

**CENTRE FOR THEORETICAL CHEMISTRY AND PHYSICS (CTCP)  
NEW ZEALAND INSTITUTE FOR ADVANCED STUDY (NZIAS)**

*The Bob-Tindall Building (E-Centre, Gate 5, Albany), 0632 Auckland, New Zealand*

# A celebration of Peter Schwerdtfeger's 60<sup>th</sup> Birthday



**09 – 11 February 2016**

## PROGRAMME AT A GLANCE

### **Tuesday, 09 February 2016, OR4 Oteha Rohe (Bldg.102)**

10h: Welcome address  
10h15-11h15: Prof Bartlett  
11h15-11h30: *Coffee break*  
11h30-12h30: Prof Gaeggeler  
12h30-13h00: Dr Borschevsky  
13h00-14h30: *Lunch break*  
14h30-15h00: Prof Calvo  
15h00-15h30: Dr Ori  
15h30-16h00: Dr Pahl  
16h00-16h15: *Coffee break*

18h00: Welcome BBQ

### **Wednesday, 10 February 2016, e-centre seminar room**

09h15-10h15: Prof Schwarz (Berlin)  
10h15-10h30: *Coffee break*  
10h30-11h00: Prof Dzuba (Sydney)  
11h00-11h30: Prof Zuelicke (Wellington)  
11h30-12h00: Dr Avery (Copenhagen)  
12h00-13h30: *Lunch break*  
13h30-14h00: Prof Urban (Bratislava)  
14h00-15h00: Prof Bohle (Montreal)  
15h00-16h00: Prof Flambaum (Sydney)  
16h00-16h15: *Coffee break*

19h00: **Sir Neil Waters public lecture**

*"The Usefulness of Useless Knowledge" – on the Vital Role of Basic Research in Preserving Societies' Dreams and Aspiration*

Prof. Dr. Drs. h.c. H. Schwarz (TU Berlin)

### **Thursday, 11 February 2016, e-centre seminar room**

09h15-09h45: Prof Tallon (Wellington)  
09h45-10h15: Prof Sadus (Swinburne)  
10h15-10h30: *Coffee break*  
10h30-11h00: Dr Lein (Wellington)  
11h00-11h30: Dr Soehnel (Auckland)  
11h30-11h45: Concluding remarks  
11h45-12h30: *Lunch*

**Concluding at 12.30 pm**

## **Excited States From Multi-Reference Coupled-cluster Theory to an Exact One-Particle DFT Theory\***

R.J. Bartlett, J. Lutz, P. Verma, Y. Jin, D. Ranasinghe, and A. Perera  
*Quantum Theory Project, University of Florida, Gainesville, FL 32611*

Several different approaches for excited states will be presented and discussed. These include the Equation-of-Motion coupled-cluster theory (EOM-CC), the similarity transformed coupled-cluster theory (STEOM-CC), and the two-determinant, multi-reference MR-CCSD. Then an alternative approach based on time-dependent density-functional theory will be considered and applied to core-excitation spectra. To conclude we will ask the question, what conditions would one have in an exact effective one-particle theory and how close can we come to realizing that?

\***This work is supported by U.S. Air Force Office of Sponsored Research & HASI (HPCMO).**

**Peter & Heinz**  
*or*  
**The two sides of the same gold medal**

H.W. Gaeggeler

*Laboratorium for Radiochemistry and Environmental Chemistry, Paul Scherrer Institut,  
5232 Villigen and Bern University, 3000 Bern, Switzerland*

Gold is the preferred surface on which the adsorption behavior of heaviest elements is currently investigated in order to determine their volatility in the elemental state. Such superheavy elements start with atomic number 112 (Cn, Copernicium), i.e. have a filled  $6d^{10}$  electronic shell and start filling the 7p shell. Experiments with these exotic members of the periodic table are conducted at accelerator centres that deliver usually very few atoms within week-long irradiation times. We, the experimentalists, then tend to conclude that e.g. elements Cn and Fl (Flerovium with  $Z = 114$ ) are very volatile metals, knowing that such statements are scientifically speaking nonsense: single atoms are not volatile nor are they metals! What we mean is that the single atoms under study behave - if they were available in macro-amounts - as stated.

Now Peter comes into play: using relativistic models he and his group members are able to calculate solid state properties of such heavy elements. The expression relativistic is absolutely instrumental in such applications since due to the very high Coulomb forces (caused by the high number of protons), electrons of heaviest elements – even of the outer shells – have such high velocities that their orbital energies and masses are significantly influenced. The cohesive energy deduced from solid state calculations then yield information on volatility.

The presentation outlines the strategy how one can deduce volatility from single-atom studies which could then be compared with theoretical prediction.

Also a recent development is addressed, the new class of volatile compounds in heaviest element chemical studies, the carbonyls.

Finally some private impressions from several visits of Peter's group in New Zealand will be addressed.

## **Relativistic coupled cluster: method and applications**

A. Borschevsky

*The Van Swinderen Institute for Particle Physics and Gravity, University of Groningen,  
Nijenborgh 4, 9747 AG Groningen, The Netherlands*

Relativistic coupled cluster is considered one of the most powerful methods for accurate calculations of properties of heavy elements. Two variants of this method are usually used. The first variant, the single reference coupled cluster approach (SRCCSD(T)) is suitable for calculations of ground state properties in systems which can be well described by a single determinant. This approach can be used to obtain, for example, ionization potentials and electron affinities. The second variant is the multireference Fock space coupled cluster method (FSCC), which is particularly useful for high accuracy calculations of excitation spectra.

The talk will provide a brief introduction to the two variants of the relativistic coupled cluster approach. The main focus will be, however, on the recent successful applications of these methods to various atomic properties of heavy and superheavy elements.

## Coating polyaromatics with helium: from classical to quantum... and back

F. Calvo

*CNRS and University of Grenoble-Alpes, France*

Helium droplets provide extremely cold temperatures and weak interactions with dopant molecules, enabling their high-resolution spectroscopy. They are also strongly quantum and in the case of  $^4\text{He}$  prone to superfluidity. However, when interactions are stronger, as in the case of atomic ions bound by polarization forces, superfluidity is suppressed and the first solvation shells become localized. In this contribution we examine the case of large aromatic dopants such as fullerenes or polycyclic aromatic hydrocarbons, and show how the interplay between the moderately strong dispersion interactions and the precise number of helium atoms produces intriguing and possibly anisotropic solvation patterns. In particular, the lesser delocalization near the graphitic planes allows metastable dimers with a nearly classical helium monolayer sandwiched between the molecules.

# Topological evolution stable-nodes in a growing 5-Nanocone

O. Ori

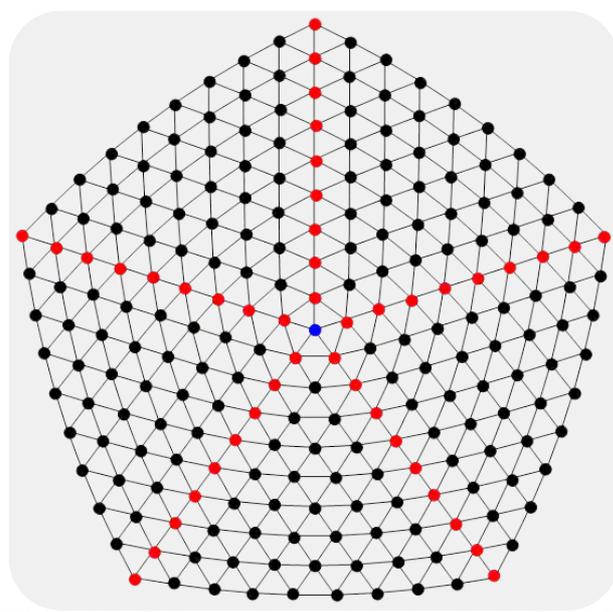
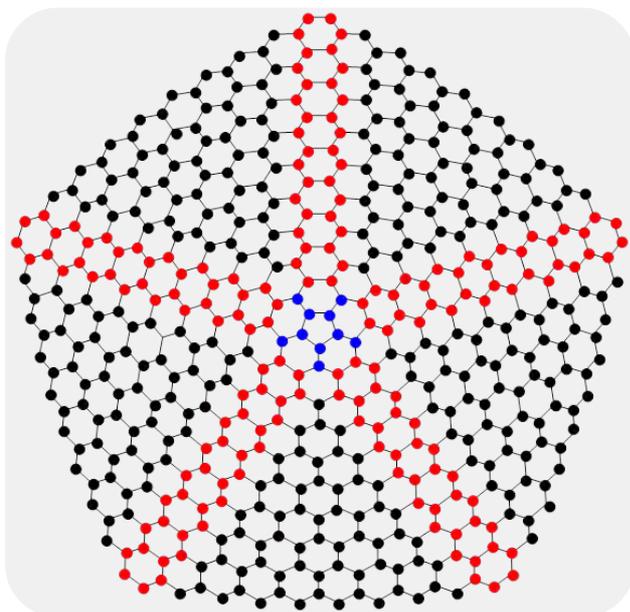
<sup>1</sup>Actinium Chemical Research, Rome, Italy

<sup>2</sup>Laboratory of Computational and Structural Physical-Chemistry for Nanosciences and QSAR, Biology-Chemistry

Department, West University of Timisoara, Timisoara, Romania

In this talk a pure topological approach provides a detailed descriptions of a 5-nanocone, e.g the basic unit for  $I_h C_n$  fullerenes, during its infinite growth around the pivotal pentagon. By adding an increasing number of concentric circles made only with hexagons, typical polynomial rules for the main topological indices related to the Wiener index  $W(N)$  are derived. We also show how a peculiar *migration* effect affecting the vertices giving minimum contribution to  $W$ ; these vertices migrate as the structure grows, drifting in the lattice along typical paths, proposing the tendency of the central pentagon area to become (topologically) chemically reactive. Moreover, topological computation not only indicate that the stable region of the lattice migrates with the size of the nanocone, but also that for some *magic* sizes the structure reaches peculiarly stable configurations.

Present results evidence the descriptive power of topological modeling methods in fullerenic structures. Computations are made in both lattices, the dual and the direct one.



## Playing Dice to Melt Clusters and Extended Systems

E. Pahl

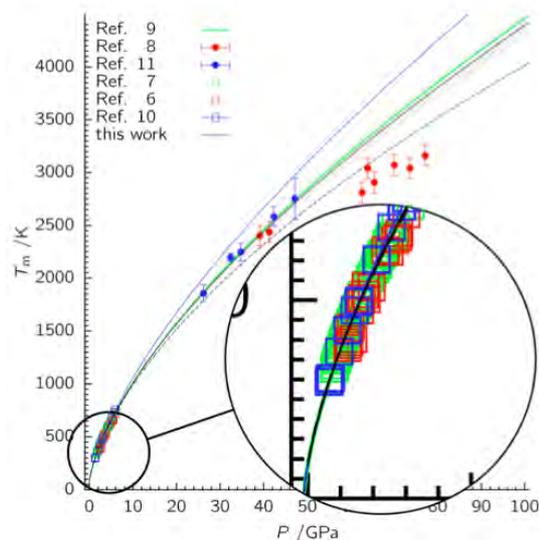
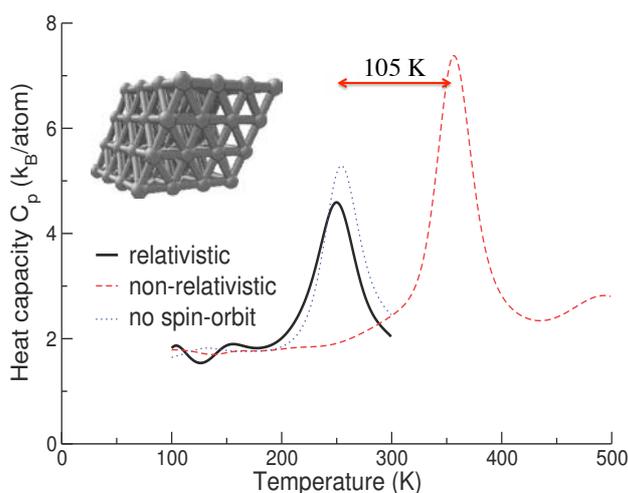
Centre for Theoretical Chemistry and Physics,  
Institute for Natural and Mathematical Sciences, Massey University Auckland

Why is mercury, Hg, liquid at room temperature? Why do rare gases always crystallize in face-centred cubic (fcc) structures at ambient conditions and not in the energetically very similar hexagonal closed packed structure; why not in a random closed (Barlow) packing? How does ultra-high pressure influence the phase transitions? Can concepts of statistical physics, derived for a very large number of particles, still be applied to the description of clusters with only a few atoms? Is an extrapolation of cluster results to the bulk behaviour possible?

Simple, fundamental questions like these provide the motivation and guidance of all work I have done together with Peter in the last 10 years since I joined Massey. Here, I will concentrate on our melting work on mercury and the rare gases: Based on very accurate interaction potentials for the  $N$ -atomic systems, Monte Carlo simulations have proven to be very successful in locating the melting transition for finite as well as extended systems. Research highlights as depicted in the figures below are:

- 1) Confirmation that indeed relativistic effects (in conjunction with complicated many-body effects) cause the exceptionally low melting temperature of mercury, see Fig.1.
- 2) Accurate *ab initio* simulation data of the melting of Argon up to pressures of 100 GPa, 1 million times atmospheric pressure, reach or even surpass experimental accuracy, see Fig. 2.

**Figure 1:** Including relativistic effects into the melting simulation of Hg lowers the transition temperature by more than 100 degrees making Hg liquid at room temperature (F. Calvo, E. Pahl, M. Wormit, P. Schwerdtfeger, *Angew. Chem. Int. Ed.*, **52**, 7583 (2013)).



**Figure 2:** High-Pressure melting simulation results compared with experimental data (J. Wiebke, E. Pahl, P. Schwerdtfeger, *Angew. Chem. Int. Ed.* **52** (2013)).

## How do Metal Oxides Activate Methane? A Mechanistic Exercise<sup>1)</sup>

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[Helmut.Schwarz@tu-berlin.de](mailto:Helmut.Schwarz@tu-berlin.de)*

Hydrogen-atom transfer (HAT) constitutes a key process in a broad range of chemical transformations as it covers heterogeneous, homogeneous, and enzymatic reactions. While open-shell metal oxo species  $[MO]^\bullet$  are no longer regarded as being involved in the heterogeneously catalyzed oxidative coupling of methane ( $2CH_4 + \langle O \rangle \rightarrow C_2H_6 + H_2O$ ), these reagents are rather versatile in bringing about (gas-phase) hydrogen-atom transfer, even from methane at ambient conditions. In this mini-review, various mechanistic scenarios will be presented, and it will be demonstrated how these are affected by the composition of the metal-oxide cluster ions. Examples will be discussed, how 'doping' the clusters permits the control of the charge and spin situation at the active site and, thus, the course of the reaction. Also, the interplay between supposedly inert support material and the active site – the so-called 'aristocratic atoms' – of the gas-phase catalyst will be addressed. Finally, gas-phase HAT from methane will be analyzed in the broader context of thermal activation of inert C–H bonds by metal-oxo species.

1) For recent reviews, see: (a) N. Dietl, M. Schlangen, H. Schwarz, *Angew. Chem. Int. Ed.* 2012, 51, 5544; (b) H. Schwarz, *Chem. Phys. Lett.* 2015, 629, 91; (c) H. Schwarz, *Angew. Chem. Int. Ed.* 2015, 54, 10090.

## **Search for local Lorentz invariance violation in atoms**

V. Dzuba

*School of Physics, University of New South Wales, Sydney, New South Wales 2052,  
Australia*

## **Quasi-relativistic behaviour of electrons in solids**

U. Zuelicke

*School of Chemical and Physical Sciences, Victoria University of Wellington, PO Box 600,  
Wellington 614, New Zealand*

## **The Shapes of Fullerenes**

J. Avery

*Niels Bohr Institute, University of Copenhagen, Blegdamsvej 17, Building C, 2100  
Copenhagen, Denmark*

Fullerenes are carbon molecules that form polyhedral cages with surfaces similar to graphene sheets, and whose bond structures are exactly those planar cubic graphs that have only pentagon and hexagon faces. Their geometrical properties make some fullerenes incredibly strong, while the 12-pentagon rule allows opening the hollow shell by changing a single pentagon to a hexagon. This makes them interesting as delivery systems, reflected by their occurrence in nature in other forms in addition to carbon structures. For example, a number of virus capsids, which protect and deliver genetic material, are fullerene analogs.

Many chemical and physical properties of fullerenes are uniquely determined by their bond graphs, and can be approximated very rapidly directly from the graph. This is important when we wish to search through millions of fullerene isomers to select a few according to desired properties, such as stability, shapes, malleability, electrical properties, etc.

In this talk, I will describe a method that derives one such property, the three-dimensional shape of a fullerene, from its graph by way of its induced Riemannian surface metric, at speeds that allows automatic study of millions of fullerene isomers. The method is in an experimental stage, but has shown promising preliminary results.

## Complexes of Au<sub>(n)</sub> clusters with closed shell and open shell ligands up to „golden“ analogues of hydrocarbons

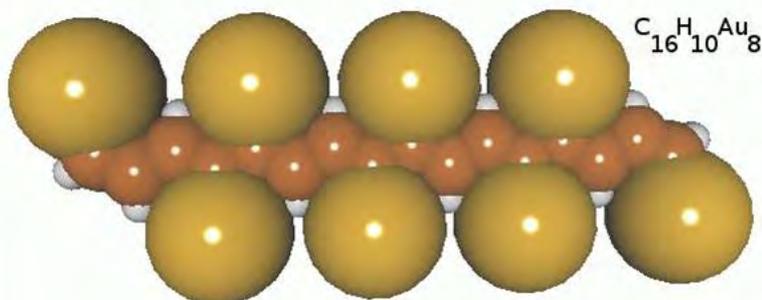
M. Urban<sup>1,2</sup>, T. Rajský<sup>1</sup>, M. Blaško<sup>1</sup>, A. Antušek<sup>1</sup>, L. F. Pašteka<sup>1,3</sup>

<sup>1</sup> Comenius University, Faculty of Natural Sciences, Department of Physical and Theoretical Chemistry, 84215 Bratislava, Slovakia

<sup>2</sup> Slovak University of Technology in Bratislava, Faculty of Materials Science and Technology, Advanced Technologies Research Institute, 91724 Trnava, Slovakia

<sup>3</sup> Massey University Auckland, NZIAS, CTCP, Auckland 0632, New Zealand

We have shown in our previous paper [1] that the interaction energy between the gold atom and a lone-pair ligand is much higher than with Cu and Ag thanks to large relativistic enhancement of the electron affinity (EA) of Au. The pattern of interaction energies ( $\Delta E$ ) in Au-L complexes is also linked with ionization potentials (IPs) of ligands. Strong interaction of Au with P containing ligands is attributed to their lower IP and the lone pair  $\rightarrow$  metal electron donation accompanied with the back-donation characteristic for P containing ligands. Small Au<sub>n</sub> clusters exhibit oscillatory pattern of EA's [2]. In line with this we confirmed that interaction energies in odd Au<sub>n</sub>L clusters ( $n=1,11$ ) are also oscillatory and follow electron affinities of Au<sub>n</sub> clusters confirming the same bonding mechanism as it holds for Au<sub>1</sub>-L complexes. The mechanism of interactions of even Au<sub>n</sub> clusters (closed shells) with ligands is different [3]. This is consistent with a view that properties of small nanoclusters are sensitive to the number and the structure of atoms in a cluster. In relation to Self Assembled Monolayers, we analysed interactions of small Au<sub>n</sub> clusters with SCH<sub>3</sub> and a model carbon containing system, the CH<sub>2</sub> radical, in different spin states. While interaction with a doubly occupied lone-pair of SCH<sub>3</sub> (leading to a triplet Au-SCH<sub>3</sub>) is similar as with closed shell ligands, the singlet Au-SCH<sub>3</sub> complex is bound by a strong covalent bond. The same holds for SCH<sub>3</sub> interacting with small Au clusters. Even stronger bonds exhibit Au<sub>n</sub>-CH<sub>2</sub> complexes. The Au<sub>2</sub>-CH<sub>2</sub> complex is a „golden“ analogue of the methane molecule. Similarly, there exists also a „golden“ analogue of ethylene. This leads us to the idea of creating other analogs, like „golden“ polyethylene, polyvinylbromine and possibly other polymers.



**Figure 1: Computational simulation of a „golden“ polyacetylene**

[1] L. F. Pašteka, T. Rajský and M. Urban, J. Phys. Chem. A **117**, (2013) 4472.

[2] B. Assadollahzadeh and P. Schwerdfeger, J. Chem. Phys. **131** (2009) 064306.

[3] D. Mollenhauer and N. Gaston, J. Comp. Chem. **35** (2014) 984.

## **New Chemistry of Coordinated NO: How Useful is the Oft Touted Isolobal Relationship of NO<sup>+</sup> and CO ?**

S. Bohle

*Department of Chemistry and Center for Self Assembled Chemical Structures, McGill University, 801 Sherbrooke Street West, Montreal, Quebec H3A 2K6, Canada*

The discovery of nitric oxide's critical biochemistry challenged many of our notions of its reactivity and chemistry. NO's biological receptors are frequently metalloproteins, and the metal's affinity and bonding to NO represent a cross of conventional organometallic and bioinorganic models. But perhaps the deeper problem is related to an idea central to teaching Ligand Field and Transition Metal Molecular Orbital theory: CO and NO<sup>+</sup> are isolobal and therefore by this simple model should have similar chemistry. But why does this frontier orbital approach fail to describe many of the key aspects of NO's remarkable coordination chemistry. In this presentation some of these failings will be outlined, and two examples of recent metallonitrosyl chemistry where theoretical insight is proving invaluable in determining key catalytic and biochemical pathways will be presented. The answer to Schwerdtfegerian question of, "are there calculations on this theme?" now becomes how do we get the most from the calculations we have?

## **Link between dark matter and variation of the fundamental constants of Nature leads to a major breakthrough in the sensitivity of dark matter searches**

V. Flambaum

*School of Physics, University of New South Wales, Sydney, New South Wales 2052, Australia*

Astrophysical observations indicate that 85% of the matter content in the Universe is due to dark matter, the identity and properties of which remain a mystery. Traditional searches for the scattering of dark matter particles off nuclei have not yet produced a strong positive result. The challenge with these traditional searches is that they look for effects that are fourth power in a very small interaction constant.

We propose to search for low mass dark matter that form coherently oscillating classical fields and topological defects, via effects that are first power in the interaction constant [1-6].

We have shown [1] that dark matter can produce a cosmological evolution of the fundamental constants of Nature. The fundamental constants govern the strength of the fundamental forces (including electromagnetism), as well as the masses of the particles that constitute the ordinary matter that we see around us. Variations in these physical constants leave characteristic fingerprints on physical processes that take place from as early as a second after the birth of the Universe until the present day.

By studying the effects of dark matter on the primordial abundance of helium produced in the first few minutes of the Universe and on atomic systems in the laboratory, we have derived limits on the quadratic interactions of dark matter with the photon, electron and quarks, which improve on existing constraints by up to 15 orders of magnitude, as well as the first ever limits on the interactions of dark matter with the W and Z bosons that mediate the weak interactions. The vastly improved sensitivity to dark matter through its effects on the fundamental constants opens exciting new paths in the global hunt for dark matter.

Other effects of dark matter include oscillating spin-precession and oscillating parity and time reversal violating effects [2-4]. Further progress may be achieved with laser interferometry experiments [5] and pulsar timing [6].

[1] Can dark matter induce cosmological evolution of the fundamental constants of Nature? Y. V. Stadnik and V. V. Flambaum. *Phys. Rev. Lett.* 2015.

[2] Axion-induced effects in atoms, molecules and nuclei: Parity nonconservation, anapole moments, electric dipole moments, and spin-gravity and spin-axion momentum couplings. Y. V. Stadnik and V. V. Flambaum. *Phys. Rev. D* **89**, 043522 (2014).

[3] Limiting P-odd Interactions of Cosmic Fields with Electrons, Protons and Neutrons. B. M. Roberts, Y. V. Stadnik, V. A. Dzuba, V. V. Flambaum, N. Leefer and D. Budker. *Phys. Rev. Lett.* **113**, 081601 (2014).

[4] Parity-violating interactions of cosmic fields with atoms, molecules and nuclei: Concepts and calculations for laboratory searches and extracting limits. B. M. Roberts, Y. V. Stadnik, V. A. Dzuba, V. V. Flambaum, N. Leefer and D. Budker. *Phys. Rev. D* **90**, 096005 (2014).

[5] Searching for Dark Matter and Variation of Fundamental Constants with Laser and Maser Interferometry. Y. V. Stadnik and V. V. Flambaum. *Phys. Rev. Lett.* **114**, 161301 (2015).

[6] Searching for Topological Defect Dark Matter via Nongravitational Signatures. Y. V. Stadnik and V. V. Flambaum. *Phys. Rev. Lett.* **113**, 151301 (2014).

## **Light ions/heavy ions - melting and superconductivity**

Jeff Tallon

Robinson Research Institute, Victoria University of Wellington, P.O. Box 33436, Lower  
Hutt 5046, New Zealand

Following Peter Schwertfeger's longstanding interest in heavy ions this talk contrasts light ions and heavy ions in melting and superconductivity. For example, the three-decades-long focus on 2D layered cuprates as the paradigm for high transition temperature superconductors seems to insist on the presence of highly polarisable heavy ions. On the other hand the recent discovery of superconductivity at 203K in compressed H<sub>2</sub>S shifts attention back to very light ions and 3D systems. Is there perhaps some way of combining these extremes to better effect still?

## Water – not your everyday triatomic molecule

R.J. Sadus

*Centre for Molecular Simulation, Swinburne University of Technology, PO Box 218,  
Hawthorn 3122, VIC, Australia*

Water is arguably one of the best-known molecules on Earth [1]. It is certainly one of the most important, playing an essential role in supporting life. We quench our thirst with it, grow our crops with it, bathe in it, ski on it and unfold umbrellas to protect us from it. It's simple. If you stop a layperson in the street, there is a very high likelihood that they will know its chemical formula ( $H_2O$ ), most will be able to identify its constituent atoms (hydrogen and oxygen) and some will also recall its triangular structure from their school days. An educated layperson might also recall the term hydrogen bonding associated with water. In view this familiarity, we should be able to predict its properties without difficulty but we can't. It's complicated. Indeed, predicting its properties has been identified [2] as one of the great challenges in science.

The theoretical treatment of water has advanced significantly since the pre-computer days that were reliant literally on "ball and stick" modelling [3]. The main theoretical advances have come courtesy of molecular simulation techniques [4] that make use of supercomputing to directly calculate the forces and energies of a given water model. Despite these computational advances, and indeed the apparent molecular simplicity of water, an accurate model has proved elusive. It has been estimated [5] that there are at least 80 water models, some more commonly used than others. Typically a model designed specifically for one property such as diffusion, yields inadequate agreement for another property, such phase coexistence. Overcoming this situation is imperative, because accurately modelling water impacts on our ability to correctly model large systems, such as biological entities. This work surveys progress in this field and highlights the importance of an often-neglected aspect of modelling water, namely correctly accounting for the effects of polarization [6].

- [1] P. Ball, *Chem. Rev.* 108, 74 (2008).
- [2] D. Kennedy and C. Norman, *Science* 309, 75 (2005).
- [3] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.* 1, 515 (1933).
- [4] R. J. Sadus, *Molecular Simulation of Fluids: Theory, Algorithms and Object-Oriented*, Elsevier, Amsterdam, 1999.
- [5] I. Shvab and R. J. Sadus, *Fluid Phase Equil.* (2015)  
<http://dx.doi.org/10.1016/j.fluid.2015.07.040>.
- [6] I. Shvab and R. J. Sadus, *Phys. Rev. E.* 92, 012124 (2015).

# Automatic optimization of transition structures from molecule-specific empirical force-fields

Matthias Lein<sup>a,b)</sup> and Kimberley J. Savill<sup>a)</sup>

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<sup>b)</sup>*New Zealand Institute for Advanced Study, Centre for Theoretical Chemistry and Physics, Massey University, Auckland, New Zealand*

While the empirical force-fields that are employed in molecular mechanics calculations provide a convenient way for the fast computation of potential energy surfaces of large molecules, their relative computational efficiency is offset by their relatively low accuracy for any particular molecular system. This is in mostly due to the combination of the neglect of the quantum nature of molecular species in combination with the necessity to parameterize force-fields to show an even performance across a wide range of systems.

It is possible however, to construct molecule-specific force-fields that draw theoretical parameters directly from highly accurate Quantum Chemical calculations using the Quantum Mechanical Derived Force Field (QMDFF) approach [1]. This allows the fast calculation of accurate potential energy surfaces within the realm of molecular mechanics.

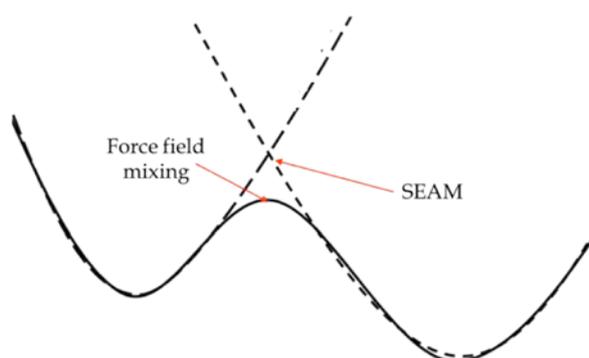
We propose a new method that combines Grimme's QMDFF approach with Jensen's SEAM procedure [2 - 4]. That optimizes transition state structures on the seam where the potential energy surfaces of reactants and products intersect. To this end, we have generalized Grimme's force-field and establish how the combination of both methods can be used to generate candidate transition state structures for subsequent optimisation by conventional quantum chemical calculations. We demonstrate the performance and general applicability of our method over a wide range of systems.

[1] Grimme, S. J. *Chem. Theory Comput.* **2014**, *10* (10), 4497-4514.

[2] Jensen, F. J. *Comput. Chem.* **1994**, *15* (11), 1199-1216.

[3] Olsen, P. T.; Jensen, F. J. *Chem. Phys.* **2003**, *118* (8), 3523-3531.

[4] Jensen, F. J. *Chem. Phys.* **2003**, *119* (17), 8804-8808.



**Figure 1: Transition Structures can be interpolated on the seam where the potential energy surfaces of reactants and products intersect.**

## Mössbauer spectroscopy on Fe, Ru and Ir-Sn cluster compounds – Some theory and experiment

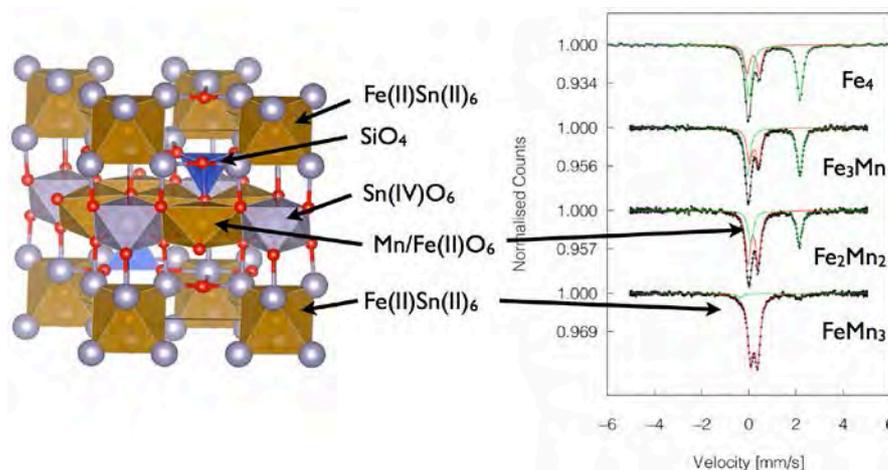
T. Söhnel

School of Chemical Sciences, The University of Auckland, Private Bag 92019, Auckland, New Zealand

Mixed tin - transition metal cluster compounds form novel nano-scale clusters with a wide variety of different combinations of metals and resulting architectures which are size tunable. The central and most striking structural feature of all these stannates is the formation  $\text{Sn}_6$ -octahedra, which are filled with the different transition metals. In this presentation some Fe, Ru and Ir containing examples will be discussed in more detail. The Fe based clusters  $\text{Fe}_{4-x}\text{Mn}_x\text{Si}_2\text{Sn}_7\text{O}_{16}$  provides a novel situation in oxide compounds. It can be described as a composite of intermetallic ( $\text{FeSn}_6$ ) clusters and  $(\text{Fe}/\text{MnO}_6)/(\text{SnO}_6)$  oxide layers within the one structure.  $\text{SiO}_4$  tetrahedra separate these layers which leads to electronic and magnetic isolation of the repeated layers by about 7 Å resulting in a nearly perfectly 2D oxide system comparable to a one layer thick oxide “thin film”.  $^{57}\text{Fe}$ -Mössbauer spectra seem to confirm a clear preference of Mn sitting in the oxide layers and Fe in the cluster layers (Fig. 1).

In  $\text{RuSn}_6[\text{FeO}_4]\text{O}_4$  the  $\text{RuSn}_6$  octahedra are isolated from each other in contrast to most of the other compounds in this group where a condensation via common corners and edges can be found. The structure of  $\text{RuSn}_6[\text{FeO}_4]\text{O}_4$  is cubic and the isolated  $\text{RuSn}_6$ - octahedra are connected via oxygen atoms and  $\text{FeO}_4$  tetrahedra. For  $\text{RuSn}_6[\text{FeO}_4]\text{O}_4$  a tetragonal distortion which should be expected for the  $d^6$  ion  $\text{Fe}^{2+}$  centering the  $\text{FeO}_4$  tetrahedra could not be observed. This can be explained with a dynamic Jahn-Teller distortion. Measurements of magnetic susceptibility confirmed the spin only behaviour of  $\text{Fe}^{2+}$  from room temperature until 56 K. Below 56 K spin - orbit coupling takes place. At the same time a distortion of the local coordination of the  $\text{Fe}^{2+}$  atoms seems to occur as Mössbauer measurements show.

In  $\text{Ir}_3\text{Sn}_8\text{O}_4$ , the oxygen poorest of all compounds in this group of clusters,  $\text{IrSn}_6$  octahedra are partly side-linked in contrast to most of the other compounds in this group. This compound shows an incommensurately modulated structure due to Ir-Ir interactions within the condensed  $\text{IrSn}_6$  octahedra.  $^{193}\text{Ir}$ - and  $^{119}\text{Sn}$ -Mössbauer spectra seem to agree with this interpretation. This paper gives an overview about the preparation, crystallographic and Mössbauer spectroscopic



characterization of this new group of cluster compounds.

Figure 1: Crystal structure (left) and  $^{57}\text{Fe}$ - Mössbauer spectra of  $\text{FeFe}_{3-x}\text{Mn}_x\text{Si}_2\text{Sn}_7\text{O}_{16}$ .