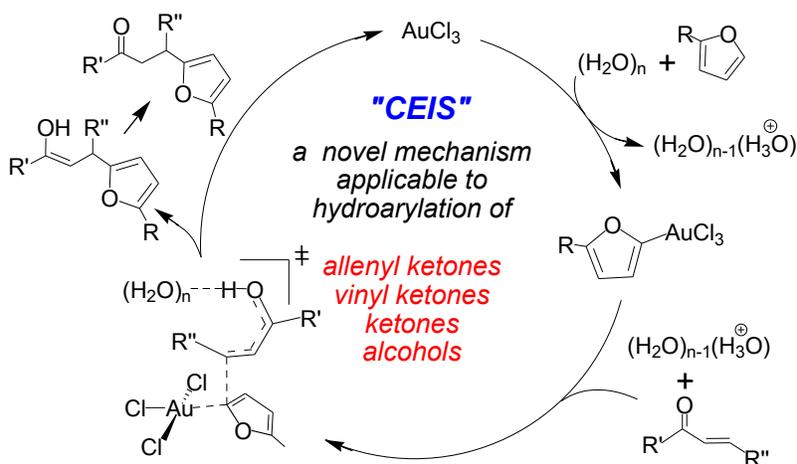
Gold-catalysed hydrofurylation of C–C multiple bonds

B. F. Yates¹, A. S. K. Hashmi² and A. Ariafard¹

¹ School of Physical Sciences, University of Tasmania, Hobart, Tasmania, Australia

² Organisch-Chemisches Institut, Universität Heidelberg, Heidelberg, Germany

In the literature, two major mechanisms have been proposed for gold-catalysed formation of C–C bonds with unsaturated substrates: inner-sphere syn-addition and outer-sphere anti-addition (a Friedel–Crafts-type mechanism). In this work, the AuCl₃-catalysed hydrofurylation of allenyl ketone, vinyl ketone, ketone and alcohol substrates has been investigated with the aid of density functional theory calculations and it is found that the corresponding functionalisations are best rationalised in terms of a novel mechanism called “concerted electrophilic ipso-substitution” (CEIS). We suggest [1] that the gold(III)-furyl σ -bond produced by furan auration acts as a nucleophile and attacks the protonated substrate via an outer-sphere process. This unprecedented mechanism needs to be considered as an alternative plausible pathway for gold(III)-catalysed arene functionalisation reactions in future studies.



[1] Bagi, A. H. et al. *J. Am. Chem. Soc.*, **2016**, *138*, 14599-14608.

Directionality and the Role of Polarization in Electrostatic Catalysis

M. L. Coote¹ and G. Gryn'ova²

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

² *Institut des Sciences et Ingénierie Chimiques, École polytechnique fédérale de Lausanne, CH-1015 Lausanne, Switzerland*

It is well known that the rate of redox reactions can be manipulated by means of an electrical potential gradient. However, as elegantly demonstrated by Shaik and co-workers, external electric fields should also be able to catalyse non-redox processes by electrostatically stabilizing the dipoles associated with charge-separated valence bond contributors of transition states, thereby enhancing resonance and lowering the barrier [1]. However, since these effects are directional in nature, implementing electrostatic catalysis in practice has been a challenge. Recently we have addressed this problem, and experimentally demonstrated practical electrostatic catalysis using two complementary approaches. First, we have used charged functional groups on the substrate, auxiliary or catalyst to deliver a localized oriented electric field that can be modulated by simple pH changes [2-3]. Second, we have used surface chemistry techniques to control the orientation of reagents in an external electric field [4]. Interestingly, our own theoretical studies of some of these systems indicate that, due to polarization, electrostatic effects on reaction barriers and enthalpies actually have a significant non-directional component [5-6]. This suggests we may one day be able to design reactions where alignment in an electric field is not necessary for catalysis, thus broadening its scope. This presentation will briefly outline our progress toward practical electrostatic catalysis, but with a focus on the role of polarization in determining the strength of these effects.

[1] Meir, R.; Chen, H.; Lai, W.; Shaik, S. *ChemPhysChem* **2010**, *11*, 301–310

[2] Gryn'ova, G.; Marshall D.L.; Blanksby S.J.; Coote, M.L. *Nature Chem.* **2013**, *5*, 474-481.

[3] Klinska, M.; Smith, L. M.; Gryn'ova, G.; Banwell, M. G.; Coote, M. L., *Chem. Sci.*, **2015** *6*, 5623–5627.

[4] Aragonès, A.C.; Haworth, N.L.; Darwish, N.; Ciampi, S.; Bloomfield, N.J.; Wallace, G.G.; Diez-Perez, I.; Coote, M.L., *Nature* **2016**, *531*, 88-91.

[5] Gryn'ova, G.; Coote, M.L. *J. Am. Chem. Soc.* **2013**, *135*, 15392-15403.

[6] Gryn'ova, G.; Coote, M.L. *Aust. J. Chem.* **2016**, in press.

Personal Reflections on 47 Years in Computational Quantum Chemistry

L. Radom

School of Chemistry, University of Sydney, Sydney, NSW 2006, Australia

In this presentation I will discuss the journey that I have taken during my 47 years in the field of computational quantum chemistry. With the assistance of my photo collection, I will discuss a selection of the people and organisations that have helped me along the way.

How single are your doubles?

G. M. J. Barca, A. T. B. Gilbert and P. M. W. Gill

Research School of Chemistry, Australian National University, Canberra, Australia

What am I asserting if I claim that a molecule is a “singly-excited electronic state”? Or, for that matter, a doubly- or triply-excited state? Do these descriptions correspond to an experimentally observable feature of the molecule? If not, do they correspond to a universally agreed theoretical definition? If not, which definition have we been using and are we confident that it’s a good one?

In this lecture and the associated poster, we argue that these questions have been either ignored or treated superficially by many researchers and that, as a result, it is likely that some states have been incorrectly classified in the past.

We propose a simple definition of the excitation number η that is easy to calculate and easy to interpret. We have computed η for a variety of excited states of a selection of organic and inorganic molecules and we find that it is almost always close to an integer. The rounded form of η provides clean and compelling answers to the opening questions above in all of the cases that we have investigated [1].

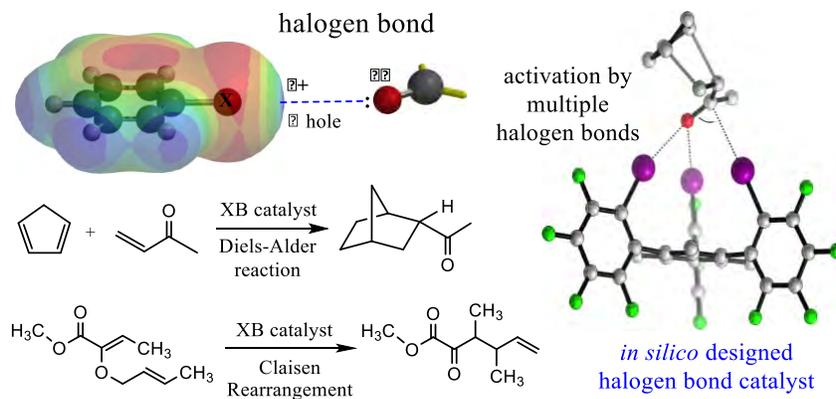
[1] Barca, G. M. J.; Gilbert, A. T. B.; Gill, P. M. W., *submitted*.

Application of Halogen Bonding to Organocatalysis

R. M. W. Wong and C. W. Kee

Department of Chemistry, National University of Singapore, 3 Science Drive 3,
Singapore 117543

Halogen bond, a noncovalent interaction involving a halogen atom as an acceptor of electron density, has emerged in recent years as an important element of molecular recognition and has numerous applications such as molecular self-assembly of functional materials and protein-drug interaction. Due to its bond strength and directionality, halogen bonding has great potential to become a complementary molecular tool to hydrogen bonding in rational catalyst design. Using density functional calculations, we have shown the use of halogen-bond donors as noncovalent activators in Lewis acid catalysis. In particular, we have proposed a new type of triaryl benzene organocatalysts via multiple halogen bond donors (e.g. perfluoro-iodophenyl group). This *in silico* designed halogen bonding (XB) based catalyst was applied to several important types of organic reaction, namely Diels-Alder reaction, Claisen rearrangement and cope-type hydroamination. The calculated catalytic mechanisms and activation barriers of these reactions readily demonstrate that the designed system is a promising Lewis acid catalyst via halogen bond mode of activation.^[1] On the basis of our DFT calculations and calculated turnover frequencies, the XB-catalyzed reactions are found to be competitive with the corresponding hydrogen bonding catalysis reported in literature. The calculated transition states unravel multiple halogen bonds between the iodine atoms and various types of halogen bond acceptors (lone pair, π and σ bonds). These cooperative non-covalent interactions provide efficient binding between the catalyst and substrate (~15 kcal/mol binding energy) and are the key factors for transition-state stabilization and molecular recognition.



[1] Kee, C. W.; Wong, M. W. *J. Org. Chem.* **2016**, *81*, 7475.

Hardware and software technology for coupled-cluster theory

J. R. Hammond

Data Center Group, Intel Corporation, Portland, Oregon, United States

Quantum many-body methods such as coupled-cluster theory pose unique challenges for computer hardware and software. On the hardware side, these methods stress essentially every component of a high-performance computing system, including floating-point computation, memory and network bandwidth, as well as storage capacity. On the software side, these methods require dozens if not hundreds of different tensor contractions to be expressed efficiently, often motivating the use of automatic code generation or generic programming techniques.

This talk will describe some of the recent developments in software technology for coupled-cluster methods, such as the Cyclops Tensor Framework [1], as well as the effort to port NWChem to Intel® Xeon Phi™ processors [2].

[1] E. Solomonik, D. Matthews, J. Hammond, J. Stanton and J. Demmel. *J. Par. Dist. Comp.* **74** (12), 3176–3190 (2014).

[2] E. Apra, K. Kowalski, J. R. Hammond, and M. Klemm. “NWChem: Quantum Chemistry Simulations at Scale” in *High Performance Parallelism Pearls*, eds. J. Reinders and J. Jeffers (Morgan Kaufmann, 2014).

Fragmentation and Direct Ab Initio Molecular Dynamics – Early Days

M. A. Collins

Research School of Chemistry, Australian National University, Canberra, Australia

Systematic molecular fragmentation decomposes molecules, crystals and liquids into relatively small molecules or clusters. The electronic energy or any other property of these fragments can be combined to give an accurate estimate of the energy or property of the whole system. Can this approach be usefully applied to the direct ab initio molecular dynamics of large (bio) molecules in solution? If so, chemical reactions of molecules in solution could be investigated with chemically accurate methods. This talk presents a solution to one of the (many) difficulties involved.

Walking in the Footsteps...

M. J. T. Jordan

School of Chemistry, The University of Sydney, NSW 2006, Australia

As our knowledge of chemistry and chemical systems evolve, new challenges come out of “old” problems. As we reassess our understanding of photochemical reactivity or as we attempt a theoretical problem as seemingly simple as the first principles prediction of the proton affinity of methane, the literature provides a road map of those who have been there before, either by studying the same problem in a different context or by providing the tools with which to answer it. This presentation is a testament to the influence and impact of our Honourees and how good methodologies and calculations do indeed stand the test of time.

Carbon fragments stabilized by donor ligands

D. J. D. Wilson¹, J. L. Dutton¹ and G. Frenking²

¹ *La Trobe Institute for Molecular Science (LIMS), La Trobe University, Melbourne, Australia*

² *Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse 1, D-35032 Marburg, Germany*

We report results from a computational investigation of low-oxidation state donor-acceptor complexes of the form L-En-L, where E is an element and L is a donor ligand – typically an N-heterocyclic carbene (NHC) [1-5]. In particular, results will be presented for ligand stabilised C₂ and C₃. The C₂ molecule has sparked much debate regarding its bonding – does it really have four bonds? The NHC-C₂-NHC compound exhibits a cumulene-type geometry around the central C₂ fragment, yet the reactivity is consistent with readily available carbon lone-pair electrons. Results will be presented from molecular orbital (MO), natural bond orbital (NBO) and energy decomposition analysis (EDA) to probe the fundamental nature of the bonding, thermodynamic stability and electronic structure of these fascinating systems (Fig.1).

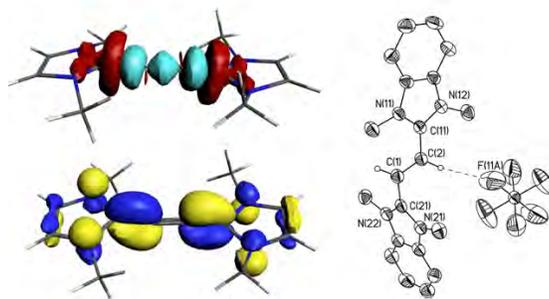


Figure 1. Donor-acceptor (density difference) plot of sigma donation and HOMO of the NHC-CC-NHC complex, and X-ray crystal structure of the related NHC-C(H)C(H)-NHC complex.

[1] Wilson, D.J.D.; Couchman, S.A.; Dutton, J.L. *Inorg. Chem.*, **2012**, *51*, 7657.

[2] Dutton, J.L.; Wilson, D.J.D. *Angew. Chem. Int. Ed.*, **2012**, *51*, 1477.

[3] Wilson, D.J.D.; Dutton, J.L. *Chem., Eur. J.*, **2013**, *19*, 13626.

[4] Couchman, S.A.; Holzmann, N.; Frenking, G.; Wilson, D.J.D.; Dutton, J.L. *Dalton Trans.*, **2013**, *42*, 11375.

[5] Georgiou, D.C.; Stringer, B.D.; Hogan, C.F.; Barnard, P.J.; Wilson, D.J.D.; Holzmann, N.; Frenking, G.; Dutton, J.L. *Chem. Eur. J.*, **2015**, *21*, 3377.

To acidity and beyond

B. J. Smith and N. A. Smith

Department of Chemistry and Physics, La Trobe Institute for Molecular Science, La Trobe University, Melbourne, Australia

In a series of papers dating back to 1991 [1-4], Smith and Radom reported the accurate prediction of gas-phase proton affinities using model chemistries and density functional theory. Today, composite methods routinely predict gas-phase proton reaction energies to within chemical accuracy. *Ab initio* prediction of condensed phase proton reaction energies is less well resolved. We will describe a QM+MM approach for the prediction of pKa values in aqueous solution that accounts explicitly for electrostriction of the solute and requires no parameterisation against experimental solvation energies.

[1] B.J. Smith, L. Radom. Evaluation of accurate gas-phase acidities. *J. Phys. Chem.* **1991**, *95*, 10549-10551.

[2] B.J. Smith, L. Radom. Assigning absolute values to proton affinities: a differentiation between competing scales. *J. Am. Chem. Soc.* **1993**, *115*, 4885-4888.

[3] B.J. Smith, L. Radom. An evaluation of the performance of density functional theory, MP4, F4, G2(MP2) and G2 procedures in predicting gas-phase proton affinities. *Chem. Phys. Lett.* **1994**, *231*, 345-351.

[4] B.J. Smith, L. Radom. Calculation of proton affinities using the G2(MP2,SVP) procedure. *J. Phys. Chem.* **1995**, *99*, 6468-6471.

Homolytic Cleavage of B-B Bond via the Cooperative Catalysis of Two Lewis Bases: Computational Design and Experimental Verification

S. Li

School of Chemistry and Chemical Engineering, Nanjing University, People's Republic of China. Email: shuhua@nju.edu.cn

In this talk, we report the computational design of an unprecedented diborane B-B bond activation mode and its experimental verifications. In this new B-B activation mode, the B-B bond of $B_2(\text{pin})_2$ can be homolytically cleaved via the cooperative catalysis of two 4-cyanopyridine molecules.¹ Free radical trapping and electron paramagnetic resonance (EPR) experiments provide strong support for the generation of the boryl radical. With this novel activation mode, we have experimentally realized the catalytic reduction of azo-compounds, the deoxygenation of sulfoxides and reduction of quinones with the present 4-cyanopyridine/ $B_2(\text{pin})_2$ system. Recently, our density functional theory investigations revealed that the pyridine-boryl radical generated *in situ* using 4-cyanopyridine and $B_2(\text{pin})_2$ could be used as a bifunctional “reagent”, which serves as not only a pyridine precursor but also a boryl radical. With the unique reactivity of such radicals, the 4-substituted pyridine derivatives could be synthesized under mild reaction conditions using α , β -unsaturated ketones and 4-cyanopyridine *via* a radical migration/C-C coupling mechanism.² The homolytic B-B activation mode via a cooperative Lewis base mechanism reported here may provide a new strategy for the diborane involved reactions.

[1] G. Wang, H. Zhang, J. Zhao, W. Li, J. Cao, C. Zhu*, and S. Li,* *Angew. Chem. Int. Ed.* 2016, 55, 5985

[2] G. Wang, J. Cao, L. Gao, W. Chen, W. Huang, X. Cheng,* and S. Li* submitted, 2016.

Big Chemistry

R. Kobayashi

*National Computational Infrastructure, The Australian National University, Canberra
2601, Australia*

The formal scaling of high-accuracy *ab initio* quantum chemical methods is such that they become impractical for sizeable systems of interest, such as biological molecules and bulk systems. There are many strategies for tackling the accurate computation of properties for large systems, making use of novel methodology or exploiting high-performance computing hardware. The first part of this talk will give an overview of some of the methods in popular use today, including recently obtained results using the systematic molecular fragmentation by annihilation approach. The second part of the talk will cover HPC issues, discussing how to make the most of the NCI infrastructure, and just what does Big Data mean to a chemist.

Quantifying the strength of intramolecular hydrogen bonds

J. R. Lane

*School of Science, Faculty of Science and Engineering, University of Waikato, Hamilton,
New Zealand*

Hydrogen bonding is important in a diverse range of applications in the fields of chemistry and biology including solvation, crystal packing, DNA base pairing, enzyme-drug binding, and protein folding. While several theoretical approaches exist to estimate the strength of intermolecular hydrogen bonds, the absence of a zeroth-order wavefunction for the donor and acceptor fragments of intramolecular hydrogen bonds makes this task non-trivial. In this work, we show that the integrated kinetic energy density can be used as a predictor of hydrogen bond strength. A series of complexes exhibiting intermolecular hydrogen bonds is used to predict the strength of some prototypical intramolecular hydrogen bonds.

Soil Water Repellence at a Molecular Level:

Molecular Dynamics of Amphiphilic Compounds on Mineral Surfaces

D. J. Henry¹, S. M. Uddin², N. Daniel,¹ L. Kitchens¹ and R. J. Harper²

¹ *Chemical and Metallurgical Engineering and Chemistry, Murdoch University, Perth, Western Australia, Australia*

² *School of Veterinary and Life Sciences, Murdoch University, Perth, Western Australia, Australia*

Hydrophobic soils are found under different climates and land uses all across the world [1]. However, this is a particularly common phenomenon in Australia with up to five million hectares affected [2]. Unfortunately, these non-wettable soils cause both environmental and economic problems including increased surface runoff, enhanced erosion rates and chemical leaching, decreased nutrient storage and plant-available water and reduced crop yields [3]. The hydrophobicity in these soils is generally attributed to organic compounds that originate from plant materials [4]. Our experimental investigation of this phenomenon is complemented by computer modelling of the structuring and interaction of organic species, on different soil types, to identify key driving forces. This study uses classical molecular dynamics simulations to examine the interactions of monolayers of various organic compounds on quartz, silica and kaolinite as a function of surface density. The simulations reveal quite different packing and interfacial interactions between wax molecules on sand/quartz (Fig. 1a) and clay/kaolinite surfaces (Fig. 1b), respectively [5]. Consequently, higher levels of wax material are required to render clay particles hydrophobic compared with sand particles.

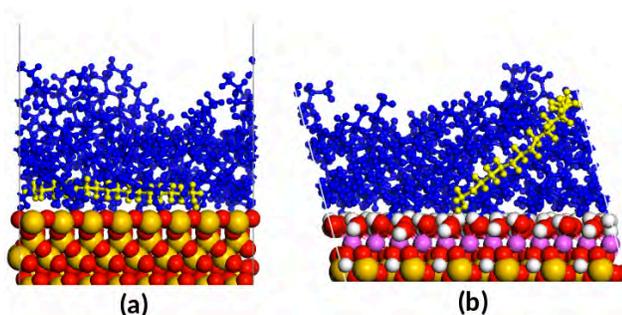


Figure 1. Alignment of $\text{CH}_3(\text{CH}_2)_{15}\text{OH}$ on (a) Quartz and (b) Kaolinite

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Leo Radom: Great Scientist, Great Friend

H. F. Schaefer III

*Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia
30602, United States*

The Lennard-Jones Potential Revisited: Analytical Solutions for the Solid State from Lattice Sums and Epstein Zeta Functions

P. Schwerdtfeger, E. Pahl and A. Burrows

Centre for Theoretical Chemistry and Physics, The New Zealand Institute for Advanced Study (NZIAS), Massey University, Auckland, New Zealand

The Lennard-Jones potential is the most widely used interaction potential between atoms with widespread applications in physical, chemical and biological sciences. This simple potential also has the advantage that the cohesive energy, pressure and the bulk modulus of a simple solid (simple cubic, body-centered cubic, and face-centered cubic) can be expressed analytically as a function of volume using lattice sums in three dimensions, originally developed by Hund, Born and Lennard-Jones. In a similar procedure to Lennard-Jones we derive analytical expressions for the zero-point vibrational energy and first-order anharmonicity corrections for these crystals by an inverse power expansion in terms of the internuclear distance, which we call the Extended Lennard-Jones potential. These new expressions are applied to the Lennard-Jones systems of rare gas solids from helium down to superheavy element oganesson ($Z=118$). We will show how to deal with slow converging lattice sums by expansion techniques such as the Epstein zeta function or Van der Hoff-Benson expansions in terms of Bessel functions. We also give an analytical solution for the hcp lattice for the first time. By doing so we can solve some old problems, e.g. why a simple Lennard-Jones potential always prefers hcp over fcc contrary to what is known from experiment. Moreover, through many-body expansions using computer intensive relativistic coupled cluster methods we can get the cohesive energy for solid Argon accurate to within 1 J/mol and within experimental accuracy [1].

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The dispersion force: what is it, and how it can compete with covalent bonding

J. R. Reimers^{1,2}, M. J. Ford², S. M. Marcuccio^{3,4}, J. Ulstrup⁵, T. Gould,⁶ and N. S. Hush⁷

¹ *International Centre for Quantum and Molecular Structures, College of Sciences, Shanghai University, China.*

² *School of Mathematical and Physical Sciences, The University of Technology Sydney, Australia.*

³ *Department of Chemistry and Physics, La Trobe Institute for Molecular Science, La Trobe University, Australia.*

⁴ *Advanced Molecular Technologies Pty Ltd, Scoresby, Vic. Australia.*

⁵ *Department of Chemistry, Technical University of Denmark, Denmark.*

⁶ *Queensland Micro- and Nanotechnology Centre, Griffith University, Nathan 4111, Australia*

⁷ *School of Molecular Bioscience, The University of Sydney, NSW 2006 Australia.*

The basic nature of the van der Waals dispersion interaction beyond the London approximation is described, along with modern computational methods for its treatment over a wide range of nanotechnological environments.¹⁻² Traditionally this has been regarded as being too weak to compete against covalent bonding for the determination of chemical structure, but recent examples showing valence tautomerization involving interchange of covalent and van der Waals bonds will be discussed.³ These include Fe(III)-thiolate to Fe(II)-thiyl transformations⁴ in cytochrome P450 and Au(I)-thiolate to Au(0)-thiyl transformations on gold metal and nanoparticle surfaces.⁵ All interactions between soft atoms are susceptible to dispersion forces.

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Double Hybrids: The Third Way of Quantum Chemistry

J. M. L. Martin¹, S. Kozuch², A. Karton³ and M. K. Kesharwani¹

¹ *Department of Organic Chemistry, Weizmann Institute of Science, 76100 Rehovot, Israel*

² *Department of Chemistry, Ben-Gurion University of the Negev, 84015 Beer-Sheva, Israel*

³ *School of Chemistry and Biochemistry, University of Western Australia, Perth, WA 6009, Australia*

On Perdew's "Jacob's Ladder" of DFT, the fifth rung is occupied by functionals dependent on the unoccupied orbitals. Double hybrids [1], in which both the exchange term contains some global (Hartree-Fock like) exchange and the correlation term contains some global (MP2-like) correlation are a special case of the fifth rung. The computational 'surcharge' over conventional DFT methods is actually quite modest if RI approximations are applied to the MP2-like step.

By introducing spin component scaling [3] and an empirical dispersion correction, we were able [4,5] to reach thermochemical accuracy rivalling G3-type composite thermochemistry schemes, while for harmonic frequencies we can reach about 10 cm⁻¹ accuracy with our DSD-PBEP86 functional. The earlier assertion [1,2] that double hybrids require LYP correlation for accuracy is an artefact of not introducing spin component scaling.

The use of the Caltech [7] rather than Grimme [1] form of the double hybrid — i.e., employing full GGA correlation in the KS orbitals — was found [8] to have a much smaller effect on accuracy if spin component scaling is used.

Very recently, following the work by Kállay and coworkers [9], we considered the use of dRPA rather than MP2 correlation. While this surprisingly yields somewhat poorer results for atomization energies of molecules with some static correlation, this is offset by outstanding performance for noncovalent interaction energies.

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Double-hybrid density functionals: an old hat or is there anything new to tell?

L. Goerigk

School of Chemistry, The University of Melbourne, Victoria 3010, Australia

Double-hybrid density functionals (DHDFs) can be considered as an extension of the hybrid density functional theory (hybrid-DFT) idea. Similarly to the latter, nonlocal Fock-exchange replaces a fraction of semi-local DFT exchange, but additionally, DHDFs also contain a nonlocal term substituting parts of semi-local DFT correlation. DHDFs have become established methods for electronic ground-state properties and combined with London-dispersion corrections, they can be considered as the currently most accurate DFT approximations for (main-group) thermochemistry, kinetics, noncovalent interactions, geometries, and frequencies [1].

In this talk, I will first give a brief overview of the current state of double-hybrid DFT for electronic ground states before I will discuss recent studies that explored strategies to further modify the current approximations [2,3].

Most researchers in the DFT community are probably unfamiliar with earlier work that has shown DHDFs to be accurate candidates for the calculation of excitation energies [1]. In the second part of my talk, I will therefore review these previous findings before I will outline our recent efforts to revive this area and to also make relatively new ground-state DHDFs applicable within a time-dependent DFT framework [4].

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Double-Hybrid Density Functional Theory: Development and Application to Fullerene Chemistry

B. Chan

*Graduate School of Engineering, Nagasaki University, Bunkyo 1-14, Nagasaki 852-8521,
Japan*

Double-hybrid density functional theory (DH-DFT) has over the past decade been established as an accurate and, at the same time, fairly economical computational chemistry tool. We have in recent years contributed to this development by devising methods to improve the efficiency of DH-DFT while maintaining its accuracy. Our strategies will be presented in this talk [1,2]. We will also demonstrate the use of DH-DFT to calculate the properties of fullerenes with unprecedented accuracy, and how such information lead us to gaining a deeper understanding of their unique chemistry [3,4].

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The right tool for the right job: Adventures around the Pople table

A. J. Wallace and D. L. Crittenden

Department of Chemistry, University of Canterbury, Christchurch, New Zealand

Conventional wisdom holds that the optimal balance between accuracy and computational cost in quantum chemistry calculations is achieved by traversing the Pople table [1] diagonally, from the bottom left (small basis, mean-field model) to the top right (large basis, highly correlated model).

However, we contend that substantial chemical insight into systems whose behaviour is dominated by static correlation may be derived by exploring the less popular upper left corner (small basis, highly correlated model), while the bottom right quadrant (large basis, mean-field and perturbation theory models) holds the key to assessing the importance of dynamic correlation. Two case studies will be presented by way of example.

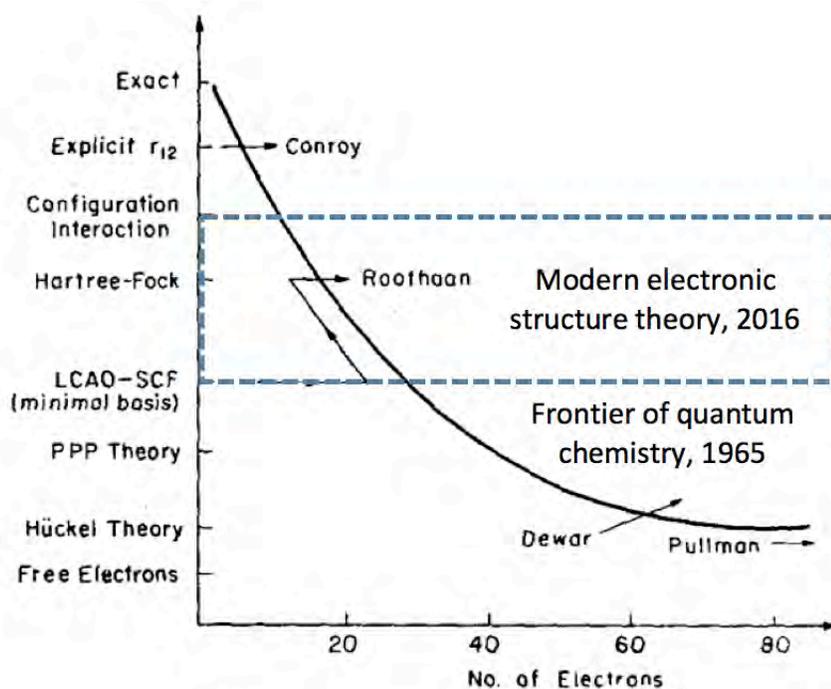


FIG. 1. A chart of quantum chemistry.

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Factors Impacting the Accuracy of ^{13}C NMR Chemical Shift Predictions Using Density Functional Theory – The Advantage of Long-Range Corrected Functionals

M. A. Iron

*Computational Chemistry Unit, Department of Chemical Research Support, Weizmann
Institute of Science, Rehovot, Israel*

Nuclear magnetic resonance (NMR) is an indispensable tool in organic, organometallic and inorganic chemistry. Its use is key in determining structure of compounds – including stereochemistry – and in following reactions.¹ On occasion, however, it is not always definitive, and the actual structure may be debated. The use of calculated chemical shifts is becoming indispensable in helping resolve the structure,² yet sometimes the results can be either inconclusive or even incorrect.

There have been a number of studies published each looking at the impact of certain factors on the accuracy of the calculated chemical shifts. Here, an in-depth study is presented where the key factors are considered: exchange-correlation functional – where over 70 are considered, basis set, integration grids, and the NMR calculation method. For the first time (to the best of my knowledge), long-range corrected functionals were considered and are shown to be more accurate than other functionals.

Recently, Smith and Goodman proposed the DP4 probability as a reliable tool in selecting which amongst a set of potential structures is the most likely based on comparison of the calculated and experimental NMR spectra.³ This method has found significant use in the determination of the stereochemistry of natural products with several chiral centres. The parameters for DP4 were determined for the method of choice found in this study.

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NMR Shieldings Using a Fragment Approach

R. Amos

*National Computational Infrastructure, The Australian National University, Canberra
2601, Australia*

There are many factors which determine the accuracy of calculated NMR shielding parameters – choices of basis sets and methodology, whether to include solvent effects, vibrational effects, and, in large molecules the ambiguity as to what is meant by the structure. The effect of basis set choice is greater than is generally realised. Specialised and very large basis sets, for example those of Jensen, are needed to reach the basis limit. We have applied (1) the Jensen basis sets to a moderately large molecule – a 10 peptide section of a protein – and have demonstrated that it is possible to reach the limit, and that it is very expensive. Fortunately the expense can be greatly reduced, by at least two orders of magnitude using a combination of a fragmentation technique and locally dense basis sets.

[1] Roger Amos and Rika Kobayashi, *Journal of Physical Chemistry A*, 2016,
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Hydrogen atom positions and other derived properties from in molecular crystals from combined X-ray diffraction and quantum chemistry refinements

D. Jayatilaka

School of Chemistry and Biochemistry, University of Western Australia, Nedlands, Australia

Physical experiments may be broadly characterised as spectroscopic or scattering. So far quantum chemistry has almost exclusively concerned itself with energy-related properties which are best measured by spectroscopic methods. However there is a wealth of data on molecular systems, in the form of crystals, from diffraction experiments on crystals.

In this talk I will outline our research program to combine quantum chemistry methods and X-ray diffraction methods.

1. I will concentrate on deriving accurate positional parameters from X-ray diffraction experiments where a quantum chemistry calculations is “geometry optimised” to the X-ray data rather than by minimising the energy. (The X-ray experiment gives the magnitude of the Fourier components of the electron density, typically comprising thousands or hundreds of thousands of individual measurements). I will concentrate on such refinement results for hydrogen atoms which usually cannot be seen in X-ray experiments [1]. Ideas for extending this to protein refinement will be discussed.
2. I will also briefly describe other kinds of electronic properties, especially refractive indices and in-crystal polarisabilities, derivable from “experimental wavefunctions” i.e. model quantum chemical wavefunctions whose electronic variables, the molecular orbitals, have been refined in order to fit the X-ray diffraction data [2].

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Simulating the physical performance of molecular crystals

D. J. Carter¹, I. A. Olson², A. G. Shtukenberg², S. Nilsson-Lill³, P. Raiteri¹, J. D. Gale¹, C. Boissier³, B. Kahr² and A. L. Rohl¹

¹*Curtin Institute for Computation and Department of Chemistry, Curtin University, WA, 6845 Australia*

²*Department of Chemistry and Molecular Design Institute, New York University, New York City, New York 10003, United States*

³*AstraZeneca, SE-431 83 Mölndal, Sweden*

Most material used in pharmaceutical development is crystalline in character. Consequently, simulation methods to predict the structures and energies of crystals and the defects within are of significant interest to the pharmaceutical industry as crystal properties are determined by these factors [1]. Despite this importance, there are few studies of extended defects in molecular crystals in the literature, a situation that we strongly believe needs to change. We will report on two studies that we have undertaken to extend knowledge in this area.

The first aims to build a computational methodology for the identification and relative quantification of slip planes, allowing also for distinguishing between elastic and plastic deformations and creation of dislocations. We will discuss the complex behaviour observed even for the simplest of molecular systems. In the second, a methodology for calculating the structure and energetics of screw dislocations in molecular crystals will be presented. The methodology is applied along [001] in *n*-hexane, *n*-octane, and *n*-decane crystals. The detailed structures of the dislocations will be discussed and the distribution of strain compared to linear elastic theory.

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Excited States of Wigner crystals

P. F. Loos and F. J. M. Rogers

*Research School of Chemistry, Australian National University, Canberra ACT 2601,
Australia*

Wigner crystals (WC) are electronic phases peculiar to low-density systems [1], particularly in the uniform electron gas [2]. Since its introduction in the early twentieth century, this model has remained essential to many aspects of electronic structure theory and condensed-matter physics. Although the ground-state WC (GSWC) has been thoroughly studied, the properties of excited-state WCs (ESWCs) are basically unknown [3]. In this talk, I will present a well-defined procedure to obtain an entire family of ESWCs in a one-dimensional electron gas using symmetry-broken Hartree-Fock calculations [4]. While the GSWC is a commensurate crystal (i.e. the number of density maxima equals the number of electrons), these ESWCs are incommensurate crystals exhibiting more or less maxima. Interestingly, they are lower in energy than the (uniform) Fermi fluid state. For some of these ESWCs we have found asymmetrical band gaps, which would lead to anisotropic conductivity. These properties are associated to unusual characteristics in their electronic structure.

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Exploring precursors to biomineral nucleation

J. D. Gale¹, P. Raiteri¹, R. Demichelis¹ and D. Gebauer²

¹ *Department of Chemistry, Curtin Institute for Computation and The Institute for Geoscience Research, Curtin University, Perth WA*

² *Department of Chemistry, Physical Chemistry, University of Konstanz, Konstanz, Germany*

Biomineralisation is a key natural process that leads to the formation of everything from bones and teeth, through to the structures that form the basis of coral reefs. One of the most ubiquitous such minerals is calcium carbonate, whose formation both influences ocean acidity and leads to the creation of problematic industrial scale. Because of the broad relevance of the crystallisation of this mineral there has been extensive interest in the mechanisms of nucleation. This was further piqued when it was proposed that pre-nucleation clusters existed for this system [1] leading to a re-evaluation of classical nucleation theory for this, and other systems [2].

While experiment provided evidence for the existence of clusters beyond ion pairing prior to the nucleation of calcium carbonate, structural information regarding the nature of such species was lacking. Computational investigations found that dynamic polymeric species could be formed at elevated concentrations [3], and this was later extended to propose that the initial nucleation event could involve a liquid-liquid phase separation [4].

In this study, we use computational methods to re-evaluate the possible pathways to nucleation for calcium carbonate in light of new experimental evidence that demonstrates that monodispersed nanoparticles can be created in the presence of appropriate ligands [5].

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Polarization effects in the stimuli-responsive molecular monolayers under external electric field

J. Ma¹, X. Wang, J. Zhao, Q. Zhu

¹ *School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P. R. China*

Under the exerted external electric field, significant polarization effects are demonstrated in the switching process of positively charged oligopeptide chains on gold surface by using the polarizable force field-based molecular dynamics (MD) simulations. [1-3] The changes of electrostatic environment during the conformation switching are described by calling density functional theory (DFT) calculations of atomic charges or fragment-centered dipole moments. The charge-variable polarizable force field (Q-POL) model shows a good agreement with all the experimental observations of open-circuit state (OC) without E_{ex} , extended conformation (ON) with upward E_{ex} , and bent conformation (OFF) with opposite E_{ex} , while the non-polarizable force field (Non-POL) with the fixed atomic partial charges fails in reproducing experiments for ON state. [2,3] A qualitative picture is depicted for understanding the polarization phenomena in the dielectric monolayer in OC/ON/OFF states. With the applied electric field, the rearrangement of ions leads to the induced internal E-field, E_{in} , in the direction opposite to external electric field. [3] The analysis of the induced internal E-field and interfacial potential may shed light on the further modification of theoretical models to better understand the electrical-induced switching mechanism.

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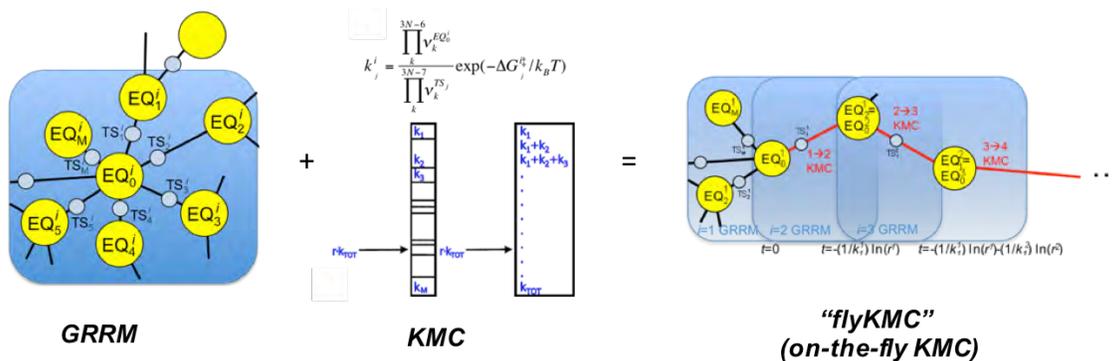
Extended Timescale Simulations - Combining Global Reaction Route Mapping with Kinetic Monte Carlo Theory

I. Mitchell¹, S. Irle² and A. J. Page²

¹ *The University of Newcastle, Australia*

² *Nagoya University, Japan*

I will present a new on-the-fly kinetic Monte Carlo (KMC) method, based on exhaustive potential energy surface searching carried out with the global reaction route mapping (GRRM) algorithm [1]. Starting from any given equilibrium structure, this GRRM-KMC algorithm performs a one-step GRRM search to identify all surrounding transition state barriers. Intrinsic reaction coordinate pathways are then calculated to identify potential subsequent equilibrium states. Harmonic transition state theory is used to calculate rate constants for all potential pathways, before a standard KMC accept/reject selection is performed. The selected pathway is then used to propagate the system forward in time, which is calculated on the basis of 1st order kinetics. I will discuss the performance of this new method in the context of molecular and nanoscale chemical problems, and demonstrate its capabilities for simulating emergent phenomena, such as self-assembly.



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Generation of Nanoporous Carbon-Derived Carbons by Molecular Dynamics

I. Suarez-Martinez, C. de Tomas, N.A. Marks

Department of Physics & Astronomy, Curtin University, Perth, Australia

Carbide-derived carbons (CDCs) are an important class of nanoporous carbons with applications including gas separation, hydrogen storage, catalyst supports and electrodes in batteries. The advantage of CDCs over other porous materials is that the pore size distribution is narrow and tunable through the choice of precursor material and processing conditions. Atomistic models of CDCs are highly sought after as they provide direct simulation of gas absorption. Historically, a range of different approaches have been employed (simply two infinite graphene sheets, manual construction by fullerene fragments or more complex Monte Carlo methods) in some cases with little correlation to experiments.

Here we present a fully mimetic method for the generation of CDCs atomistic structure based on Molecular Dynamics employing the Environment Dependent Interatomic Potential. Our large simulation cells allows the formation of both nanopores and mesopores giving a realistic CDC structures maintaining strong contact with experiments. Our correlation between experimental and simulation temperatures bridges the gap between experimental and simulations time scale mismatch in a rigorous way.

Entropy driven ion association

P Raiteri¹, M. Kellermeier², R. Demichelis¹, W. Zhao¹, E. H. Byrne¹, A. Schuitemaker¹, N. Garcia¹ and J. D. Gale¹

¹ *Department of Chemistry, Curtin Institute for Computation and The Institute for Geoscience Research, Curtin University, Perth WA*

² *Material Physics, BASF SE D-67056 Ludwigshafen (Germany)*

Minerals are ubiquitous materials that are present in our everyday life. They form rocks, scale around taps or in pipes, or, as in the case of biominerals, they constitute the hard parts in teeth, bones or skeletal material of invertebrates and marine life. On the Earth biominerals form almost exclusively from an aqueous solution where dissolved ions come together to form aggregates that eventually precipitate and grow to macroscopic sizes. Although this process is conceptually very simple there is still no definitive experimental or computational evidence of the molecular mechanisms that lead to the nucleation of mineral particles. In particular, in the last decade there has been a strong debate about whether classical nucleation theory could be applied to mineral growth or not, with the most controversial point being the existence of stable pre-nucleation clusters [1,2]. This idea is based on the assumption that multiple ion binding events have the same binding constant, which is well known in polymer chemistry [3], but has not yet been demonstrated for minerals and ionic systems.

In this presentation I will report on our recent all-atom classical molecular dynamics simulations of ion association [4]. I will discuss how the aggregation of ions and larger species is enthalpically unfavourable and driven by entropy, and what consequences this can have for the pre-nucleation stage of mineral growth.

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Abstracts:

Poster Presentations

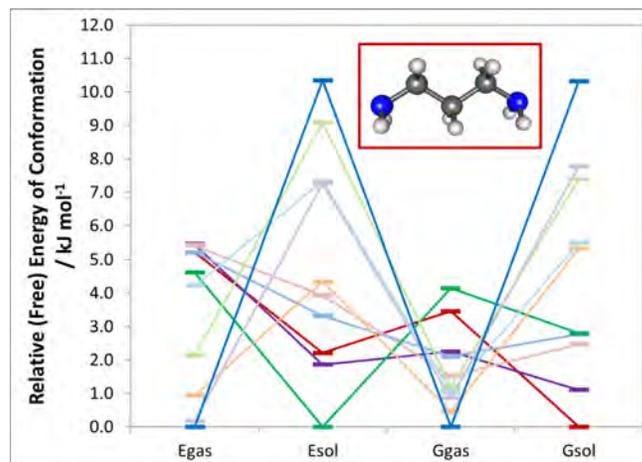
Predicting pKa – beyond small, rigid molecules

N.L. Haworth, Q. Wang and M. L. Coote

Poster # 1

*ARC Centre of Excellence for Electromaterials Science, Research School of Chemistry,
Australian National University, ACT, Australia.*

Accurate pKa values are crucial for assigning the protonation state of molecules in solution, and for assessing their susceptibility to proton transfer reactions. Whilst there is an abundance of experimental data in the literature, accurate measurements can be challenging or impossible for many systems, particularly metastable species and transition states. Hence, the development of accurate first principles methods for predicting pKa values is of great value and the subject of intense research activity.[1] Much of this activity has focused on developing methods which can give accurate pKa predictions for small rigid molecules. However, many of the systems which are of greatest chemical or biochemical interest are neither small nor rigid. In order to make reliable pKa predictions for such species, it is critical to correctly identify the molecular conformation(s) which are adopted in solution. Here we examine various approaches to comparing conformational stabilities, and identify the factors which are important for making selections which give good pKa predictions. Factors include the metrics used to compare conformations (energy or free energy, gas phase or solution phase), the methodology used to calculate solution phase free energies (thermocycles or entirely solution phase calculations), the inclusion of explicit water molecules and the use of “quasi-harmonic oscillator” approximations to reduce errors due to poor prediction of low energy vibrational frequencies. We have been exploring these factors in the context of predicting pKa values for a series of cationic amines and polyamines. This poster will outline our results and highlight some of the ongoing challenges in first principles pKa prediction.



[1] For a review see: Ho J., Coote M.L. *Theor. Chem. Acc.* **2010**, *125*, 3 - 21.

Designing a photorechargeable organic battery

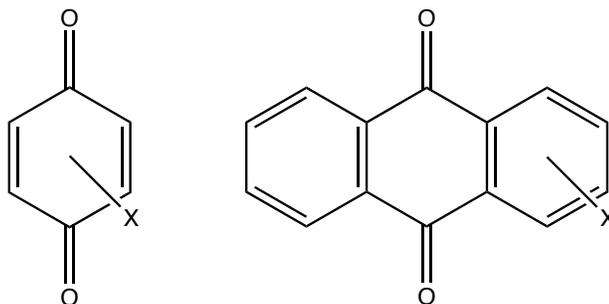
A. P. Flanagan and D. L. Crittenden

Poster # 2

Department of Chemistry, University of Canterbury, Christchurch, New Zealand

Quinones are promising species for energy storage in batteries as they are stable to multiple charge/discharge cycles and have redox potentials that can be tuned by attaching electron-donating or electron-withdrawing groups to the quinoid ring system, or altering the extent of the conjugated ring system.

The effect of chemical substitution on electrochemical energy storage capacity and charging overpotentials for pairs of substituted quinones was investigated using quantum chemical methods. Energies of all intermediates along the electrochemical charging pathway were calculated at B3LYP/6-311G+(2d,p) and solvent effects were approximated using C-PCM. Electron-withdrawing groups were found to lower activation energy barriers and enhance electrochemical energy storage capacity by stabilising reduced species, as well as stabilising radical and ionic intermediates.



Substituted benzoquinones (left) and anthraquinones were investigated.

New computational reactivity predictors of eliminative photocyclization

A. D. Dinga Wonanke and D. L. Crittenden

Poster # 3

University of Canterbury, Christchurch, New Zealand

Prediction of photocyclization reactions is a challenging task that has so far eluded resolutions by *cheap and reliable* computational chemical procedures. Previous approaches have focussed upon analysing the change in electron density upon photoexcitation, based upon bond order and atomic population density analyses. However, these methods are highly sensitive to both the quality of the underlying electronic structure method and the arbitrary nature of analysis schemes. Therefore, we have instead investigated geometrically-based reactivity predictors of eliminative photocyclization for a series of 40 molecules, of which 28 have been experimentally observed to photocyclize and 12 have not. Ground-state geometry optimizations were performed at HF/STO-3G, with subsequent single-point excited state calculations at the same level of theory accomplished using the maximum overlap method. Instantaneous changes in bonding patterns upon photoexcitation were analysed by projecting the induced forces onto bond vectors. In all cases, including molecules that are not experimentally observed to photocyclize, these results are consistent with the photocyclizing ring system becoming more aromatic in character. Forces along sigma bonds indicate that these will shorten in the excited state, with concomitant pi-bond lengthening. While these results do provide evidence of excited-state bond rearrangement, they don't explicitly indicate whether a molecule will photocyclize. Further studies will investigate the effects of changes in planarity and leaving-group efficacy.

Formation of Environmentally-Persistent Free Radicals (EPFR) on α - Al_2O_3 . A hydrated surface

N. W. Assaf¹, M. Altarawneh¹, M. Radny² and B. Z. Dlugogorski¹

Poster # 4

¹*School of Engineering and Information Technology, Murdoch University, Perth, Australia*

²*School of Mathematical and Physical Sciences, The University of Newcastle, New South Wales, Australia*

There is a growing body of literature that investigates the catalytic role of metal oxides in producing phenolic EPFRs. Alumina, as one of the metal oxide profuse with a high concentration in fly ash and the PM of the combustion systems, performs an active tendency toward producing EPFRs. This study presents a computational study of the catalytic role of α - Al_2O_3 (100) surface in producing phenolic EPFRs. First, we present the geometric and electronic properties of bulk α - Al_2O_3 . Then, we followed by a detailed investigation of the molecular and ionic (dissociation) interaction of phenol over α - Al_2O_3 (100). Molecular phenol is found to interact strongly, in a vertical and flat configurations, with requires binding energies of -114.5kJ, 146.5 kJ, respectively. Hydrated alumina surface is very active toward attack phenol molecule and form a phenoxy moiety, via H_2 elimination mechanism. Si- α - Al_2O_3 (100) substituted surface has also been considered. The energy required to form phenoxy moiety, over Si- α - Al_2O_3 (100) substituted surface, is found to be much smaller when compared to the clean hydrated alumina surface.

Remarkable selectivity of photoredox catalysts towards RAFT agents of thiocarbonylthio moieties

P. Seal and S. C. Smith

Poster # 5

*Integrated Materials Design Centre (IMDC), School of Chemical Engineering, UNSW
Australia, NSW 2052, Sydney, Australia*

It has been experimentally reported [1,2] that organic photoredox catalysts, pheophorbide *a* (PheoA) and zinc tetraphenylporphine (ZnTPP) has exceptional selectivity towards reversible addition-fragmentation chain transfer (RAFT) agents of dithiobenzoate, xanthate, and trithiocarbonate moieties. The present work provides a theoretical understanding on this selectivity. Our analyses based on energetics reveal the importance of non-bonded interactions present in the complexes formed by the catalysts with different RAFT agents. The most interesting observations lies in the molecular orbital analyses and their corresponding energies in the excited state, where we found a clear distinction and origin of this selectivity issues. Molecular orbitals analyses of the complexes reveal that it is the electron transfer between LUMO and LUMO + 1 orbitals in PheoA-RAFT agent complexes that plays the key role in this selectivity of PheoA towards dithiobenzoates, in particular that of CPADB. The complex PheoA-CPADB shows the least value for the crucial transition amongst all the other complexes studied in the excited state. For the complexes formed between RAFT agents and ZnTPP, it is the transition between LUMO and LUMO + 2, which occurs for the trithiocarbonate family of RAFT agents, thereby favouring their complex formation relative to that of xanthates and dithiobenzoates.

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Success and challenges in modelling photochemical reactions

M. F. Shaw¹, S. H. Kable² and M. J. T. Jordan¹

Poster # 6

¹ *School of Chemistry, University of Sydney, Sydney, NSW*

² *School of Chemistry, University of New South Wales, Sydney, NSW*

Our research involves a combined experimental and theoretical approach to the study of the photochemistry of small, atmospherically relevant molecules. Although photochemistry typically occurs from electronically excited states, there has been increasing evidence that previously overlooked reactions occurring on the S₀ surface are also significant.[1][2] We have used a range of computational methods to explore the potential energy surfaces of a series of aliphatic aldehydes and ketones, focusing on the interaction between the S₁, T₁, and S₀ surfaces and the reactive channels available in the actinic UV range. The more robust DFT and composite methods were found to give the best performance overall in predicting experimental barriers on all surfaces, while multi-reference and coupled cluster methods gave, surprisingly, generally less reliable results.

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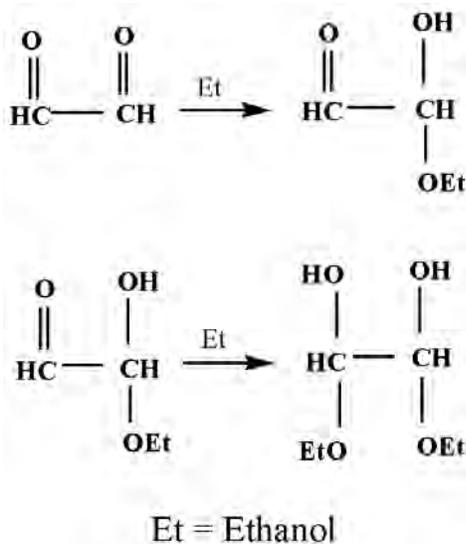
The reaction of glyoxal and ethanol: Formation of organic aerosol precursors

F. Sarrami, W. Wan, L.-J. Yu and A. Karton

Poster # 7

School of Chemistry and Biochemistry, The University of Western Australia, Perth, WA 6009, Australia

Glyoxal is an important contributor to secondary organic aerosols (SOA) formation. The present work examines the reaction of ethanol with glyoxal to form hemiacetal using high-level G4(MP2) quantum chemical calculations. We found that water and sulphuric acid catalysts can effectively catalyse this reaction. There are two important implications arising from these findings. First, the results suggest that under the catalytic influence of sulphuric acid, glyoxal hemiacetalisation can impact the growth of atmospheric aerosols. The hydrogen bonds between the polar OH groups in the di-hemiacetal products significantly lower the vapor pressure in the product relative to the parent glyoxal molecule; hence the product can more readily partition into the particle phase and contribute to the growth of SOA. Second, our findings provide valuable insights into how hemiacetal might be formed under atmospheric conditions and strongly suggest that the formation of this precursor for secondary organic aerosol growth is not likely restricted solely to the bulk aqueous phase as is currently assumed.



Theoretical study of the hydride transfer mechanism catalyzed by cholesterol oxidase

L.-J. Yu¹, N. Chen², E. Golden¹, Y. Zhao³, A. Vrieling¹ and A. Karton¹

Poster # 8

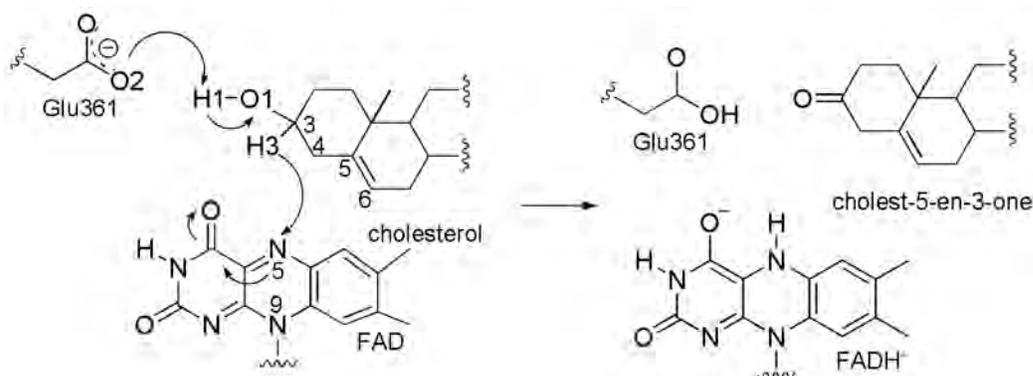
¹ School of Chemistry and Biochemistry, The University of Western Australia, Perth, WA 6009, Australia

² School of Pharmaceutical Sciences, Sun Yat-sen University, Guangzhou 510006, China

³ The Key Laboratory of natural Medicine and Immuno-Engineering, Henan University, Kaifeng 475004, China

Cholesterol oxidase (COx) is a flavoenzyme that catalyzes the oxidation and isomerisation of cholesterol to cholest-4-en-3-one. The recent high resolution X-ray structure of COx enables us to build a model of the COx reactive site composed of Glu361, the FAD cofactor, and the steroid substrate (Sub) (Scheme 1). It is proposed that COx catalyzes the oxidation of cholesterol *via* a hydride transfer from the substrate to the reactive center N5 of FAD and concomitant abstraction of the hydroxyl proton from Glu361. In this study we carried out extensive combined quantum mechanics and molecular mechanics molecular dynamics (QM/MM MD) simulations and classical molecular dynamics (MD) simulations to obtain an in-depth understanding of the flavoenzyme catalysis.^[1,2] These simulations were augmented by high-level double-hybrid density functional theory (DHDFT) calculations, which further elucidate the catalytic roles of a number of key residues in the hydride transfer (namely, Glu361, Gly120, and His447).

Scheme 1. Proposed mechanism for the oxidation reaction catalyzed by COx.



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Interatomic potentials for carbon

C. de Tomas¹, I. Suarez-Martinez¹ and N. A. Marks¹

Poster # 9

¹ *Department of Physics and Astronomy, Curtin University, Perth WA 6102, Australia*

Carbon has proved a difficult element to study using molecular dynamics (MD). The principal difficulty is that the interatomic potential is non-trivial to establish due to the complexity of the competing hybridizations and long-range effects associated with pi-electrons. Unlike metals and oxides, where useful potentials were developed decades earlier, the first useful potential for carbon only appeared in 1988 from Tersoff. Two years later Brenner built upon Tersoff's method to create the hydrocarbon-oriented Reactive Empirical Bond-Order (REBO) potential. Today, these two pioneering articles have a combined footprint of nearly 4000 citations, the balance in favour of REBO by slightly more than 2:1.

Many other potentials have subsequently been developed, often directed towards a specific application or niche. At the present time, nearly 40 different carbon potentials can be identified in the literature, some suited only to carbon, while others also treat interactions with species such as hydrogen, oxygen and silicon. Many of these potentials have not been made publicly available to the computational community, and only a handful have been coded into open-source packages such as LAMMPS, DLPOLY or GULP. In recent years LAMMPS has emerged as the default MD package in materials science and for many carbon scientists if a potential is not in LAMMPS it may as well not exist. While LAMMPS has made the life of a computational researcher easier due to its accessibility and high level of parallelization, the transferability of the underlying potential is often not questioned. This opens the risk that a potential will be applied to a system where the potential itself is unsuitable.

In this work we perform a systematic comparative study of five common carbon interatomic potentials: Tersoff, REBO-II, ReaxFF, EDIP and LCBOP-I. All of the potentials are used exactly as implemented in LAMMPS. Using the liquid quenching method we generate amorphous carbons at different densities, and subsequently anneal to high temperature. The amorphous carbon system provides a critical test of the transferability of the potential, while the annealing simulations illustrate the graphitization process and test bond-making and bond-breaking. A wide spread of behavior is seen across the five potentials, with quantities such as sp^2 fraction, morphology, ring statistics, and 002 reflection intensity differing considerably [1]. These results highlight the importance of choosing the appropriate potential, and motivate this study as a reference point to assess future studies.

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Thumbs up for PcTx1 – mechanistic insight into the binding of the venom peptide PcTx1 to the acid sensing ion channel 1a from free energy calculations

E. Deplazes^{1,2,3}, M. Stroet, G. F. King³ and A. E. Mark^{2,3}

Poster # 10

¹*School of Biomedical Sciences Curtin University, Perth, Australia*

²*School of Chemistry & Molecular Biosciences; ³Institute for Molecular Bioscience, The University of Queensland, Brisbane, Australia.*

The acid sensing ion channel 1a (ASIC1a) is a proton-gated channel involved in many physiological processes and a drug target for treating neurological disorder and pain. PcTx1, a 40-residue peptide isolated from the venom of the tarantula *Psalma cabridgei*, is the most potent selective inhibitor of ASIC1a. Recent crystal structures of the ASIC1a-PcTx1 complex have revealed an extensive network of peptide-channel contacts. Our subsequent study combining simulations and mutagenesis of the peptide and the channel revealed that only a subset of the many contacts in the ASIC1a-PcTx1 crystal structure are critical for PcTx1 activity, thus defining the main pharmacophore of PcTx1. Despite the large amount of structural and functional information on the binding of PcTx1 to ASIC1a, little is known about the thermodynamics and pathway of binding.

In this study we use free energy calculations as well as unrestrained MD simulations of the apo channel and the ASIC1a-PcTx1 complex to investigate the binding of PcTx1 to ASIC1a at atomistic resolution. The free energy calculations predict a binding free energy (ΔG) of -52 kJ mol^{-1} , which is in very good agreement with experimental binding affinities. The simulations reveal that binding of PcTx1 is a highly dynamic, two-state process that involves formation of transient interactions and previously unseen conformational changes in the channel. Furthermore, the simulations revealed that the binding of a single peptide induces the same conformational changes in all three subunits of the channel indicating that the binding of PcTx1 is cooperative. This investigation represents the first extensive simulation study of a peptide-ASIC complex and provides new mechanistic insight into the binding of PcTx1 that is likely relevant to the binding of other venom peptides to ASIC1a.

As part of this study we have also developed a freely available Python implementation of the UI method that include error analysis and convergence checks.

Growth Mechanism of Boron Nitride Nanotubes in Chemical Vapour Deposition: Nonequilibrium Molecular Dynamics Simulations

B. McLean¹, G. B. Webber¹ and A. Page¹

Poster # 11

¹ *Discipline of Chemistry, The University of Newcastle, Callaghan, NSW, Australia*

Boron nitride nanotubes (BNNTs), first predicted in 1994 [1] and experimentally realised in 1995 [2], are structural analogues to carbon nanotubes (CNTs). Unlike CNTs, BNNTs exhibit the same physical properties independent of the tube chirality, with a wide band gap of 5-6 eV [3]. Among other techniques [4], BNNTs can be synthesised effectively via chemical vapour deposition (CVD) [5]. While numerous reaction conditions and precursors have been tested, the so-called boron oxide CVD (BOCVD) method produced the first successful synthesis of patterned, vertically aligned, pure BNNTs. A reaction at high temperatures between boron powder and MgO and/or FeO produces gaseous B₂O₂. This reacts with ambient NH₃ to form solid BN on a metal catalyst surface [6-8]:



The mechanism of growth during this process is not well understood. Here we report nonequilibrium molecular dynamics simulations of CVD BNNT growth from B₂O₂ and NH₃ precursors, based on the ReaxFF reactive force-field [9]. We demonstrate how this mechanism is influenced by pertinent experimental parameters, such as reactor temperature, pressure and the presence/absence of catalytic (Ni/Fe) nanoparticles.

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Unphysical nucleation of diamond in the Extended Tersoff potential

A. Aghajamali, C. de Tomas, I. Suarez-Martinez and N. A. Marks

Poster # 12

Department of Physics & Astronomy, Curtin University, Perth, Australia

Molecular Dynamics simulations of carbon materials is a challenging problem. This is mainly due to the difficulties in constructing an interatomic potential that represent carbon's complexity of the competing hybridizations as well as long-range effects associated with π -electrons. More than 40 carbon potentials and modifications have been published but their transferability across different situations is not always appropriate [1]. The first useful potential for carbon only appeared in 1988 from Tersoff [2] and since then a number of modifications and reparametizations have been pulished in order to correct some its deficiencies.

Here we reveal an up-to-now unknown deficiency of the Tersoff potential associated with modification of its cut-off radius. We show that the common modification known as 'extended Tersoff' expands the cutoff of the potential into the second neighbour coordination shell, resulting in the unphysical nucleation of diamond during annealing of amorphous carbon.

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[2] Tersoff, J. *Phys. Rev. Lett.*, **1988**, 2879.

Reaction of Alkyl Halides with the Copper (100) Surface

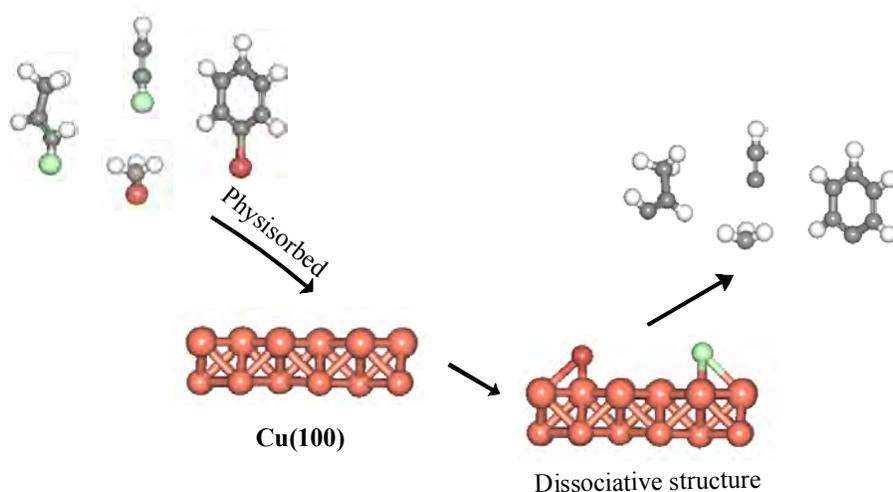
O. H. Ahmed^{1,2}, M. Altarawneh¹, Z. T. Jiang¹ and B. Z. Dlugogorski

Poster # 13

¹ *School of Engineering and Information Technology, Murdoch University
Murdoch, WA 6150, Australia*

² *Department of Physics, College of Education, Al- Iraqia University, Baghdad, Iraq*

The interplay of alkyl halides with metal surfaces has been the focus of many experimental studies. These investigations have mainly aimed to illustrate the potential role of transitional metals and their oxides in mediating formation of toxic halogenated aromatics from the fragmentation of smaller C₁-C₃ cuts as well as from condensation of halogenated benzenes. An initial and prominent step in conversion of these precursors into heavier halogenated aromatics signifies their dissociative adsorption on metallic species present in the combustion media. This contribution represents a systematic computational study to examine thermo-kinetic parameters underlying rupture of Cl/Br-C bonds in halogenated model compounds (namely; chloromethane, 2-chloropropane, chloropropene, chlorobenzene, chloroethyne, bromomethane, 2-bromopropane, bromopropene, bromobenzene and bromoethyne) over the Cu (100) surface). These compounds adapt very weak physisorbed molecular states in several flat and vertical orientations. Calculated reaction barriers for Cl/Br-C bond fissions are scattered in the range of 40 – 120 kJ/mol. Stronger Cl – C bonds in reference to Br – C bonds translate into higher corresponding reaction barriers for the former. Results from this study should provide an insight into the heterogeneous formation of halogenated pollutants in thermal systems.



Solvation Effects with Hybrid Quantum Monte Carlo and Polarizable Molecular Mechanics Method

N. M. Thellamurege, A. S. Barnard and M. C. Per

Poster # 14

*Molecular & Materials Modelling, Data61, CSIRO, The Goods Shed Docklands,
710 Docklands VIC 3008*

Inclusion of solvation effects in quantum mechanical calculations is important to make accurate and realistic predictions of molecular properties. The main challenge in this kind of calculations is to include a considerable region of the solvent or the environment in the quantum mechanical calculations to capture all the important solute solvent interactions. Because of the high computational cost it is not feasible to include all the solvent molecules in a calculation using a high-level quantum mechanics method. One solution to this problem is to treat the solute or the chemically interesting region of the system with a high level of theory while the solvent or the environment with a much more efficient low cost method. There are two common approaches of including the solvent region in such calculations i.e. 1) using explicit solvent models, in which force fields are used to describe the solvent molecules, and 2) using the continuum solvent models, where the solvent region is treated with a dielectric medium and the interaction with the solute molecule is evaluated by some charges induced on the solute molecular surface. When using force fields it is important to take polarization into account to capture the electrostatic effects accurately [1].

When considering high level quantum mechanical methods, coupled-cluster method is known as the gold standard but also has the drawback of high computational cost, poor scaling with system size and high memory requirements. This limits it from being applied to large molecular systems. Alternatively, Quantum Monte Carlo (QMC) methods have emerged as a similarly accurate method [2]. The most attractive feature of QMC is that it scales better than the coupled-cluster methods as the number of electrons of the system becomes larger. In this work, we demonstrate the implementation of a combined approach where QMC method is, combined with polarizable force fields to model solute-solvent interactions. Partial charges and induced dipoles are used to describe the electrostatics of the molecular mechanics region. Then we apply this approach to calculate the solvent effect on the deprotonation energy of some model carbon acids.

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Atomistic simulation of AFM imaging of calcite surfaces with point defects in solution

B. Reischl, P. Raiteri, Julian D. Gale and A. L. Rohl

Poster # 15

*Curtin Institute for Computation and Department of Chemistry,
Curtin University, Perth, Western Australia*

While the atomic force microscope (AFM) is able to image mineral surfaces in solution with atomic resolution, so far the theory for whether imaging point defects is also possible under these conditions has not been established. Even though AFM images of atomic-scale isolated features have been reported on surfaces such as calcite in solution [1], they are difficult to interpret, due to the limited knowledge of what types of defects may be stable in the presence of an AFM tip, and the complex imaging mechanism in water, involving interactions between hydration layers over the surface and around the tip [2].

Here, we present atomistic molecular dynamics and free energy calculations [3] as well as simulated AFM images [4] of vacancies and ionic substitutions in the calcite (10.4) surface in water, obtained with a new silica AFM tip model [5]. Our results indicate that both calcium and carbonate vacancies, as well as a magnesium substitution, could be resolved in an AFM experiment, albeit with very different imaging mechanisms: the calcium vacancy and the magnesium substitution are imaged as a change in the structure of the first hydration layer, above the calcium sub-lattice, and may lead to very similar contrasts in a 2D AFM image. The carbonate vacancy is best imaged at closer tip-surface distances, when the tip comes into hard contact with the surface ions. These results also highlight the need for 3D AFM imaging [6] of the interfacial space, in order to attempt a proper characterization of point defects.

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Elucidating the Structure/Property Relationships of Peptide-promoted Catalytic Au Nanoparticles

Z. E. Hughes and T. R. Walsh

Poster # 16

Institute for Frontier Materials, Deakin University, Geelong, Vic. 3216, Australia

The ability to exploit the structure-function relationship of peptide-decorated nanoparticles (NPs) in solution offers a promising method for the green production of catalytically-active nanomaterials with controllable functionality [1]. A recently synthesized series of peptide-promoted catalytic Au nanoparticles (PEPCANs) is one example of these promising new nanomaterials [2]. However, to fully realise the potential of these new materials, clear connections between the catalytic performance of these systems and their structures, both of the metallic nanoparticle and the adsorbed multi-peptide overlayer, must be established. Experimental studies have determined the atomistic-level structure of these metallic NPs, as well as investigating their catalytic ability [2], but resolution of the structures of the adsorbed peptide overlayer via experimental techniques alone is challenging. Molecular simulation provides a complementary approach to predicting the structure(s) of biomolecules adsorbed at aqueous metal interfaces [3]. However, the majority of these studies have investigated the behaviour of peptides adsorbed at periodic surfaces or ideally faceted NPs, rather than NP surfaces with irregular features occurring on the nanoscale. In contrast, recent experimental evidence shows that peptide-synthesised AuNPs feature surface irregularities.[2] We predict the structure and binding properties of the non-covalently adsorbed peptide overlayer for ten different PEPCANs (ten different peptide/Au NP combinations) that have been shown to support varying degrees of catalytic activity [2]. The structure of the underlying Au NP was determined from atomic pair distribution function analysis of high energy X-ray diffraction data [2]. Using a Hamiltonian replica-exchange molecular technique [4], essential for ensuring sufficient conformational sampling, we predict the morphology of the adsorbed peptide overlayers. Our simulations reveal the major factors responsible for the catalytic activity of the PEPCANs. From these results we devise a simplified computational method for the prediction of catalytic performance, thus providing a screening approach for future studies and enabling the development of rational design rules for catalytic bio-nano-materials.

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Subsurface Oxygen Vacancy Diffusion in Cubic SrTiO₃

J. J. Brown¹ and A. J. Page¹

Poster # 17

¹ *Department of Chemistry, University of Newcastle, Newcastle, New South Wales, Australia*

The formation of oxygen vacancy defects and their diffusion through perovskite materials important in considerations of material stability for synthesis as well as bulk and surface properties need for various applications¹. Strontium Titanate (SrTiO₃) has attracted attention in this field due to its insulating properties, thermal stability, optical transparency and electronic properties that are ideal for hydrogen and oxygen evolution reactions^{2,3}. SrTiO₃ has also been the focus of several band gap engineering and surface catalysis investigations^{4,5}. While oxygen vacancy formation and diffusion in bulk cubic SrTiO₃ has been studied previously,^{3,4,6} oxygen defect diffusion barriers at the catalytic interface (i.e. surface/subsurface region) remain unexplored.

Herein we consider formation and diffusion energy barriers of oxygen vacancies in the surface/subsurface region of [0001] SrTiO₃ using density functional theory. We report an optimised DFT+U+J protocol for modelling the SrTiO₃ catalytic interface and present a systematic study demonstrating how oxygen vacancy defects migrate between the surface and the bulk material.

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Empirical molecular modelling of the interactions of PIBSA-based surfactants with Ammonium Nitrate (IV)

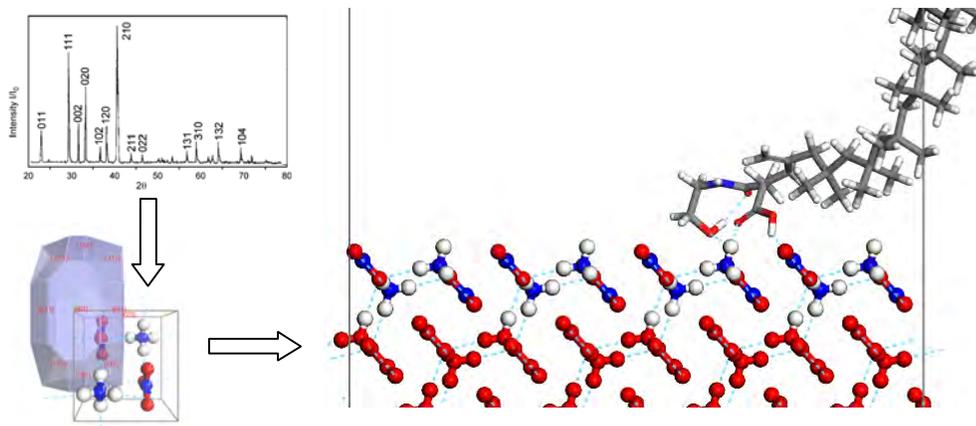
M. M. van der Merwe¹, M. Landman², P. H. van Rooyen³ and M. Meunier⁴

Poster # 18

^{1,2,3} Department of Chemistry, University of Pretoria, Pretoria, South Africa

⁴Dassault Systèmes BIOVIA Ltd. 334 Milton Road Science Park, Cambridge, U.K.

PIBSA-based surfactants are widely used by mining industry to achieve a long term kinetic stability of high internal phase emulsions - HIPEs [1]. Shelf life and stability of these emulsions have been affected by the droplet coalescence and crystallization of the salt over time. The mechanism of stability has been partially attributed to the interactions of the surfactants with the internal phase, which typically consists of a supersaturated salt solution in water. However, previous reports of the nature of these interactions at the interphase were inconclusive [2-3]. It was hypothesised that some useful insight could be derived from computational study of the interactions of the three widely used PIBSA-based surfactants, which render various levels of emulsion stability, with the morphologically important faces of the salt. Empirical molecular modelling of the salt with *ab-initio* optimised CompassII force field allowed to identify morphologically important crystal faces of the salt [4-5]. These findings correlated well with the experimental and theoretical XPD patterns of the salt [6-7]. The adsorption energies of the three surfactants with some of the crystal surfaces were found to correlate with the stability pattern derived from the experimental studies of the HIPEs. To the best of our knowledge these findings have not been previously reported.



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Basis-set convergence of equilibrium geometries for CCSD(T)

P. R. Spackman, D. Jayatilaka and A. Karton

Poster # 19

School of Chemistry and Biochemistry, The University of Western Australia, Perth, Australia

We examine[1] the basis set convergence of the CCSD(T) method for obtaining the structures of the 108 neutral first- and second-row species in the W4-11 database (with up to five non-hydrogen atoms). As reference values, geometries optimized at the CCSD(T)/aug'-cc-pV(6+d)Z level of theory are used. We consider the basis set convergence of the CCSD(T) method with the correlation consistent basis sets cc-pV(n+d)Z and aug'-cc-pV(n+d)Z (n = D, T, Q, 5) and the Weigend–Ahlich def2-n ZVPP basis sets (n = T, Q).

The double-zeta and triple-zeta quality basis sets systematically and significantly overestimate the bond distances. A simple and cost-effective way to improve the performance of these basis sets is to scale the bond distances by an empirical scaling factor.

The basis set convergence of larger basis sets can be accelerated via standard basis-set extrapolations. In addition, the basis set convergence of explicitly correlated CCSD(T)-F12 calculations is investigated in conjunction with the cc-pVnZ-F12 basis sets (n = D, T). Typically, one 'gains' two angular momenta in the explicitly correlated calculations. Overall, the CCSD(T)-F12/cc-pVDZ-F12 level of theory offers a stellar price-performance ratio and we recommend using it when highly accurate reference geometries are needed (e.g., in composite ab initio theories such as W4 and HEAT).

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Algorithmic comparison and analysis of decorated molecular surfaces in the crystalline context.

P. R. Spackman, S. P. Thomas and D. Jayatilaka

Poster # 20

School of Chemistry and Biochemistry, The University of Western Australia, Perth, Australia

Molecular shape is important in both crystallisation and supramolecular assembly, yet its role is not completely understood. We present[1] a computationally efficient scheme to describe and classify the molecular shapes in crystals. The method involves rotation invariant description of Hirshfeld surfaces in terms of spherical harmonic functions. Hirshfeld surfaces represent the boundaries of a molecule in the crystalline environment, and are widely used to visualise and interpret crystalline interactions.

The spherical harmonic description of molecular shapes are compared and classified by means of principal component analysis and cluster analysis. When applied to a series of metals, the method results in a clear classification based on their lattice type. When applied to around 300 crystal structures comprising of series of substituted benzenes, naphthalenes and phenylbenzamide it shows the capacity to classify structures based on chemical scaffolds, chemical isosterism, and conformational similarity.

The computational efficiency of the method is demonstrated with an application to over 14 thousand crystal structures. High throughput screening of molecular shapes and interaction surfaces in the Cambridge Structural Database (CSD) using this method has direct applications in drug discovery, supramolecular chemistry and materials design.

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Assessment of Orbital-Optimisation for Double-Hybrid Density Functionals and Second-Order Møller-Plesset Perturbation Theory

Methods

A. Najibi and L. Goerigk

Poster # 21

School of Chemistry, The University of Melbourne, Melbourne, Victoria, Australia

Orbital-optimisation for methods based on Møller-Plesset perturbation theory have been shown to be useful for the quantum-chemical description of open-shell systems and transition states [1]. In addition, double-hybrid density functionals (DHDFs) have been shown to be the most robust and accurate class of density functionals [2].

Double-hybrid density functionals (DHDFs) contain a portion of MP2-type correlation energy obtained from Kohn-Sham orbitals, thus orbital-optimisation can be achieved for them. Preliminary studies suggest that orbital-optimisation could be a viable technique to improve DHDFs [3]. However, these studies were limited to three ‘non-empirical’ DHDFs that were all based on Perdew-Burke-Ernzerhof (PBE) exchange and correlation contributions. There have not been any extensive studies on orbital-optimised DHDFs that also take into account other underlying exchange and correlation functionals. Also, the effect of spin-component scaling (SCS) on orbital-optimised DHDFs has not been investigated.

This presentation thoroughly discusses orbital-optimisation for DHDFs, MP2 and the spin-component-scaled MP2 (SCS-MP2) and spin-opposite-scaled MP2 (SOS-MP2) methods, for 20 different sets of chemical situations.

We find that orbital-optimisation does not remedy the inability of DHDFs to properly describe van der Waals forces, but gives improvements for SCS-MP2 and SOS-MP2 when dealing with non-covalent interactions.

Calculations involving transition states only improve with orbital-optimisation for open-shell systems using the MP2 methods.

The overall effect of orbital-optimisation is found to be mostly negligible for closed-shell systems for the DHDFs and SCS/SOS-MP2. However, orbital-optimisation mostly improves SCS-MP2, SOS-MP2, and slightly improves some DHDFs for open-shell systems (but this does not sufficiently exceed the accuracy of other underlying DHDFs).

Our extensive study therefore shows that orbital-optimisation may not be justified for DHDFs and that other strategies to improve these already highly accurate methods need to be employed.

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Predicting the highest intensity peak (primary fragment) in electron impact mass spectroscopy using Roby bond indices

K. Alhameedi and D. Jayatilaka

Poster # 22

School of Chemistry and Biochemistry, University of Western Australia, Nedlands, Australia

In 2001 Mayer and Gömörý proposed using the largest difference in the bond index to predict the highest peak in the electron impact mass spectrum (EIMS) of organic compounds [1]. Those authors proposed using the Mayer bond index, and for the cation wavefunction, they proposed using Koopman's approximate wavefunction. Moreover, those authors did not test their method systematically. In this poster we revisit this idea to predict mass spectra, testing it more thoroughly, and with several modifications and improvements:

1. We use the Roby bond index method [2], which, unlike the Mayer bond index, is stable to basis set extension. The Roby method also provides an ionic bond index, which may be used to predict the charged fragment.
2. We use fully optimised BLYP/6-31G(d) cation wavefunctions.
3. We investigate there is a variation in the quality of the predicted results for certain types of compounds, for example alcohols, aldehydes, are predicted more accurately.
4. Most important, we test to see whether we can distinguish the correct isomer purely on the basis of predicting the primary fragment, even for several biologically important compounds.

The last point opens the possibility of using EI-MS as a structure determination method for unknown compounds.

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The excitation number: characterizing multiple excitations

G. M. J. Barca, A. T. B. Gilbert and P. M. W. Gill

Poster # 23

Research School of Chemistry, Australian National University, Canberra, Australia

What is a multiply excited state? How can it be unambiguously characterized? In this Poster, we formally respond to these fundamental questions by introducing a new quantity, the excitation number η , as a measure of the number of electrons which have been excited from the ground state. Additionally, we show that within the new metric the concept of multiply excited state is univocally defined and how the previous informal definitions were inconsistent and led to cases of misassignment. We conclude that the excitation number metric can be generally used in chemistry in order to significantly enhance the theoretical characterisation and the physical understanding of excited states.[1]

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

Theoretical Application of Pressure Predicts Piezomagnetic Properties of Electride

S. G. Dale¹, A. Otero-de-la-Roza² and E. R. Johnson³

Poster # 24

¹ *Department of Chemistry and Chemical Biology, The University of California, Merced, California, United States*

² *Department of Chemistry, The University of British Columbia, Okanagan, British Columbia, Canada*

³ *Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada*

Electrides are a unique class of ionic materials in which the anions are stoichiometrically replaced by localised electrons. It has recently been shown that some metals, under extreme pressure, localize electrons within crystal vacancies, providing evidence for elemental electride behaviour. While electrides have previously been suggested to resemble expanded metals this new evidence implies they may in fact be compressed metals.

We have previously used density-functional theory (DFT) to show the presence of a localised electron and high lying "electride" valence state in all of the known electrides. In this current work we use a similar approach to investigate the effect of pressure on the simplest electride, $\text{Cs}^+(15\text{-crown-5})_2\text{e}^-$. We find that the electride shows a significant change in its electronic properties over a much smaller range of pressures than those used for investigation of elemental metals. Further, we examine both the ferro-magnetic and anti-ferromagnetic state of the localised electron within the electride and find that the most stable magnetic state can switch with a modest application of pressure demonstrating piezomagnetic properties.

This has implications not only for the future of electride development but our fundamental understanding of metallic behaviour, especially under abnormal circumstances.

