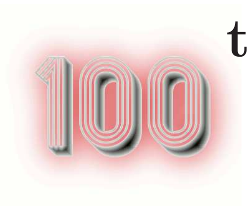
Ψ_k Newsletter

AB INITIO (FROM ELECTRONIC STRUCTURE) CALCULATION OF COMPLEX PROCESSES IN MATERIALS

Number 100 August 2010



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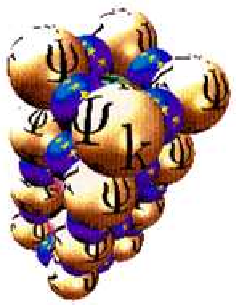

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Sponsored by: UK's CCP9
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Contents

1 Editorial

This is already the 100^{th} issue of the Psi-k Newsletter, which we did not think possible when starting the Psi-k Network activities in 1993. Of course, all of this would not have happened without you, the readers and members of the Psi-k community. Thus, on the occasion of this small jubilee, we would like to thank each and every one of you who contributed to our newsletters. Without your continuous support, this 100th issue would have not materialized.

This issue is started with the call for workshop proposals for 2011, followed by four reports on recent workshops sponsored or endorsed by the Psi-k Network.

We would like to turn readers attention especially to the announcement of the KKR Hands-on Course which will take place in Daresbury Laboratory and Chester, U.K., on 4-6 October, 2010.

The position announcements and abstracts of the newly submitted or recently published papers can be found in their usual sections.

The scientific highlight of this issue is on "Ab initio Random Structure Searching", by Chris J. Pickard (London, U.K.) and Richard J. Needs (Cambridge, U.K.).

For details, please check the table of contents of this newsletter. The *Uniform Resource Locator*

(URL) for the Psi-k webpage is:

`http://www.psi-k.org.uk/`

Please submit all material for the next newsletters to the email address below.

The email address for contacting us and for submitting contributions to the Psi-k newsletters is

	function
psik-coord@stfc.ac.uk	**messages to the coordinators, editor & newsletter**

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2 Call for Psi-k Workshop Proposals for 2011

Herewith we ask for proposals for workshops, small conferences, hands-on tutorials and summer schools in the field of ab-initio calculations to be held in 2011 and to be partially funded by the Psi-k network.

The deadline for Psi-k proposals is Friday, October 1, 2010.

Collaboration with CECAM: As in the past years we strongly encourage joint CECAM/ Psik Workshops as well as joint tutorials about electronic structure calculations. The collaboration with CECAM is working very well and has effectively increased our funding substantially..

The deadline for CECAM proposals was July 19, 2010.

The importance of CECAM, which is now located at Lausanne, is strongly increasing. This year CECAM organizes and/or co-sponsors a more than 60 activities, many more than in previous years (see the CECAM website). Please notice that CECAM also funds tutorials. In addition 'Sponsored Events' are included in the program, e.g. tutorials or schools, which do not take place at CECAM in Lausanne, at Zuerich or at other CECAM nodes.

New Psi-k Funding Policy: In the last years Psi-k has acted more or less like a funding agency, instead as a bottom-up network which funds workshops from membership fees of our Psi-k groups. In order to respond to this and in order to distinguish us from CECAM the board of Psi-k has decided that in the future we should concentrate the Psi-k activities on the fields of our working groups and should give priority to workshops coming from or supported by these groups. We believe that with the concentration on the working groups we will strengthen the cohesion of Psi-k and preserve our identity as Psi-k family in view of the future cooperation with CECAM. In order to distribute the responsibility of the working groups on more shoulders, we have created for each group a coordination committee of experienced scientists in the field which will be headed by the spokesperson and which should plan and coordinate the activities for the next two years.

The Working Groups of Psi-k, the Spokespersons and the Coordination Committee members are listed on the Psi-k Web Site ((http://www.psi-k.org). If you want to organise a workshop in the field of one of the working groups, please contact the spokesperson and the committee members.

Training activities and interdisciplinary workshop activities like Industry Workshop or Total Energy and Force Conference will not be affected by this restriction.

New ESF Proposal 'Advanced Concepts in Ab-initio Simulations of Materials': The proposal, published on the Psi-k Website, has been approved by the ESF Physical and Engineering Science Committee (PESC) and will soon be send to the national agencies for decisions about funding. If successful, the network could start in 2011. Thus we urge you now already, to consider in your plans workshops or sessions within workshops, which focus on new concepts and methods in the field.

How to submit a proposal: You need to login to the Psi-k Portal, accessed from the Psi-k web pages (http://www.psi-k.org). First you will have to create an account (if you do not have it already). For this please use your e-mail address as user-id. After the successful creation of an account you will end up in the PSI-K workspace. Click on the 'Workshop Proposal' button, and then click on the number 1 (left column) of the 'Call For Workshop Proposal List' to view its details, including the option to submit a proposal.

Then to submit a proposal for a workshop, click the 'Submit Workshop Proposal' button:

Fill in all form fields correctly and then you will be able to preview your proposal as a pdf-file by clicking on 'Preview(PDF)' button. If the preview button does not produce a pdf-file please check carefully that all input fields have been filled in, valid dates are used (format dd/mm/2009-dd/mm/2009) and budget (Euros) is provided. You can then make any changes to your proposal or 'Submit' your proposal as it is. To view any proposals you have already submitted, first go to the relevant proposal page then click on the 'Show My Proposal(s)' button. You can view or modify your proposal, or download it as a pdf-file.

Funding for US participants: Very often the workshops have an American co-organizer, who can bring in additional support for US participants by funding from NSF or other agencies. European organizers can also apply for support of US participants from: U.S. Office of Naval Research Global (http://www.onrglobal.navy.mil) European Office of Aerospace Research and Development (http://www.london.af.mil).

Please contact us, if you have questions.

With best regards,

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Chairman, Psi-k	Vice-Chairman, Psi-k

3 Psi-k Activities

”Towards Atomistic Materials Design”

3.1 Reports on Psi-k Sponsored/Endorsed Workshops

3.1.1 Report on Workshop Electronic Structure of Fe-based Superconductors

Max-Planck-Institute for Solid State Research, Stuttgart, Germany

10-12 May 2010

Sponsors:

Psi-k Network, Max-Planck Society, Office of Naval Research Global (ONRG)

Organizers:

O. K. Andersen, L. Boeri (MPI-FKF), I. Mazin (NRL), H. Rosner (MPI-CPS)

Web Page:

`http://www.fkf.mpg.de/conf/fesc2010`

Scientific Report

The Fe-based superconductors (FeBSC) are generally considered to be the most important discovery in superconductivity since the cuprates. What sets them apart is their complex, multiband electronic structure that plays the pivotal role for both normal state properties and superconductivity. First-principles calculations have had an unprecedented impact in this field. The unusual and unexpected magnetic state of the parent compound was predicted theoretically and the now accepted unconventional s+- superconducting symmetry was proposed long before any experimental evidence was found, also based on first-principles calculations. Rarely have so many people in the field of superconductivity, both theorists and experimentalists, had their ears so sharply attuned to what band theorists say. The goal of the proposed workshop was to bring together most European groups engaged in the band theory of FeBSC, in order to have a profound and more detailed discussion of the electronic structure of FeBSC than what usually takes place in more general conferences. Selected experimentalists whose work is closely related to the electronic structure also presented talks and posters.

The most energetically discussed subject was the origin and the microscopic picture of the parent compounds. Three basic points of view emerged from the talks and the discussions.

1. **Fully itinerant picture**. *Eremin, Graser, Arita, Honerkamp (also e.g. Chubukov, D-H Lee)*

   - Magnetism is driven by nesting
   - Magnetic interaction of itinerant (RKKY) nature, defined by the Fermi surface geometry
   - Similar to 1D spin-Peierls
   - Spin fluctuations can be described by RPA/FLEX/RG

2. **Fully localized picture.** *Lu (also e.g. J.P. Hu, Q. Si)*

   - Magnetism is driven by combination of Hubbard U and Hund's J
   - Magnetic interaction are local, of superexchange nature
   - Similar to cuprates, 3d oxides
   - Spin fluctuations can be described by the $J1 + J2$ model

3. **Orbital ordering picture.** *Wei Ku (also e.g. R. Singh, P. Phillips)*

   - SOME electrons are localized, others itinerant
   - Magnetic interactions are set by competition between the orbital ordering (Jahn-Teller) in the localized orbitals, and metallic double exchange of the other electrons
   - Similar to CMR manganites
   - Spin-fluctuations can be described by orbital-dependent superexchange + double exchange?

4. **Local-itinerant picture** *D. Singh, Johannes, Antropov (also e.g. Yildirim), Hansmann, Arita. Reznik/Heid*

   - Magnetism is driven by Hund
   - Magnetic interaction of itinerant (not always RKKY) nature, affected, but not fully defined by the Fermi surface geometry, cannot be described in terms of superexchange
   - Similar to 3d metals (Cr, Mn, Fe)
   - Spin fluctuations can be described, with reservations, by RPA/FLEX/RG

The next important issue that was discussed was **the correlation strength and possible proximity to the Mott-Hubbard transition.** This issue has been discussed in many details by the DMFT practitioners: *Anisimov, Aichorn,Hansemann.* A better consensus has been acieved in the sense that all parties argue that FeBSCs are in a week to moderate correlations regime. *Liebsch* also supported this conclusion but argued that for an integer doping (one electron or one hole) a Mott transition would be supported. It was pointed out though that experiments for KFe_2As_2 do not agree with this prediction.

A number of experimental talks (*Borisenko, Coldea*) raised the question of the band width and the effective mass renormalization. What is the origin? Is there a QCP-associated m* divergence? These questions remain a challenge to the theorists.

Further there was a discussion of a possible role of electron-phonon copling. *Calandra* showed improved calculations that place an upper limit λ as 0.3-0.4, *Fink* presented an experimental estimate of 0.2, and Borisenko showed a kink in the electronic dispersion corresponding to a phonon-driven Fermi velocity renormalization of 1.4 (corresponding to a conventional λ of 0.4).

The k_z **dispersion** was discussed by *Singh* and, experimentally, by *Brouet, Jepsen* and by *Fink. Graser* emphasized the importance of this factor for superconductivity.

The coupling of magnetism (within LDA) with other degrees of freedom was addressed in several talkes: *Johannes, Antropov, Yaresko, Kasinathan, Valenti.* It was discussed from the phenomenological Ginzburg-Landau point of view by *Lorenzano.*

Methodological papers by *Hansmann, Buenemann/Schikling* discussed possibilities of speeding up the traditional DMFT calculations by reducing the basis (*Hansmann*) or by using the Gutzwiller approximation (*Buenemann/Schikling).*

Finally, *Benfatto, Ortenza, Plakida, Ummarino, Ciechan, Golubov* presented various results regarding multiband effects in superconductivity and normal properties.

The programmme of the conference, and the list of participants are attached to this report.

Program

Monday, 10th May 2010

8:45-9:00 L. Boeri: Opening remarks
9:00-9:30 D. Singh: Electronic structure of iron superconductors: not oxides
9:30-10:00 V. Anisimov: Coulomb correlation effects in pnictide superconductors from LDA+DMFT calculations
10:00-10:30 S. Graser: Superconducting pairing in Fe-based superconductors via weak-coupling approach
10:50-11:20 M. Calandra: Effects of magnetism and doping on the electron-phonon coupling in $BaFe_2As_2$
11:20-11:40 D. Reznik: Interplay between phonons and magnetism in 122 ferropnictides
11:40-12:00 R. Heid: Lattice dynamics of Fe-based superconductors from first principles
12:00-13:00 Oral presentations of Posters
13:00-14:00 Lunch Break
14:00-14:30 Oral presentations of Posters
14:30-15:00 M. Johannes: Dual character of magnetism in pnictides
15:00-15:30 S. Borisenko: ARPES studies of Fe-based superconductors
15:30-16:00 A. Coldea: Quantum oscillation experiments in Fe-based superconductors

16:00-... Poster Session + Beer and Snacks

Tuesday, 11th May 2010

9:00-9:30 Z. Lu: Electronic structures and magnetic properties of iron-pnictides by the first-principles study.
9:30-10:00 M. Aichhorn: Correlated electronic structure of iron-based superconductors from an LDA+DMFT perspective
10:00-10:30 Wei Ku: What does the rich magnetic structures of parent compounds tell us about the essential low-energy electronic structure?
11:00-11:30 A. Yaresko: Spin-spiral calculations of the magnetic properties of Fe-based superconductors
11:30-12:00 S. Massidda: Magnetism in Fe-based superconductors
12:00-12:30 R. Arita: LDA+FLEX study for Fe-based superconductors based on ab-initio downfolding
12:30-13:00 A. Boris: Criticality-induced optical anomalies in 122 Fe pnictides
13:00-14:00 Lunch Break
14:00-14:30 I. Eremin: Magnetism, superconductivity and pairing of Fe-based superconductors in the RPA formalism
14:30-15:00 K. Koepernik: Bulk and surface electronic structure of Fe-pnictides: TB-models, cleavage behavior and surface states
15:00-15:30 S. Dugdale: Probing the Fermi surface with Compton scattering: theory and experiment
16:00-16:30 D. Inosov: Normal-state spin dynamics and temperature-dependent spin resonance energy in an optimally doped iron arsenide superconductor
16:30-17:00 D. Kasinathan: Relation of structure, magnetism, doping and pressure in AFe2-xTxAs2 (A=Ca,Sr,Ba,Eu; T=Co,Rh,Ru)
17:00-17:30 R. Valent: Effect of pressure on the electronic structure of Fe-based superconductors
18:30-... Conference Dinner

Wednesday, 12th May 2010

9:00-9:30 A. Liebsch: Correlation induced spin freezing in FeSe and FeAsLaO: a dynamical mean field study
9:30-10:00 C. Honerkamp: Iron pnictides viewed by the functional renormalization group
10:00-10:30 B. Büchner: Nanoscale electronic order in underdoped iron pnictides
11:00-11:20 P. Hansmann: Dichotomy between large local and small ordered magnetic moment in iron-based superconductors
11:20-11:40 J. Lorenzana: First principle Landau theory of competing orders in LaOFeAs
11:40-12:10 A. Golubov: Strong coupling theory of superconducting pnictides: multiband scenario
12:10-12:40 L. Benfatto: Eliashberg approach to multiband pairing in pnictides
12:40-13:25 I. Mazin: Summary of the conference

13.25-13.30 O.K. Andersen: Closing remarks

List of participants

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3.1.2 Report on the KITP Program

Excitations in Condensed Matter: From Basic Concepts to Real Materials (excitcm09)

October 5, 2009 - December 18, 2009

Coordinators: Claudia Ambrosch-Draxl, Kieron Burke, Roberto Car, and Matthias Scheffler

Partially sponsored by Psi-k

Materials Science requires a qualitative and quantitative description of processes from an atomistic point of view. In this context, electronic-structure theory is the first level in the hierarchical set of models needed to quantitatively describe and understand phenomena that are observed in condensed matter and in the behavior of real materials. For polyatomic systems, density-functional theory (DFT) has proven to be an excellent technique for the calculation of structures and molecular dynamics. Limits are, however, encountered in several major current research topics. For example, the accurate treatment of excited states, strong electronic correlations, hydrogen bonding, van der Waals interactions, non-adiabaticity and of out-of-equilibrium scenarios such as transport are still demanding issues, where improvements are not only important, but crucial.

While great progress has been made in different areas, such as many-body perturbation theory (MBPT), time-dependent density-functional theory (TDDFT), ab-initio molecular dynamics, DFT for superconductivity, and, last but not least, in density-functional theory itself, the relationship of the different techniques and domains of applicability is still a challenging task. The aim of this program is to survey the state-of-the-art and recent achievements in the individual research areas, to discuss their future perspectives, and to seek new approaches to interrelating these fields with each other. It should include basic aspects as well as the application to real functional materials.

The topics discussed during this program, comprised first-principles methods for excitation processes in solids, covering electronic excitations, electron-phonon coupling, non-adiabaticity, and transport, but also recent developments towards a most reliable description of the ground state, which is a prerequisite of all those approaches.

The number of applications that we had received was overwhelming, i.e., the program was significantly oversubscribed. Thus, we were in the good but also difficult position to do a careful (and somewhat tough) selection. This selection was guided by mainly two criteria, which were scientific excellence, obviously normalized with respect to the age of the researcher, and the aim to achieve a good mix of people, i.e., the respective research fields. In particular, the latter point made our program different to others that we had attended (or observed) in the past. We took utmost care that we did not get a group of colleagues who all think along the same line but tried to achieve the opposite. Indeed, our group consisted of a few hard-core DFT practitioners, colleagues who are top experts in many-body perturbation theory (Green functions), others employing or developing many-electron wave function methods from physics (e.g. quantum Monte Carlo approaches), representatives from quantum chemistry (Hartree-Fock Mller-Plesset perturbation theory and coupled cluster theory), people from dynamical mean-field theory, and some experts concentrating on electronic transport. This concept worked just perfectly. The discussions were numerous. They focused on concepts and faithfully identified weak points of the respective theories and implementations. These open discussions were intense, honest, success-oriented and most enjoyable, indeed.

Several methods and problems were assessed, limits of current methodologies identified, and possible errors quantified. To give just a few examples, we could mention the critical analysis of modern treatments of van der Waals interactions in DFT and in MP2, and the starting point dependence of the G_0W_0 approximations and the EX+cRPA approach. Another key issue concerned the limits of dynamical mean field theory, were just a single electronic level is correlated (neglecting changes of its hybridization with other states). This was contrasted by MBPT that correlates all the electrons but needs a somewhat empirical approach for electrons that are very localized (e.g. GW@GGA+U).

Altogether the scientific atmosphere and the constructiveness of the debates could not have been better. This also applies to the social atmosphere, where the enthusiastic participation in the Thursday night dinners (taking place every Thursday) is indicative of. They, indeed, added much to the enjoyment.

The list of participants can be found on the web at:
`http://online.kitp.ucsb.edu/online/excitcm09/directory.html`.

Most talks were recorded and slides were put on the web. However, the discussions in the afternoon were typically not recorded, because people felt more freely by that.

Details of most talks and some discussions can be found here:
`http://online.itp.ucsb.edu/online/excitcm09/`.

Altogether, the program ran for eleven weeks. It started on Monday, October 5 and ended on Friday, December 18. Five of the 11 weeks we decided to run as so-called focus weeks. One week was the conference, and the remaining 5 weeks were un-focused, as we called them. For the latter, we still had about 3 talks per week in the morning and typically every afternoon a scheduled discussion.

A so-called focus week had a certain topic and a main coordinator. There was typically a talk in the morning and a discussion in the afternoon. The latter was rather open and not necessarily fully related to the morning talk.

Maybe it is worth noting that this was the initial concept but we carefully watched if we should actually implement or abandon it, as we did not want to over-regulate the program. The clear conclusion was that the concept was good and therefore was carried through.

The focus weeks were as follows:

Limitations of DFT: Oct. 5 - 9, organized by Kieron Burke
Since DFT is the standard starting point for most ground-state electronic structure calculations, this week covered its limitations from several disparate viewpoints: L. Mitas (NCSU) talked

about latest developments in quantum Monte Carlo, which is a rival method to DFT mainly in terms of energetics. He also provided an outlook to how excitations could be calculated with it. Suchi Guha (Univ. Columbia, Missouri, experiment) and Marilia Caldas (Univ. Sao Paolo, theory)discussed what they needed (but could not yet get) from theory in order to model the organic photo-voltaics at the heart of energy research. Scheffler's (FHI Berlin & UCSB) presentation entitled At the Fifth Rung of Jacob's Ladder: Closer to Heaven or to Hell? gave a critical overview of developments and limitations of DFT from within the solid-state calculational community. These formal talks were complemented by several informal presentations.

Transport: Oct. 19 - 23, organized by Roberto Car
Again, many disparate views were aired highlighting the breadth of this field. During this week, Kieron Burke (UC Irvine) gave a tutorial on DFT for Molecular Electronics. Stefan Blgel (FZ Jülich) talked about Spintronics, while Giulia Galli (UC Davis) focused on Thermal Transport. The program continued with talks by Stefan Kurth (Univ. San Sebastian) about Multiple Steady States and Derivative Discontinuities in Time-dependent Transport, Rex Godby (Uni. York) about GW-like Approaches to Quantum Transport, Carsten Ullrich (Univ. Columbia, Missouri) about The Spin Coulomb Drag, Jose Pitarke (Univ. Bilbao) about Some Lessons from the KS Exact Exchange Potential at Metal Surfaces, and by Roberto Car (Univ. Princeton) about Anharmonicity.

Theoretical spectroscopy: Nov. 16-20, organized by Rex Godby
This week was dedicated to various approaches to compute excitation spectra. Speakers where Robert van Leeuwen (University of Jyvaskyla, Conserving Approximations in TDDFT: Connections to Many-body Perturbation Theory), Ulf von Barth (Lund University, Guiding Principles in Theoretical Spectroscopy), John Rehr (University of Washington, Real-time Approaches for Linear and Nonlinear Optical Response), Paolo Umari (SISSA, Trieste, Non Resonant Hyper-Raman Spectra From First Principles: Application to Vitreous Silica), Werner Hanke (ITPA, Superconductivity in the Iron Pnictides: from DFT to a Functional-Renormalization-Group Study), Wei Ku (BNL, Local Approach for Excitations in Strongly Correlated Materials: Frenkel Excitons and their Propagation), and Gian-Marco Rignanese (University Louvain, Vibrational Spectroscopy). A discussion about TDDFT Functionals for Spectroscopy of Finite Systems completed the program.

Beyond DFT: Nov. 30 Dec. 4, organized by Matthias Scheffler As DFT, obviously, exhibits limitations in various aspects, methods beyond are a very hot topic. The talks listed below reflect the variety of approaches discussed in the community: Hong Jiang (Peking Univ, Localized and Itinerant States in a Unified Picture beyond DFT), Sergey Savrasov (UC Davis, Electronic Structure Calculations with Dynamical Mean Field Theory), Mark van Schilfgaarde (ASU, Quasiparticle Self-consistency), Kai-Ming Ho (ISU, Beyond LDA - The Gutzwiller Approach). For this focus week, we could even attract speakers who, for time-constraints, could not stay as long-term participants (Savrasov, Ho).

Code development: Dec. 13-17, organized by Claudia Ambrosch-Draxl
The success of all approaches discussed during the entire duration of the program also relies on efficient implementations into computer codes. To this extent, we have dedicated the last focus week to code development. Also for this week, we could attract additional speakers

like Filipp Furche (UC Irvine, The Fastest RPA in the West) and Francois Gygi (UC Davis, Scalable Algorithms for Electronic Structure Calculations). Other sessions where dedicated to the following questions / topics: Which Code to Use? Best of ...: Oral contributions were given by John Rehr (Univ. Washington), Claudia Ambrosch-Draxl (Univ. Leoben), and Volker Blum (FHI Berlin); Excited States with contributions by Stephan Sagmeister Univ. Leoben), Mark van Schilfgaarde, Xingo Ren (FHI Berlin), Hong Jiang, and John Rehr; Large Scale Computing, Speedup, Scaling with contributions from Volker Blum, Kieron Burke, and Francois Gigy; Code Sharing, Organization, I/O with contributions by Rex Godby (Univ. York) and Christian Meisenbichler (Univ. Leoben). A general discussion about Challenges: Multiplets, RIXS, PES, EMCD, NMR ... could round up the program.

Obviously, we could provide a more detailed summary of all the talks that were presented and topics that were discussed. However, we feel that the web page is nearly complete and gives a sufficient impression:
`http://excitcm09.wikispaces.com/Schedule`.

From November 2 to 6 two of the organizers (Ambrosch-Draxl and Scheffler) were running the Conference From Basic Concepts to Real Materials. (Details can be found at
`http://online.itp.ucsb.edu/online/excitcm_c09/`). Analogously to the whole program, the conference brought together scientists from various fields that we consider closely related though the communication between these fields was not always optimum.

The idea behind the conference is summarized in its announcement which reads:

Bridging the gap between the fundamental concepts of condensed matter theory, cluster-, and biophysics and a quantitative description and prediction of real materials' properties and functions is one of the biggest challenges in computational materials science and engineering. A variety of exciting methodologies is currently being developed and probed, ranging from extensions to density functional theory (DFT), like time-dependent DFT, to "beyond DFT" approaches such as many-body perturbation theory, quantum chemistry concepts, and quantum Monte Carlo methods. The goals are to reliably describe and predict the ground state (also for strongly correlated and/or van der Waals bonded materials), electronic excitations, as well as transport properties.

This conference will critically assess state-of-the-art and novel approaches in these fields, scrutinizing the applicability of various procedures to the most demanding systems and phenomena. Moreover, the theoretical achievements will be confronted with recent progress and challenging questions in different experimental techniques. To this extent, we will bring together scientists from different areas and generations to discuss forefront research and future perspectives.

Again, the concept had worked very well. All talks and more can be found at the conference web site
`http://online.itp.ucsb.edu/online/excitcm_c09/`. It should be explicitly noted here that we got overwhelming feedback from the speakers as well as the participants about the outstanding program and atmosphere of this event. For this conference, we could raise additional funding from the Psi-k Network (`http://www.psi-k.org/`) to enable the participation of 9 young researchers from Europe.

Finally, we also point out that many collaborations have been established or strengthened during this program. Examples are those between Ceperley and Zhang; Allen and Ku; Rehr and Bohnen; Burke and Gross; Ariyasetiawan and Manghi; Caldas, Blum, and Scheffler; Manghi and Rehr; Maitra and Burke; Pankratv and Ku; Ullrich and van Leeuwen; Guha and Ullrich; Thonhauser and Galli; Thonhauser and Bohnen; Thonhauser and Tateyama; Romaner, Ambrosch-Draxl, Ren, and Scheffler; and others.

Joint publications are mentioned by Lucia Reining, R. Martin and D. Ceperley who have worked on a book about Interacting electrons: theory and computational approaches; S. Kurth together with C. Verdozzi and E.K.U. Gross. Further manuscripts benefitting from the program are mentioned by Burke, Magyar, Godby, Ullrich, and Tkatchenko.

Summarizing, we can say that workshop has been a great success, judged by the energy and enthusiasm of the participants. The program succeeded in all the major goals, which were bringing together prominent researchers in many disparate areas, including solid-state physics, chemistry, and biochemistry, and finding a common language for meaningful discussions. Unusually, many researchers focused on the failures of their methods and calculations rather than successes, which was both refreshing and very productive. A clear theme evolved, that could only come about in a KITP program, showing that ab-initio calculations of excitations in condensed matter is currently in a great state of flux.

3.1.3 Report on the Psi-k Tutorial: Hands-on Siesta Code

”Efficient density-functional calculations with atomic orbitals”

University of Cantabria, Santander, Spain

June 7th-10th 2010

Organized by
Javier JUNQUERA
Departamento de Ciencias de la Tierra y Física de la Materia Condensada
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Scientific Summary

This was a four-day hands-on tutorial on the use of the Siesta code (http://www.icmab.es/siesta), aimed at researchers from different disciplines who already use, or plan to use, Siesta in their work and who would like to go beyond simply managing the code, to better understand its essential foundations and to learn to which problems and how exactly the code can be most successfully applied. Aimed also at students, the tutorial also offered a brief introduction into density-functional theory in a more general frame, to put the Siesta code in context.

Apart from the consideration of standard tasks implemented in most *ab-initio* codes, such as how to calculate the electronic (band) structure, perform structure (geometry) relaxation, calculate lattice vibrations or run molecular dynamics simulations, some specific Siesta topics were covered, such as the generation and use of pseudopotentials, the construction of basis sets of strictly localized numerical atomic orbitals, the efficient computation of the matrix elements with linear scaling methods, the role and behaviour of the real-space grid manipulations, and the smart use of parallelization. Also post-processing and visualization tools, which are becoming essential, were taught during the tutorial.

The tutorial consisted of morning lectures followed in the afternoon by practical “hands-on” sessions. Some basic knowledge of quantum mechanics, solid-state physics, and statistical physics was assumed, along with basic knowledge of UNIX and Fortran programming.

Motivation

Electronic structure codes have become mature enough to be used by scientists not trained in the development of the methods themselves. This is a shift away from traditional practice, in which the know-how and the right to use the code was acquired through a long “internship” (a PhD thesis or a postdoc appointment) in one of the groups dedicated to method and code development. Nowadays most codes are distributed with very light licensing restrictions or for affordable fees. While this ease of access is in principle a good thing, it carries the risk of uncritical or poor use of the codes by untrained people. There is thus an increasing demand for training in the sensible use of these methods, with the goal that the prospective user understands the physical and main technical approximations behind a method and can assess its reliability and its usefulness for a particular problem.

In the past few years, the possibility of treating large systems with some first-principles electronic-structure methods has opened up new opportunities in many disciplines, and ever more people not familiar with *ab-initio* calculations are being attracted to these codes. In particular, the SIESTA program (http://www.icmab.es/siesta) has become quite popular and is increasingly being used by researchers in geosciences, biology, and engineering (apart from the "home base" of materials physics and chemistry). Currently there are more than 2500 registered users all over the world (almost 40 % of the licensees are located in Europe, mostly in ESF-member countries), and the paper describing the method [J. Phys.: Condens. Mat. **14** 2745-2779 (2002)] has more than 2100 citations. SIESTA's efficiency stems from the use of strictly localized basis sets and from the implementation of linear-scaling algorithms which can be applied to suitable systems. A very important feature of the code is that its accuracy and cost can be tuned in a wide range, from quick exploratory calculations to highly accurate simulations matching the quality of plane-wave methods.

SIESTA is distributed freely to academics, and a special effort has been made over the years to train people in its use. Previous SIESTA schools [addressing specific communities in Barcelona (1999), Lyon (1999), Rio de Janeiro (2000), Cambridge (2002), Lyon (2003), Lyon (2007), Barcelona (2007), San Sebastián (2007), Barcelona (2009)] were very succesful, typically with more applicants than could be accomodated, and the demand for a new one is noticeable in the pace of new registrations and the postings to the program's mailing list.

This was the man reason why we proposed a four-day hands-on tutorial on the use of the SIESTA code, intended for researchers who want to use the code and need, apart from basic practice, a grounding on the capabilities of the method and the approximations used.

Aims

A first aim of the tutorial was to show the students the thread between fundamental laws of physics and the properties of atomic aggregates, and, in so doing, transmit the difficulty of the problem and the essence of the approximations along that thread. The main take-home knowledge was: (i) what can be computed, (ii) how to do it, (iii) how good the results can be, and (iv) how bad they can be if things are not done critically and carefully (even if *ab initio*). Apart from the basics of density-functional theory, molecular dynamics simulation and geometry relaxation, which are common to most codes, the specific SIESTA topics covered were the generation and use of pseudopotentials, the construction of basis sets of strictly localized numerical atomic orbitals, localization issues for linear scaling both in the computation of the matrix elements and in the resolution of the hamiltonian, as well as more technical ones such as the influence of the real-space grid and parallelization. Also post-processing and visualization tools, which are becoming essential, were covered during the tutorial.

It was not the purpouse of this school to train new method developers (even if this is a possible first step for it), but to train future users of these methods. It is always very important to educate future *ab-initio* users in the critical use of these codes. We taught them to control and assess the main approximations involved (LDA/GGA, pseudopotentials, basis sets, localization for linear scaling, etc.) as well as the more technical ones.

Audience

The tutorial was addressed to young people who plan on using electronic structure methods in their research. Some fundamental knowledge of quantum mechanics was assumed, as well as basic statistical mechanics for the molecular dynamics part. Basic solid state physics background was not strictly required. The basics of these areas will be covered quickly to establish the language. We have decided not to assume any previous *ab-initio* training, as our experience is that many prospective users are interested in self-contained courses. Experts in other electronic structure methods could still profit from most of the lecturers of interest, even if the course was less intensive for them.

The course was very succesful form the point of view of the interest raised. The final number of attendees was of 24. We could not expand the numbers because of limitations in the confirmed finantial support. During the practical sessions, each student worked alone in a PC computer.

The origin of the students was also very varied, both geographically (14 different nationalities: Russia, Spain, Belgium, Chile, Argentina, Germany, United Kingdom, Uzbekhistan, Poland, Mexico, France, Colombia, India, and China) and in terms of the scientific field.

A list of attendees follows in the corresponding section below.

Format

The main scheme adopted was that of morning lectures followed by afternoon practical sessions. The lectures were split into: (1) Formal lectures in the early morning, giving the theoretical background and fundamental aspects of the physics and/or methodology of the calculations, and (2) practical lectures in the late morning, with more practicalities related to the implementation and the actual SIESTA usage, preparing for the afternoon session.

Documentation and bibliography

All the information related with the organization of the tutorial (including the programme, venue, accomodation, sponsors and even some touristic information) is accesible through:
http://www.siesta.unican.es

The materials related to the course (talks and exercises) can be found in the Documentation section of the Siesta web site (http://www.icmab.es/siesta).

The key references used in the tutorial were:

J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal. *The Siesta method for ab initio order-N materials simulations*, J. Phys.: Condens. Matter **14**, 2745-2779 (2002)

D. Sánchez-Portal, P. Ordejón, and E. Canadell. *Computing the properties of materials from first principles with Siesta*, Principles and applications of density functional theory in inorganic chemistry II: Structure and bonding **113**, 103-170 (2004)

D. Sánchez-Portal, E. Artacho, P. Ordejón, and J. M. Soler. *Density-functional method for very large systems with LCAO basis set*, Int. J. Quantum Chem. **65**, 453-461 (1997)

E. Artacho, D. Sánchez-Portal, P. Ordejón, A. García, and J. M. Soler. *Linear-scaling ab-initio calculations for large and complex systems.*, Phys. Stat. Sol. (b) **215**, 809-817 (1999)

J. Junquera, O. Paz, D. Sánchez-Portal, and E. Artacho. *Numerical atomic orbitals for linear-scaling calculations*, Phys. Rev. B **64**, 235111 (2001)

E. Anglada, J. M. Soler, J. Junquera, and E. Artacho. *Systematic generation of finite-range atomic basis sets for linear-scaling calculations*, Phys. Rev. B **66**, 205101 (2002)

P. Ordejón, D. A. Drabold, M. P. Grumbach, and R. M. Martin. *Linear system-size scaling methods for electronic-structure calculations*, Phys. Rev. B **51**, 1456-1476 (1995)

E. Artacho, E. Anglada, O. Diéguez, J. D. Gale, A. García, J. Junquera, R. M. Martin, P. Ordejón, J. M. Pruneda, D. Sánchez-Portal, and J. M. Soler. *The Siesta method. Developments and applicability*, J. Phys.: Condens. Matter **20**, 064208 (2008)

E. Artacho, J. D. Gale, A. García, J. Junquera, R. M. Martin, P. Ordejón, D. Sánchez-Portal, and J. M. Soler. *Electronic structure calculations within localized orbitals: The Siesta method*, Handbook of materials modeling, Volume 1. Electronic scale. Edited by S. Yip (Springer 2005), Chapter 1.5, p. 1-15

together with the basic DFT references

R. M. Martin. *Electronic structure: Basic theory and practical methods*, (Cambridge University Press, Cambridge, UK, 2004)

J. Kohanoff. *Electronic structure calculations for solids and molecules*, (Cambridge University Press, Cambridge, UK, 2006)

Lecturers

The lectures and practical sessions were conducted by members of the Siesta development team and very experienced users. The detailed list of invited speakers and assistants for the practical sessions can be found at the corresponding Section.

Budget

Our purpouses were, at the very least, to cover the hotel, breakfast, lunch, and coffee break expenses of the participants, and the living and travel expenses of the speakers/presenters.

We got partial support from:

- The Psi-k network (5000 Euro).
- The University of Cantabria (2000 Euro).

We have also asked for support to the local Autonomous Government of Cantabria. We have not got any answer yet with the final figure we will be awarded with (if any).

To close the budget, we were forced to ask for a fee of 275 Euro per student.

Conclusion and perspectives

The tutorial was very succesful both in attendance and satisfaction of the attendees. There is still considerable interest in learning the basic of *ab-initio* methods for their use (this is a relatively new trend), and size-efficient methods are still very sought-after options. We do not see any indications of decline of the interest of young scientists in these methods, which allow us to suggest some form of continuity. The success of this and previous courses is quite evident in view of the number of papers published using Siesta and the number of citations of the main technical paper (over 2100, being the second most cited paper in the history of the review Journal of Physics: Condensed Matter).

Acknowledgments

We acknowledge finantial support of the ESF Programme Psi-k, the University of Cantabria and the local Autonomous Government of Cantabria. We are indebted with the people of the Fundación Leonardo Torres Quevedo for their invaluable help in managing the Tutorial. We thank Esteban Stafford for his help with the computer setup.

Program

Day 1: June, 7th

8:30 Registration.

10:00 Welcome and practical issues. (Javier Junquera)

10:15 Introduction: Computer simulations and their role in research. (Alberto García)

11:00 Coffee break ———

11:30 Fundamentals: the quantum-mechanical many-electron problem and the Density Functional Theory approach. (Julian D. Gale)

12:15 Brief introduction to SIESTA. What is SIESTA good and efficient for?. Where does it stand in relation to other methods or codes?. (José Antonio Torres)

12:45 Introduction to the basic execution of SIESTA (input, output, tools, k-points, SCF...). (José Antonio Torres)

13:30 Lunch —————

15:00 Practical session: first runs on simple examples. Basic visualization tools.

16:30 Coffee break ———

17:00 Practical session continued.

Day 2: June, 8th 2010

9:00 Pseudopotentials. General overview. (Alberto García)

9:45 Atomic orbitals of finite range as basis sets. (Javier Junquera)

10:30 Coffee break ———

11:00 How to generate and test pseudopotentials (including dealing with partial core corrections and semicore states). (Alberto García)

11:45 How to generate and test basis sets. (Javier Junquera)

12:30 How to generate variationally optimized basis sets. (Alberto García)

13:00 Lunch —————

15:00 Practical session: How to generate smooth and transferable pseudopotentials. Converging the basis sets for realistic systems.

16:30 Coffee break ———

17:00 Practical session continued.

Day 3: June, 9h 2010

8:30 Brief introduction to the internal algorithms for computation of matrix elements and the electronic structure. (Javier Junquera)

9:15 Fundamentals on linear scaling. (Julian D. Gale)

10:00 Simulations of periodic systems. The sampling in reciprocal space. Computation of band structures in solids. (Andrei Postnikov)

10:45 Coffee break ———

11:10 The parallelization of SIESTA. (Julian Gale)

11:55 Simulation of magnetic systems: ferro and antiferromagnetic ordering. (Andrei Postnikov)

12:40 Systematic convergence for realistic projects: from quick and dirty to converged calculations. Filtering atomic orbitals to avoid the eggbox. (Daniel Sánchez-Portal)

13:10 Lunch —————

15:00 Practical session: Systematic convergence for realistic problems.

16:30 Coffee break ———

17:00 Practical session continued.

Day 4: June, 10th 2010

8:30 Relaxations and geometry optimizations. (Alberto García)

9:15 Molecular Dynamics (MD) in different ensembles. (Julian Gale)

10:00 Calculations of vibrational spectrum and phonons. (Andrei Postnikov)

10:45 Coffee break ———

11:10 LDA+U: a primer and implementation in Siesta. (Daniel Sánchez-Portal)

11:55 Tools for the analysis of the electronic structure in relation to bonding properties. (Alberto García)

12:40 Practical code-handling matters: licences, updates and compilation. (José Antonio Torres)

13:10 Lunch ——————

15:00 Practical session: Computation of vibrational properties of materials. Molecular dynamic simulations on different ensembles. Beyond bare DFT simulations: the effect of correlation.

16:30 Coffee break ———

17:00 Practical session continued.

List of invited speakers

- Julian D. Gale (julian@ivec.org)
  Curtin University of Technology, Perth, Australia.
- Alberto García (albertog@icmab.es)
  Institut de Ciència de Materials de Barcelona, ICMAB-CSIC, Barcelona, Spain.
- Javier Junquera (javier.junquera@unican.es)
  Universidad de Cantabria, Santander, Spain.
- Andrei Postnikov (postnikov@univ-metz.fr)
  Université Paul Verlaine, Metz, France.
- Daniel Sánchez-Portal (qsapod@sc.ehu.es)
  Donostia International Physics Center, DIPC-CSIC, San Sebastián, Spain.
- José Antonio Torres (jose.torres.alonso@uam.es)
  Universidad Autónoma de Madrid, Madrid, Spain.

List of assistants in practical sessions

- Pablo Aguado-Puente (pablo.aguado@unican.es)
  Universidad de Cantabria, Santander, Spain.
- Marcos Verissimo-Alves (marcos.verissimo@unican.es)
  Universidad de Cantabria, Santander, Spain.
- Esteban Stafford (esteban.stafford@gestion.unican.es)
  Universidad de Cantabria, Santander, Spain.

List of Attendees

Name	Age	Nationality	Affiliation	Country
Mikhail Akhukov	28	Russia	Radboud University	Netherlands
Valentín Alba	43	Spain	UNED	Spain
Ludovic Briquet	28	Belgium	CRP Gabriel Lippman	Luxembourg
Pepa Cabrera-SanFélix	32	Spain	DIPC-CSIC	Spain
Diego Carrascal	35	Spain	University of Oviedo	Spain
Enrique Comesaña	32	Spain	University of Santiago	Spain
Sergio Conejeros	29	Chile	University of Barcelona	Spain
Griselda Noemi García	39	Argentina	Catholic University of Chile	Chile
Nuria García	24	Spain	University of Barcelona	Spain
Hannes Huebener	29	Germany	Echole Polytechnique of Paris	France
Elisa Jiménez	25	Spain	University if the Basque Country	Spain
Karen Johnston	24	United Kingdom	Max Plank Institute for Polymer Research	Germany
Smagul Karazhanov	46	Uzbekistan	Insitute for Energy Technology	Norway
Jaromir Kryszczak	27	Poland	Marie Curie-Sklodowska Univeristy	Poland
Xochitl López-Solano	37	Mexico	The University of Texas at San Antonio	USA
Ludovic Martin	30	France	University of the Basque Country	Spain
Gonzalo Recio	23	Spain	University of Madrid	Spain
Ángela Rojas		Colombia	National University of Colombia	Colombia
Juan Salafranca	32	Spain	ORNL-University of Tennessee	USA
Suchismita Sanyal	33	India	General Electric India	India
Jing Shen	29	China	Centrale Recherche SA	France
Begoña Torres	41	Spain	University of Burgos	Spain
Montserrat Vallejo	26	Spain	University of Cantabria	Spain
Colin Van Dyck	23	Belgium	University of Mons	Belgium

3.1.4 Report on the CECAM Workshop "Actinides: Correlated Electrons and Nuclear Materials"

Organizers:
Bernard Amadon (CEA) and Leon Petit (STFC Daresbury Laboratory)

14-16 June, 2010, Manchester, U.K.

Brief Report

The workshop was held at the Ramada Jarvis Hotel in Manchester (U.K.) from the 14-16th of June 2010. Altogether 47 participants were registered for the workshop. 27 invited talks were presented. Plenty of time was given for discussions, including a round table. The focus of the workshop was on investigating the impact that the study of correlations in the actinides can have on our understanding of the materials of the nuclear cycle. Whilst the main thrust was on the theoretical first principles tools that are currently being developed, close contact was made to experimental investigations. The latter included presentations on the state of the art of developing improved nuclear fuels, as well as new approaches to nuclear waste disposal.

Summary of Presentations:

The workshop was opened by Claude Guet (CEA), who presented an outlook on the role that nuclear energy will play in guaranteeing the future sustainable energy mix. The speaker emphasized the need for substantial R&D into nuclear materials, both with respect to experiment and computer simulations. The goal is among others to develop materials capable of sustaining intense irradiation in order to extend the lifetimes of reactors, fuels for the next generation of reactors, fuels that incorporate the minor actinides to achieve improved recycling, and glasses for long term safe waste disposal. Rudy Konings (JRC-ITU) presented results on the performance of nuclear fuels under extreme conditions. The talk gave a comprehensive insight into the fuels for the next generation of nuclear reactors, and the modeling and experimental investigations that will be required for improving their performance under reactor conditions, i.e. high pressure and temperature. Understanding the materials related problems requires understanding their electronic structure, and given the strongly correlated nature of the actinide 5f electrons, theories that go beyond the LSD approximation have to be developed and applied.

One of the most studied and still not fully understood problems in actinide physics, is nature of the ground state in δ-Pu, and which was also the subject matter of several presentations at the workshop. Using the so-called magnetic cancellations model, Sung Woo Yu (LLNL) argued that the absence of magnetic moment might be explained in terms of the cancellation of the spin and orbital moments. Indications of the validity of this model could come from spin resolved photoemission experiments. Mike Brooks (Uppsala University and Daresbury Laboratory) suggested a different model, given the strong indications from experiment that both spin and orbital moments in δ-Pu are individually zero. He proposed that the non-magnetic ground state in some of the actinides can be obtained if the exchange enhanced spin-orbit coupling is correctly taken into account. The importance of taking the spin-orbit coupling correctly into account was also emphasized by Alexey Lukoyanov (Russian Academy of Sciences), who presented results for a range of actinide metals and compounds obtained by means of the LDA+U+SO method. With respect to the metals the calculated electrical resistivities under pressure compare rather well to experiment, and a non-magnetic f^6 groundstate configuration is derived for δ-Pu. In a further presentation on δ-Pu, Chris Marianetti (Columbia University), by solving the periodic Anderson model within Hartree-Fock, derived the double-well potential known to occur in the more complex DMFT approach. The double well arises from correlations switching hybridization. It was shown that whilst Hartree-Fock reproduces DFT and gives a magnetic moment, DMFT gives a Fermi liquid. In his minimal model Jindrich Kolorenc (University of Hamburg), using the LDA+Hubbard-I (HIA) approximation studied the spectroscopy of actinide metals Pu, Am and Cm, finding good agreement between theory and PES studies. The methodology was furthermore applied to the Pu115 compounds $PuCoGa_5$ and $PuRhGa_5$, with the intention of understanding their electronic structure and superconductivity. The calculations show a relative reduction of the f spectral weight at the Fermi level.

The actinide (A) oxides remain the most used fuel form in current nuclear reactors, and a considerable number of presentations focused on giving an improved description of AO_2 with the actinide A ranging from U to Cf. After giving a short introduction on the hybrid functional methodology, Richard Martin (LANL) presented the results for energy gaps, lattice constants and magnetic behavior for the actinide oxides from ThO_2 to EsO_2 in good agreement with available experimental data. The calculations also seem to indicate a distinction between early more 'ionic' actinide dioxides, and late more 'covalent' dioxides. Axel Svane (Aarhus University) presented results for the actinide dioxides from U to Am obtained using quasiparticle self-consistent GW method. The insulating ground state and the position of the lower and upper Hubbard bands was shown to emerge from the calculations without having to rely on parameters. A third methodology, the so-called self-interaction corrected (SIC)-LSD, was presented by Zdzislawa (Dzidka) Szotek (Daresbury Laboratory), where the electronic structure of the actinide monoxides, sesquioxides and dioxides was derived from first principles based on total energy considerations. The predicted ground-state properties and valencies are in agreement with experiment, and indicate an overall very ionic bonding in actinide oxides. Fei Zhou (University of California) using a combination of improved LDA+U and model Hamiltonian presented his latest results on UO_2, with the calculated ground state and crystal field excitations in good agreement with experiment.

Peter Oppeneer (Uppsala University) discussed his results regarding the hidden order in URu_2Si_2, arguing that a delocalized 5f electron manifold is in good agreement with the available experimental data. The localized 5f electrons as described in the LDA+U are required to describe the electronic structure and complex multipolar ordering in the actinide oxides. Paolo Santini (University of Parma) showed that the dynamics observed in UO_2 results from the complex interplay of spin, phonon and quadrupole degrees of freedom. Quadrupolar waves are a major component of the dynamics with some of them carrying along a magnetic component.

Using the LDA+U methodology Michel Freyss (CEA) presented his results on Oxygen self-diffusion in UO_2. It was shown that controlling the $5f$ occupation matrices can prevent metastable states. The experimentally observed stability of the Jahn-Teller distortion was investigated as was the formation energies of oxygen interstitials and vacancies. Using the GGA+U, Eugene Kotomin (University of Latvia), discussed his results on PuO_2, comparing the use of a single rotationally invariant effective U parameter, U_{eff}, as proposed by Dudarev, to the use of two independent parameters U and J, as proposed by Liechtenstein. Using an optimized U, supercell calculations were performed for Pu and O vacancies in PuO_2. Jean-Paul Crocombette (CEA) presented results on charged point defects in UO_2, obtained using the hybrid functional methodology. From the calculations it emerged that whilst O interstitials and U vacancies are negatively charged, oxygen vacancies turn out to be slightly positive charged. The formation energies of point defects in ThO2, UO_2, and PuO_2 was similarly addressed by Younsuk Yun (Paul Scherrer Institut) who furthermore discussed the diffusion behavior of Xe and He, calculating their incorporation and migration energies.

At the workshop, a number of presentations were given, addressing all aspects of experimental investigation into the actinide materials. Thomas Gouder (JRC-Karlsruhe) presented results on the surface reactivity of nuclear systems, discussing issues such as the corrosion of spent nuclear fuel and the radiation assisted reduction of PuO_2 by water. Ladislav Havela (Charles University) addressed the magnetism of Pu metal based on susceptibility measurements and XPS studies concluding among others that the details of the 5f occupancy, rather than the Pu-Pu distance are relevant for magnetic properties. Gerry Lander (JRC-ITU) presented an overview of both theory and experiments over the years studying the behavior of actinide metals, and the change in bonding properties under pressure. Gerrit van der Laan (Diamond Light Source) argued that the actinides show strong 5d-5f electric-multipole transitions that can be probed bulk sensitive using non-resonant inelastic scattering (NIXS) experiments. For localized 5f electrons in UO_2 good agreement is obtained with many-electron spectral calculations in intermediate coupling. Kevin Moore (LLNL) gave a very comprehensive overview on the insights gained from applying X-ray and electron spectroscopy to actinide materials, and the impact on understanding nuclear materials was discussed. The possibility of deriving information on the ground state valency of the actinide ions was furthermore investigated. Michael Manley (LLNL) discussed the recently observed intrinsic localized modes (ILM) in metallic Uranium, and the impact they have on thermal and electrical conductivity, the annealing rate of radiation damage, and interstitial diffusion among others. The resulting brittle to ductile fracture transition in Uranium was furthermore investigated in this context. Sung Woo Yu (LLNL) presented furthermore recent BIS and RIPES data for CeO_2 and UO_2 that were obtained from the new system at LLNL.

A number of delegates work in the field of actinide chemistry, and the workshop provided interesting potential for future cross-field collaborations. The interest in MD simulations was obvious given the potential for developing a multiscale approach to describing nuclear fuels. John Purton (Daresbury Laboratory) gave a presentation on the use of molecular dynamics in nuclear materials. Radiation damage in Gadolinium pyrochlores, a potential storage material for nuclear waste, was investigated through the numerical modeling of radiation cascades. Nick Kaltsoyannis (UCL) gave a talk on actinide chemistry, investigating the effect of spin-orbit coupling and the oxidation state in f-element organo metallics. It emerges that configurational admixture is not a reliable tool to describe the electronic structure of $Ce(COT)_2$ which is best described as Ce(IV) system. Indications are that the ground states of the late actinocenes are strongly multi-configurational.

Round Table: 'The challenges of linking fundamental theoretical modeling to practical applications in reactor core materials' moderated by Malcolm Stocks (ORNL).

The purpose of the round table was to establish what kind of difficulties the community encounters when trying to obtain insight into nuclear materials, and how these difficulties can be overcome. The discussions pointed out a number of issues:

- Energetics, how important is the ground state electronic structure for real materials at reactor operation temperatures?

- Radiation damage implies huge kinetic energies, what relevance has the ground state.

- Methodologies well suited for studying the effect of correlations are not necessarily adequate for calculating the structural properties of materials. One might therefore consider using a combination of methodologies to study the different aspect of the nuclear materials.

- Benchmark for condensed matter results. Different LDA+U calculations for example depending on the double counting term used, or whether one uses Dudarev's U_{eff}=U-J compared to Liechtensteins independent U and J.

- Are pseudopotentials approaches useful for benchmarking, is FLAPW? Do we have good pseudopotentials for the actinides?

- VASP. Pseudopotential is a problem, as we loose accuracy since we are not solving the all-electron relativistic problem. Pseudopotential fitted to smoothed spherical charge, and therefore l-decomposed but not m-decomposed

- Is it relevant to create a database for our results?

- How well is relativity accounted for in the different codes, and is it important to solve the Dirac equation as is done in molecular calculations? As far as the quantum chemists are concerned, the solid state community seems to be satisfied with a moderate level of accuracy.

- LSDA, GGA, have a non relativistic exchange correlation squeezed into relativistic code.

- The multiple minima that occur in LDA+U calculations, do they have a specific meaning.

- What can be done to achieve a simple phase diagram? Is a multiscale approach realistic? Should one instead use the atomic information as reference in for example CALPHAD, i.e. go from ab-initio to the phase diagram without the need for MD.

- Much more experimental evidence is required. This is a considerable problem, given the high costs due to the associated security and safety concerns. Even more problematic is the fact that high quality crystals of Bk, Cm, Am, etc., are no longer available.

- Suggested future experiments: * Most experimental tools investigate surface: need more bulk measurements. * Theoretical support for surface phenomena: leaching, surface reactions, absorption. * Energy gaps of the dioxides: plenty of theory but no experiments! * Need well defined surfaces before doing calculations. * Magnetism of strongly disordered actinide systems. Are the observed effects due to the loss of periodicity or frustration? * Theoreticians need pair correlation functions of the disordered structure. * Bond energies and cohesive energies: no calorimetric results available.

From the talks it emerged that considerable progress has been made in the last couple of years concerning the fundamental description of correlations in nuclear materials. It also became clear however that the next step will have to involve a certain level of validation and verification of the different methodologies, both compared to each others and compared to experiment. With respect to experiment, it would appear that not enough capabilities exist worldwide to guarantee, that on one hand the required crystals can be grown, and on the other hand, due to the prohibitive costs associated with security arrangements around actinide experiments, crucial experiments can no longer be performed within an overseeable future.

A collaboration between the Ile de France and the Hartree Center CECAM nodes is planned, with respect to validating and verifying the LDA+U and SIC-LSD codes and applying them to the study of mixed oxide fuels. A third partner at the University of Warwick, specialist on DLM and CPA, would be involved.

List of Participants:

Mike Brooks (Uppsala University and STFC Daresbury Laboratory)
Jean-Paul Crocombette (CEA, Centre de Saclay)
Michel Freyss (CEA, Centre de Cadarache)
Thomas Gouder (European Commission JRC-Karlsruhe)
Claude Guet (CEA)
Ladislav Havela (Charles University)
Gerald Jomard (CEA, Bruyeres-le-Chatel)
Nik Kaltsoyannis (University College London)
Jindrich Kolorenc (University of Hamburg)
Rudy Konings (European Commission JRC-Karlsruhe)
Eugene Kotomin (University of Latvia)
Gerry Lander (Institut Laue-Langevin)
Chris Marianetti (Columbia University)
Richard Martin (Los Alamos National Laboratory)
Peter Oppeneer (Uppsala University)
Asok Ray (University of Texas at Arlington)
Malcolm Stocks (Oak Ridge National Laboratory)
Axel Svane (Aarhus University)
Gerrit van der Laan (STFC Diamond Light Source)
Younsuk Yun (Paul Scherrer Institut)
Kevin Moore (Lawrence Livermore National Laboratory)
Paolo Santini (University of Parma)
Sung Woo Yu (Lawrence Livermore National Laboratory)
Michael Manley (Lawrence Livermore National Laboratory)
Alexey Lukoyanov (Russian Academy of Sciences)
Zdzislawa (Dzidka) Szotek (STFC Daresbury Laboratory)
Fei Zhou (University of California)

John Purton (STFC STFC Daresbury Laboratory)
Walter Temmerman (STFC Daresbury Laboratory)
Martin Lueders (STFC Daresbury Laboratory)
Andre Severo Pereiro Gomes (CNRS)
Valerie Valet (CNRS-Lille1)
Bernd Schimmelpfennig (Indtitut for Nuclear Waste Disposal)
Matthias Krack (Paaul Scherrer Institut)
Krishnamoorty Arumugam (University of Manchester)
Simon Bennie (University of Manchester)
Neil Burton (University of Manchester)
Alexander Chew (University of Manchester)
Slimane Doudou (University of Manchester)
Christopher Green (University of Manchester)
Attafeh Hassanieh (University of Manchester)
Joe McDouall (University of Manchester)
Jack Mulroue (UCL)
Julie Staunton (University of Warwick)
Hayley Wood (University of Manchester)

Program

Monday 14.06.10

8.45 - 9.00 Welcome and Introduction

9.00 - 9.30 Claude Guet (CEA/Siege):
Basic Science Issues Associated with a Sustainable Nuclear Energy

9.30 - 10.00 Thomas Gouder (JRC-Karlsruhe):
Electronic Structure and Surface Reactivity of Nuclear Systems

10.00 - 10.30 Peter Oppeneer (University of Uppsala):
A First-Principles Route to Shedding light on Complex and Correlated Actinides

10.30 - 11.00 Coffee Break

11.00 - 11.30 Michel Freyss (CEA/Cadarache):
First Principles Study of Uranium Dioxide and Oxygen Self-Diffusion in Uranium Dioxide

11.30 - 12.00 Sung Woo Yu (LLNL):
An Alternative Model for Electron Correlation in Pu

12.00 - 12.30 Gerald Jomard (CEA/DAM Ile de France):
Ab-Initio Study of the Plutonium Dioxide Surfaces: Role of Electronic Correlation

12.30 - 14.30 Lunch and Discussions

14.30 -15.00 Ladislav Havela (Charles University):
From Pu Metal to Compounds: Magnetism and Electronic Properties

15.00 - 15.30 Richard Martin (LANL):
The localization/delocalization dilemma in the Electronic Structure of f-Elements

15.30 -16.00 Coffee Break

16.00 - 16.30 Gerry Lander (JRC-ITU):
The Actinide Elements Under Pressure

16.30 - 17.00 Eugene Kotomin (University of Latvia):
DFT+U Calculations of the Electronic Structure of Perfect and Defective PuO2

18.00 -20.00 Buffet and Poster session:

Matthias Krack (Paul Scherrer Institut):
Enabling Simulations of Actinide Materials with the CP2K Program Package

Andre Severo Pereira Gomes (CNRS):
Modeling Localized Electronic States of Actinide Species in Condensed Phase

Jack Mulroue (University College London):
Modelling Ceramics for Radioactive Waste Disposal

Tuesday 15.06.10

9.00 - 9.30 Rudy Konings (JRC-Karlsruhe):
Nuclear Fuels: Materials Under Extreme Conditions

9.30 - 10.00 Axel Svane (Aarhus University):
GW Calculations for Actinides

10.00 - 10.30 Gerrit van der Laan (Diamond Light Source):

XAS, EELS and NIXS of Actinides with Localized and Itinerant 5f Character

10.30 - 11.00 Coffee Break

11.00 - 11.30 Jean-Paul Crocombette (CEA/Saclay):
Charge State of Point Defects in Uranium Dioxide Studied by Density Functional Theory with Hybrid Functional for Correlated Electrons

11.30 - 12.00 Jindrich Kolorenc (University of Hamburg):
Electronic Structure, Photoemisson and Superconductivity in 5f-Element Materials

12.00 - 12.30 Fei Zhou (University of California):
Electronic Structure of UO2 : LDA+U Calculations od the Crystal Field and Magnetic Ground States

12.30 - 14.30 Lunch and Discussions

14.30 - 15.00 John Purton (Daresbury Laboratory):
Molecular dynamics simulations of radiation cascades in gadolinium pyrochlores

15.00 - 15.30 Nik Kaltsoyannis
(UCL):
Oxidation State Ambiguity in f-Elements Organometallics

15.30 - 16.00 Coffee Break

16.00 - 17.00 Round Table
Moderator: Malcolm Stocks (ORNL):
The challenges of linking fundamental theoretical modelling to practical applications in reactor core materials

19.00 -22.00 Conference Dinner

Wednesday 16.06.10

9.00 - 9.30 Mike Brooks (Uppsala University & Daresbury Laboratory):
Spin-Orbit Coupling Enhancement in Actinide Metals and Compounds

9.30 - 10.00 Kevin Moore (LLNL):
X-Ray and Electron Spectroscopy of Actinide Materials: Fundamental Science for Energy

10.00 - 10.30 Paolo Santini (University of Parma):
Quadrupolar waves in Uranium Dioxide

10.30 - 11.00 Coffee Break

11.00 - 11.30 Younsuk Yun (Paul Scherrer Institut):
Point Defect and Transport Properties in Nuclear Fuel Materials

11.30 - 12.00 Alexey Lukoyanov (Russian Academy of Sciences):
Magnetic State and Resistivity of Actinide Compounds from LDA+U+SO Calculations

12.00 - 12.30 Chris Marianetti (Columbia University):
Capturing the Double-Well Potential in Pu

12.30 - 14.00 Lunch

14.00 - 14.30 Zdzislawa (Dzidka) Szotek (Daresbury Laboratory):
Electronic Structure of Nuclear Materials from First-Principles

14.30 - 15.00 Michael Manley (LLNL):
Impact of Intrinsic Localized Modes of Atomic Motion on the Properties of Uranium

15.00 - 15.30 Coffee Break

15.30 - 17.00 Final Discussions

4 General Workshop/Conference Announcements

4.1 KKR Hands-On Course

Daresbury Laboratory and Chester, U.K.

4-6 October 2010

Organizers:
Hubert Ebert (Ludwig-Maximilians University Munich)
Zdzislawa (Dzidka) Szotek (STFC Daresbury Laboratory, U.K.)
`http://www.hartree.ac.uk/cecam_at_daresbury/KKR.shtml`

Course Motivation

The aim of the course is to introduce theoreticians as well as experimentalists into the KKR bandstructure method and its use to calculate spectroscopic properties of magnetic solids (see the recent Psi-k highlight at:
`http://www.psi-k.org/newsletters/News_97/newsletter_97.pdf` or directly
`http://www.psi-k.org/newsletters/News_97/Highlight_97.pdf`).

Accordingly, there will be lectures dealing with the formal background and technical details of the KKR method. Emphasis will be put on a fully relativistic formulation supplying the basis for a treatment of dichroic effects in spectroscopy. The corresponding theory for magnetic dichroism in x- ray absorption, photo emission and related spectroscopies will be reviewed. Six sessions will be devoted to applications making use of the Munich *SPR-KKR* program package that includes a graphical user interface called *xband* The various calculations on clusters and ordered as well as disordered solids, which are meant in particular to introduce inexperienced users to the field, will be guided by tutors.

Speakers and Tutors:

* Peter Dederichs, Juelich (tbc)
* Hubert Ebert, Muenchen
* Eberhard Engel, Frankfurt (tbc)
* Diemo Koedderitzsch, Muenchen
* Martin Lueders, Daresbury
* Jan Minar, Muenchen
* Leon Petit, Daresbury
* Zdzislawa (Dzidka) Szotek, Daresbury
* Walter Temmerman, Daresbury

This three day hands-on course will take place at Daresbury Laboratory, U.K., where the lectures and hands-on tutorials will be run. For the accommodation, we have provisionally secured rooms in Mill Hotel and Spa in Chester, about 18 miles away from Daresbury village and Lab. Chester is a beautiful old city with Roman walls (`http://www.chester360.co.uk/index.htm`), in the county of Cheshire. The hotel is situated right at the centre of this historic city. There will be a daily bus transportation between Chester and Daresbury Laboratory throughout the course. Please check the hotel details at

`http://www.millhotel.com/?gclid=COGyp5rn2aICFUMB4wodJVWlcg`

The registration is now fully open! For details on program, registration form and accommodation, please go to:

`http://www.cse.scitech.ac.uk/cecam_at_daresbury/KKR.shtml`.

See also the web pages of SPR-KKR and xband, respectively at:

`http://olymp.phys.chemie.uni-muenchen.de/ak/ebert/SPRKKR/`

`http://olymp.phys.chemie.uni-muenchen.de/ak/ebert/xband.html`

5 General Job Announcements

Post-doctoral Position

Computational Condensed Matter Physics at Rutgers University, USA

We are looking for an exceptional computational physicist to work as a postdoctoral fellow or research associate in the group of G. Kotliar and K. Haule at Rutgers University. We seek a candidate with research interest in theoretical physics with exceptional analytical and computer skills.

The prime scientific focus of the position will be to develop and apply computational methods to carry out studies of correlated materials.

Valuable skills for the job are the ability to carry out a large scale electronic structure calculation, familiarity with techniques of many-body physics such as Dynamical Mean Field Theory, and ability to develop high level software. Excellence in one of these areas is required. The successful candidate will have the chance to interact with many experimental groups to understand and design complex correlated materials. The Rutgers Computational Physics group is at the forefront of this area and has an excellent research atmosphere.

The pay is competitive and will be commensurate with experience and abilities and includes the standard benefit package.

Applications should be sent by email to kotliar@physics.rutgers.edu or haule@physics.rutgers.edu with a cc to our secretary fran@physics.rutgers.edu and should include CV, a cover letter, a statement of research interest, and three letters of reference.

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6 Abstracts

Response of magnetically frustrated nanostructures to external magnetic fields: stepped Cr/Fe interfaces

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Abstract

The response of typical magnetically frustrated systems to an external magnetic field is investigated in order to get insight on the qualitative trends and their origin at the electronic structure level. Electronic structure calculations are conducted for Cr overlayers of different thickness on the stepped Fe(001) substrate, using a self-consistent noncollinear tight-binding method in which the Hamiltonian has been extended to account for the interaction with the external field. The average magnetization at the Cr overlayers is obtained through the local magnetic moments distribution of the system at different external magnetic fields. The complex non-monotonous behavior of the remagnetization process as a function of the external field is explained in terms of the local geometrical and chemical environment of the inequivalent Cr atoms which leads to local magnetic couplings having different response. In particular, we find minima at low fields due to the strength of the local antiferromagnetic couplings and changes of slope at higher fields associated to spin-flip transitions taking place at certain Cr atoms when the system is trapped in collinear magnetic configurations.

(Physical Review B 81, 174426 (2010))
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Hybrid functionals within the all-electron FLAPW method: Implementation and application of PBE0

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Abstract

We present an efficient implementation of the Perdew-Burke-Ernzerhof hybrid functional PBE0 within the full-potential linearized augmented-plane-wave (FLAPW) method. The Hartree-Fock exchange term, which is a central ingredient of hybrid functionals, gives rise to a computationally expensive nonlocal potential in the one-particle Schrödinger equation. The matrix elements of this exchange potential are calculated with the help of an auxiliary basis that is constructed from products of FLAPW basis functions. By representing the Coulomb interaction in this basis the nonlocal exchange term becomes a Brillouin-zone sum over vector-matrix-vector products. The Coulomb matrix is calculated only once at the beginning of a self-consistent-field cycle. We show that it can be made sparse by a suitable unitary transformation of the auxiliary basis, which accelerates the computation of the vector-matrix-vector products considerably. Additionally, we exploit spatial and time-reversal symmetry to identify the nonvanishing exchange matrix elements in advance and to restrict the $\mathbf{k}$ summations for the nonlocal potential to an irreducible set of $\mathbf{k}$ points. Favorable convergence of the self-consistent-field cycle is achieved by a nested density-only and density-matrix iteration scheme. We discuss the convergence with respect to the parameters of our numerical scheme and show results for a variety of semiconductors and insulators, including the oxides ZnO, EuO, Al_2O_3, and $SrTiO_3$, where the PBE0 hybrid functional improves the band gaps and the description of localized states in comparison with the PBE functional. Furthermore, we find that in contrast to conventional local exchange-correlation functionals ferromagnetic EuO is correctly predicted to be a semiconductor.

Phys. Rev. B **81**, 195117 (2010)
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Fractional occupation in Kohn-Sham density-functional theory and the treatment of non-pure-state v-representable densities

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Abstract

In the framework of Kohn-Sham density-functional theory, systems with ground-state densities that are not pure-state v-representable (PSVR) in the noninteracting reference system occur frequently. In the present contribution, an algorithm, which allows the solution of such systems, is proposed. It is shown that the use of densities which do not correspond to a ground state of their noninteracting reference system is forbidden. As a consequence, the proposed algorithm considers only noninteracting ensemble v-representable densities. The Fe atom, a well-known non-PSVR system, is used as an illustration. Finally, the problem is analyzed within finite-temperature density-functional theory, where the physical significance of fractional occupations is exposed and the question of why degenerate states can be unequally occupied is resolved.

(Published in Phys. Rev. A **80**, 032115 (2009))

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7 SCIENTIFIC HIGHLIGHT OF THE MONTH: "Ab initio Random Structure Searching"

Ab initio Random Structure Searching

Chris J Pickard[1] and R J Needs[2]

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Abstract

It is essential to know the arrangement of the atoms in a material in order to compute and understand its properties. The search for stable structures of materials using first-principles electronic structure methods, such as density functional theory (DFT), has grown rapidly in recent years. Here we describe our simple approach to searching for structures with DFT which we call *ab initio* random structure searching (AIRSS). Applications to discovering structures of solids, point defects, surfaces, and clusters are described.

7.1 Introduction

Finding the most stable (lowest in energy or free energy) structure of a large assembly of atoms is a very difficult problem. The number of minima in the potential energy surface (PES) of a large system increases exponentially with the number of atoms. Finding the global minimum energy structure with certainty presumably involves visiting every local minimum and consequently the computational cost also increases exponentially with the number of atoms. This effectively prohibits an exact solution for large systems. Although the problem of structure prediction remains very difficult, steady progress has been made over the years. Advances in computing power, methods for calculating accurate energies of assemblies of atoms, and progress in searching methodologies has led to numerous successful predictions.

Predicting structure is important for a number of reasons. Structure prediction is relevant to all areas of science in which one would like to know the relative positions of atoms. Computational searching can be much easier and cheaper than experiments since a range of systems can quickly be searched, often obtaining interesting results and sometimes discovering promising new materials. The low-energy metastable minima are also interesting as they can be accessed at finite temperatures, or under pressure. Structures may also be trapped in metastable minima during growth or processing. Computational searches can augment experimental studies when the data is of poor quality or incomplete. For example, powder diffraction data may be insufficient for a complete structural determination but may suffice to yield information such as the dimensions of the unit cell and an indication of its likely space group. The experimental data can then be used as constraints in a structural search. The positions of hydrogen atoms within a crystal cannot easily be determined from x-ray diffraction data, and here one can use the positions of the heavier atoms and the dimensions of the unit cell as constraints. Computational searches can also be used to investigate materials under conditions which cannot currently be accessed experimentally, for example, the pressures within the deep interiors of massive planets. Perhaps the most exciting possibility is the discovery of new materials in the computer which can be synthesised and have useful applications.

We have used our searching strategy, AIRSS, to predict stable and metastable structures of crystals and clusters and the atomic positions at point defects in solids, and we are beginning applications to surfaces and interfaces. Only fully quantum mechanical calculations suffice to deliver the required level of accuracy because of the wide range of inter-atomic bonding that may be encountered throughout the searches. We calculate the energetics using first-principles density-functional-theory (DFT) methods [1–3] which offer a high-level description of the electronic structure at a cost which is affordable for the many thousands of structures which must be considered in the course of a reliable search.

There is a rich literature on computational searching for structures. It is not our purpose here to review the entire field, although in Appendix A we briefly summarise other approaches to structure searching and give references to the literature. In this article we describe our preferred approach in detail, illustrating the discussion with a variety of examples.

7.2 Potential energy surfaces and the global searching problem

The exponential increase of the number of local minima with system size was derived and discussed by Stillinger [4]. The basic idea can be gleaned from the following simple argument. Suppose that a large system of N atoms can be divided into M equivalent subsystems, each of N/M atoms. If the subsystems are large enough they will have independent stable configurations. The total number of locally stable configurations of the system n_s therefore satisfies

$$n_s(N) = n_s^M(N/M) \ . \tag{1}$$

The solution to equation (1) is

$$n_s(N) = e^{\alpha N} \ , \tag{2}$$

where α is a constant. Computational studies of Lennard-Jones clusters support the exponential dependence [5, 6].

The exponential increase in the number of local minima suggests that it will be very difficult to devise a reliable approach for finding the global minimum energy state of a large system. Perhaps clever methods can be found for eliminating the exponential scaling? Although it is not currently possible to give a definitive answer to this question, the prospects appear bleak. Determining the global minimum of a PES is classed as an NP-hard (non-deterministic polynomial-time hard) problem. These are problems for which it is widely suspected (but not proven) that it is impossible to find an algorithm which works without fail in polynomial time. Reducing the strength of the exponential scaling (i.e., reducing the value of α in equation (2)) is a more realistic goal, but theory also provides us with a warning about this. Wolpert and Macready have proved a "no free lunch theorem" for searching and optimisation which shows that all algorithms that search for the global minimum of an energy function perform exactly the same when averaged over all possible energy functions [7]. The implication is that it may be extremely difficult or even impossible to find a smart algorithm which works well in all circumstances.

We are interested in the energy functions which represent the PES of assemblies of atoms, and these form only a very small subset of all possible energy functions. Much of the PES of a reasonably large assembly of atoms corresponds to very high energy structures in which some atoms are much closer than an equilibrium bond length. This can readily be verified by calculating the energies of an ensemble of "random" structures, each formed by placing atoms at random positions within a box whose size gives a physically reasonable density. The average energy will be far higher than even the highest energy local minimum because of the strong short-range atomic repulsion. Other parts of the PES will correspond to fragmented structures. These may contain interesting energy minima, but if we are only interested in fully connected structures we can disregard them.

A basin of attraction of a PES is defined as the set of points for which downhill relaxation leads to the same energy minimum. A PES can therefore be divided into basins of attraction. Some rather general features of the PES of an assembly of atoms and its basins of attraction are known:

(i) The substantial fraction of the PES in which some atoms are very close together contains almost no minima.

(ii) The basins are normally arranged such that if one moves from a basin to a neighbour it is more likely that the neighbour will have a lower energy minimum if the barrier between the basins is small. This is a consequence of the relative smoothness of the PES at low energies and is related to the Bell-Evans-Polanyi principle which states that highly exothermic chemical reactions have low activation energies [8].

(iii) Another implication of the Bell-Evans-Polanyi principle is that low energy basins are expected to occur near other low energy basins. Of course low energy basins can occur in widely separated "clumps", which are normally referred to as "funnels".

(iv) Studies of Lennard-Jones clusters show that basins with lower energy minima tend to have larger hyper-areas than higher energy minima [9].

(v) The probability distribution of the energies of the local minima of a PES is close to Gaussian for large systems, as would apply for the model which leads to equation (2).

(vi) The hyper-areas of the basins of attraction appear to follow a power law distribution [10]. It seems that the power law behaviour must derive from some type of order in the arrangement of basins of different sizes, with smaller basins filling the gaps between larger ones [11]. The power law distribution does not occur in a simple model PES formed by arranging Gaussians of random width [11].

(vii) Both very-low (and very-high) energy minima tend to correspond to symmetrical structures. This principle has been annunciated in many forms over the years and it is also supported by calculations [12, 13].

(viii) It has been observed that some space group symmetries are much more common than others in crystals formed from small organic molecules [14–16]. Inorganic systems show different space group frequencies [17, 18].
(ix) As well as general features of the PES of assemblies of atoms, there are particular features which arise from chemical considerations. In fact we normally know a great deal about the chemistry of the systems we study. We often know which atomic types prefer to bond to one another and the approximate lengths of the bonds, and the likely coordination numbers of the atoms.

7.3 Random Structure Searching

If nothing is known about the likely low-energy structures it is reasonable to start searching by relaxing random structures, which gives the widest coverage of the PES and an unbiased sampling. The notion of "random structures" is explored in Subsection 7.3.1, and it will turn out that we must impose limits on the initial structures for reasons of efficiency, so that our "random structures" might better be described as "random sensible structures". Using random sensible structures is a useful approach which we have used successfully in several of the applications described in Section 7.6. The rather surprising degree of success of this approach derives from features **(i)**, **(iv)** and **(vi)** described in Section 7.2. These features imply that even random sampling has a good chance of finding low energy basins and that the wide coverage of the PES gives a chance of sampling the different "funnels" mentioned in **(iii)**. We exploit features **(vii)** and **(viii)** by imposing symmetry constraints as explained in Section 7.4. We make use of the proximity of low-energy basins of **(iii)** by "shaking" structures so that they fall into nearby minima, see Section 7.4. Following **(ix)**, we also make extensive use of chemical understanding of the system, as described in Section 7.4.

Our approach is very simple as it requires very few parameters and is very easy to implement. The biases are largely controllable, understandable, and based on sound principles. The searches run very efficiently on modern parallel computers. Our experience with the primitive method has been that we can perform highly reliable searches for the global minimum with up to at least 12 atoms (of one or two species) and sometimes more. When imposing constraints we can search successfully on much larger systems. Information from experiments, and chemical and structural information for the system in question or similar systems, and information generated by previous searches are combined to help design searches. The most successful approaches to searching are those which make the best use of the available information to bias the search towards finding the desired structures.

Our searches find many local minima, particularly if constraints are not imposed. As mentioned in Section 7.1, it is not only the ground state structure which is of interest, higher energy structures can also be important. For example, technologies such as molecular beam epitaxy (MBE) and Metal-Organic Chemical Vapour Deposition (MOCVD) allow controlled epitaxial growth of materials, which can result in structures far from equilibrium. Structure searching allows the discovery of many possible stable and metastable materials, which can then be ranked according to any property of interest such as the band gap or bulk modulus.

Random structure searching also teaches us chemistry! For example, we threw hydrogen atoms

(H) and oxygen atoms (O) in the ratio 2:1 into a box and relaxed, finding the most stable structures to consist of H_2O molecules. Of course we expected this but, studying the higher-energy structures, we found other low-energy small molecules composed of H and O atoms [19].

7.3.1 Generating random structures

What do we mean by the term "random structure"? The arrangements of atoms in real materials are not at all random because the diameters of atoms and the bond lengths between them lie within a rather small range of roughly 0.75 to 3 Å. An assembly of atoms therefore has a "natural volume" which is proportional to the number of atoms present but only rather weakly dependent on the identities of the atoms and the external conditions. We start searches from fully-connected structures because separate fragments do not "see" each other and are unlikely to join up during relaxation. We adopt different procedures for generating initial structures for bulk solids, clusters and point defects in solids. Procedures can easily be devised for other purposes such as finding surface or interface structures, see Fig. 1.

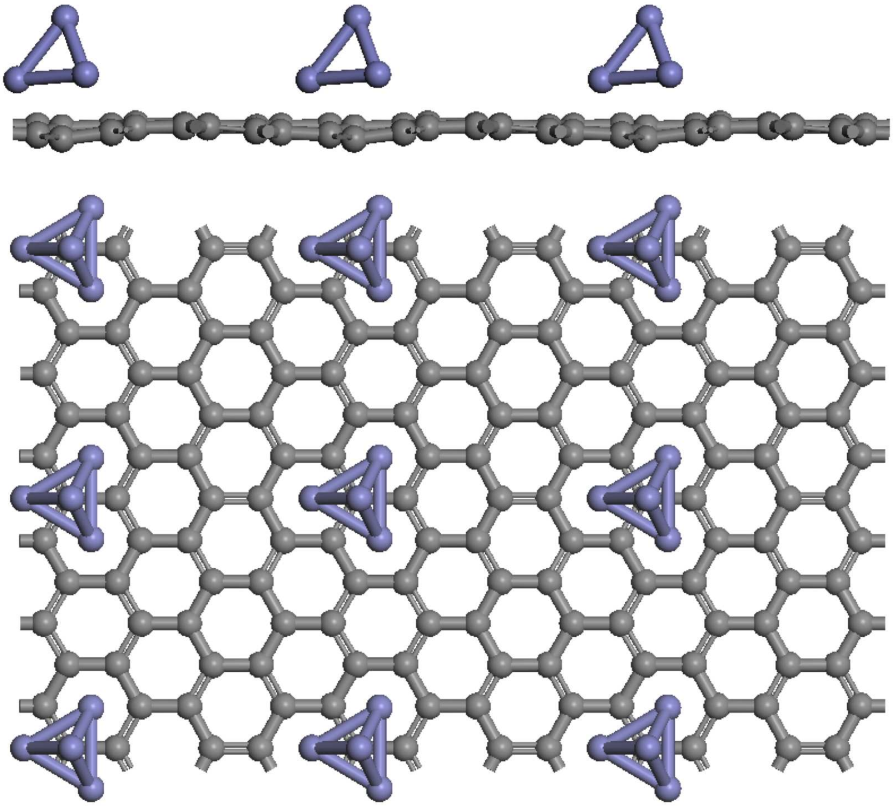

Figure 1: Iron clusters on graphene. A 24-atom supercell of graphene was set up and a (non-magnetic) four-atom iron cluster of random shape was placed at a random position on top of the graphene sheet, and all the atomic positions were relaxed. The lowest energy structure obtained after relaxing 69 structures is shown. Note the distorted tetrahedron of the iron cluster and how well the iron cluster matches the graphene lattice

Periodic solids: A random set of unit cell lengths (a, b, c) and angles (α, β, γ) is chosen and the cell volume is renormalised to a random value within ±50% (or thereabouts) of a chosen mean volume. An appropriate mean volume can be determined from known structures composed of the same atoms, by adding up atomic volumes, or by relaxing a few "handmade" structures. The results are not very sensitive to the mean volume and range chosen. It turns out that a unit cell with very large or small angles can be transformed into an entirely equivalent unit cell with angles in the range 60°–120°. The more compact transformed cells are helpful for choosing efficient grids for Brillouin zone integrations and in visualising structures. We transform to more compact cells whenever possible.

Clusters: To generate initial structures for clusters we choose a box of a reasonable size to enclose the cluster and insert the atoms at random, as in a calculation for a periodic solid. We then place the box inside a considerably larger unit cell and impose periodic boundary conditions. An example of searching in clusters is described in Fig. 2.

Point defects: We start from a supercell of the perfect host crystal. In our work on defects in diamond-structure semiconductors (see Section 7.6) we have mostly used 32-atom supercells, although some defects may require larger cells. We remove a few neighbouring atoms from the crystal to make a "hole", into which we place at random the desired host and impurity atoms.

Keeping atoms/molecules apart: Random structures may contain atoms which are very close together. Such occurrences are often harmless as the forces on the atoms are very large and they quickly move apart under relaxation. We have, however, sometimes encountered problems when transition metal atoms are nearly on top of one another which can make it very difficult to achieve self-consistency so that accurate forces cannot be obtained. A related problem occurs in searching for the structures of molecular crystals, where starting from randomly placed molecules can lead to unwanted chemical reactions. These difficulties can be avoided by rejecting starting structures in which atoms or molecules are too close. For very large systems the fraction of structures rejected will approach unity and a more efficient procedure should be used in which atoms or molecules are "nudged" apart.

7.4 Biasing the searches

Choosing stoichiometries: Does element A react with element B to form the compound AB, or perhaps A_2B, or A_2B_3 etc., or is the compound A_2B_3 unstable to the formation of A_2B + 2B, or 2AB + B ? These questions can be answered by determining the energies of the most stable structures of each compound, which allows the thermodynamically most stable state of a mixture of A and B to be determined. This problem involves searching a larger space than is required for determining the most stable structure of a particular stoichiometry, but it can be tackled by carrying out structural searches for a range of stoichiometries. Searching with a particular stoichiometry may give hints about more stable stoichiometries as phase separation can occur within the unit cell. We have often noticed such behaviour although the limited size of the cells means that calculations with other stoichiometries and cell sizes may be necessary to unambiguously identify phase separation. An example of searches over different stoichiometries is described in Fig. 14. The first source of bias in studying a system is therefore the choice of stoichiometries.

Choosing the number of units: When searching for crystalline phases of a given stoichiom-

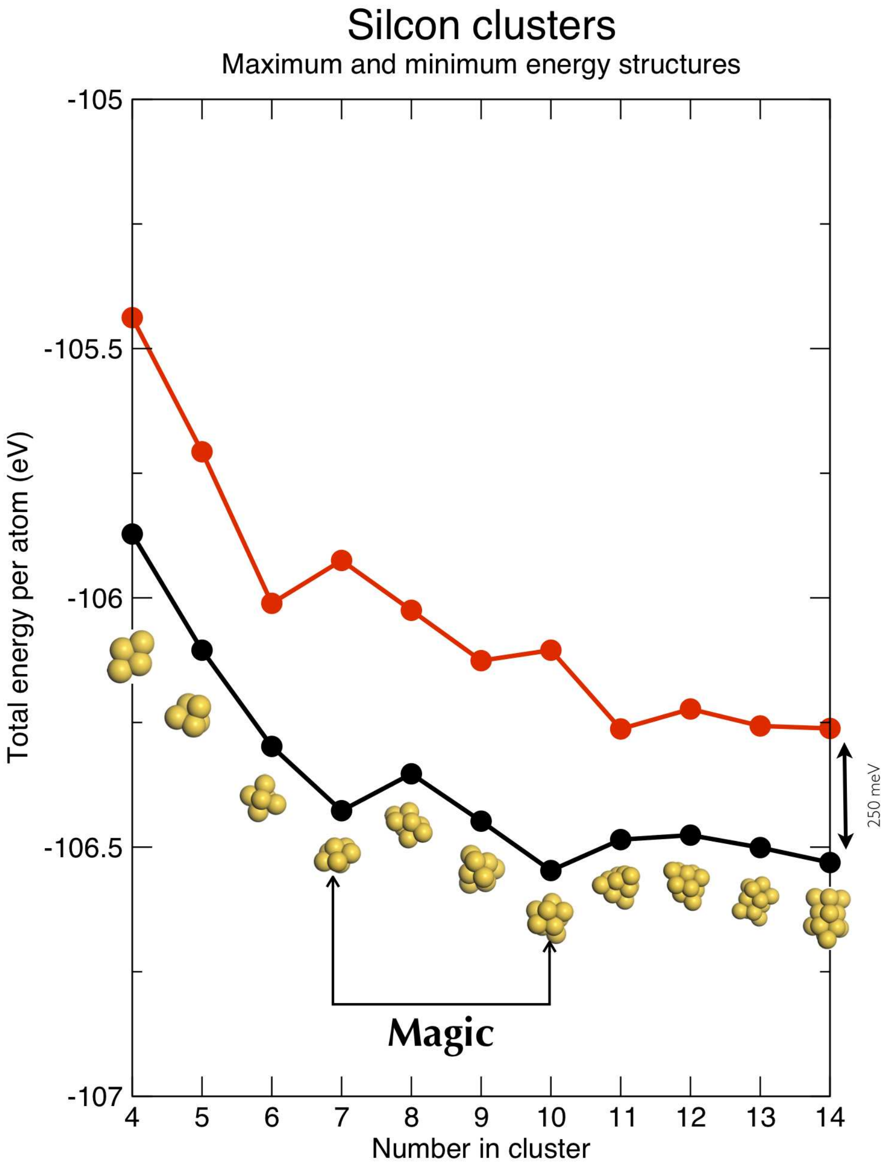

Figure 2: Silicon clusters were generated by placing atoms randomly within a small box inside a large unit cell and relaxing within DFT. The algorithm generated the same lowest-energy structures obtained in previous DFT studies [20], including the two "magic" number clusters with seven and ten atoms. We also found many local minima. The highest-energy minimum for each cluster size is only about 0.25 eV per atom higher in energy than the minimum energy structure

etry one does not *a priori* know how many formula units the primitive unit cell contains, and one should perform searches with different numbers of units. Searching using "usual" numbers of formula units, such as 2, 4, 6, and 8, will normally be an effective way to bias the search. However, it will preclude unexpected results, for example the 11 and 21 atom host-guest phases of aluminium (discussed in Section 7.6). We are fighting a computational cost which grows rapidly with system size and performing nearly exhaustive searches with more formula units rapidly becomes impracticable. Random structures are a perfectly reasonable starting point if one has no knowledge of the likely structures, but with a little thought one can often greatly improve the efficiency of the search by biasing it towards finding low energy structures. This makes it possible to perform more comprehensive searches with larger numbers of atoms.

Imposing chemical ideas: Extensive knowledge of the chemistry of a system is often available, even if we know little about the actual structures which are favoured. Under these circumstances one can use chemical ideas to bias the searching. We already mentioned the idea of choosing initial structures composed of molecular units, and other examples of imposing chemical ideas are discussed in Section 7.3. Even if the system is non-molecular it is often possible to use chemical units to increase the efficiency of the search. For example, if one is interested in structures of gallium arsenide one can make initial structures from Ga–As units. This has the effect of making the densities of the Ga and As atoms much more uniform than a random structure, which becomes increasingly important for larger system sizes. Another important chemical idea is that of coordination number. For example, we can generate initial structures of carbon with sp^2 bonding by creating random structures and rejecting all those which are not 3-fold coordinated, as illustrated in Fig. 3.

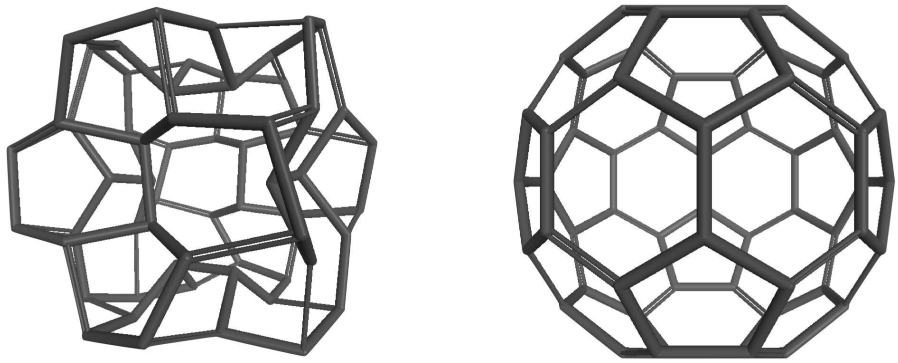

Figure 3: Left: A structure built by placing carbon atoms randomly within a small sub-box, subject to symmetry constraints. Random structures were generated and then screened to determine whether the atoms were three-fold coordinated. If not, the structure was rejected and another one was generated. Right: relaxation of this structure within DFT gave the well-known C_{60} "buckyball"

Imposing symmetry: As noted in Section 7.2, minima with very low or very high energies tend to correspond to symmetrical structures. Imposing a degree of symmetry on the initial structures and maintaining it during relaxation therefore eliminates a large amount of the PES while (hopefully) still allowing the global minimum energy structure to be found. We implement this strategy by searching randomly over all space groups with N_s symmetry operations. Such a search also allows structures to relax into space groups which are super-groups of those with N_s symmetry operations. Symmetry constraints have often been used in searching for crystalline polymorphs composed of small molecules such as the drug molecules developed within the pharmaceutical industry [21].

Using experimental data: We already mentioned the possibility of using experimental data to bias the searching in Sections 7.1 and 7.2. It may turn out that a powder diffraction spectrum is obtained with quite a few well defined peaks which, however, are insufficient for a full structural determination. In such cases it is often possible to determine the dimensions of the unit cell and perhaps an indication of the most likely space groups from the data. Such information is extremely useful when performing a structural search, and an example of this type of constrained search is described in Section 7.6 for a high-pressure phase of ammonia monohydrate, and a test calculation for a dipeptide is illustrated in Fig. 4. Knowledge of the different space group frequencies, which we mentioned in Section 7.2, could also be used to bias searches.

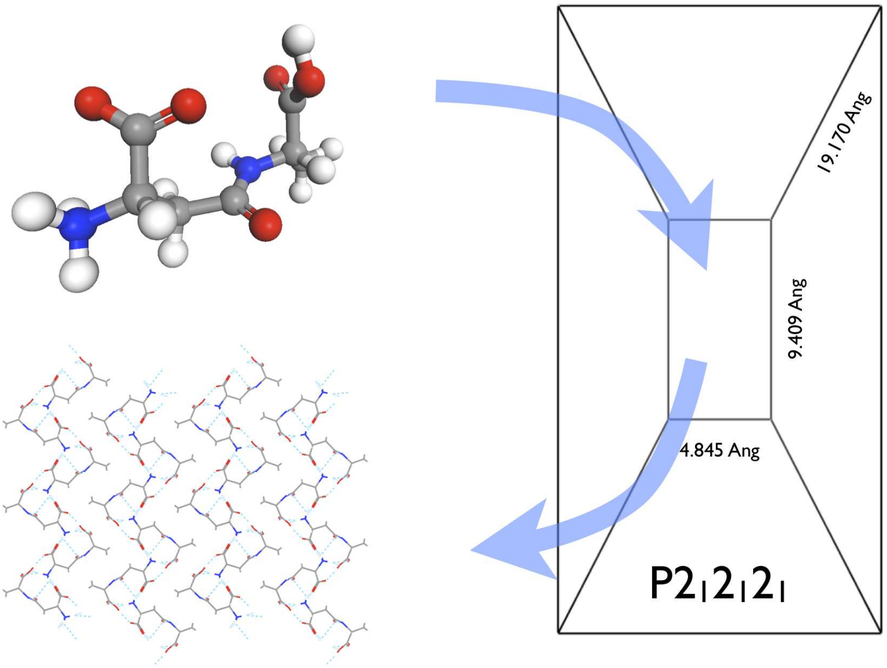

Figure 4: The crystal structure of the beta-L-aspartyl-L-alanine dipeptide is known experimentally. In this test we made structures from the experimental unit cell shown on the right and the $P2_12_12_1$ space group of the crystal and the structure of the beta-L-aspartyl-L-alanine molecule (top left). Carbon atoms are shown in grey, oxygen in red, nitrogen in blue and hydrogen in white. A single molecule was placed randomly in the unit cell and the positions of the other three molecules were determined by the space group symmetry. The structure was rejected if two molecules overlapped and a new one was generated. Each non-overlapping structure was relaxed within DFT while maintaining the size and shape of the unit cell and the $P2_12_12_1$ symmetry. The correct molecular packing (bottom left) was found after relaxing 18 structures

Shaking: In Section 7.2 we encountered the idea that low energy basins may be clustered together. This motivates the "shake", a random displacement of the atoms and, if appropriate, a random adjustment of the unit cell. Atomic displacements of a large fraction of a bond length have a reasonable chance of pushing the system into a nearby basin of attraction. We have also used shaking to look for distortions of structures into doubled (or larger) unit cells. The shake is the same as a step in the basin hopping algorithm [22–24] (see also, Appendix A), although we have used it only with zero temperature and after considerable searching has already located low-energy structures.

A related idea is to calculate the harmonic phonon modes of a structure. The phonon modes at zero wave vector of a fully relaxed structure found from random searching must be stable, and the structure must also be stable against elastic distortions. The phonon modes at non-zero wave vectors may, however, be unstable, so that the energy can be reduced by a distortion in a larger unit cell. Calculating the second derivatives of the energy to obtain the phonon frequencies and displacement patterns is expensive and we only perform such calculations on a few structures of interest after extensive searching. If unstable phonon modes are found then the energy-reducing distortions of the corresponding phonon eigenvectors can be followed to find more stable structures.

7.4.1 Have we found the global minimum?

The searching is not exhaustive and therefore we cannot be sure that we have found the global minimum. One way to gauge the quality of a search is to look for known "marker" structures (if available). We happily terminate searches when the same lowest-energy structure has been found several times. This criterion is reasonable because we relax a very wide range of initial structures. When we apply constraints to the initial structures and maintain them during the relaxation we obviously cannot obtain structures which violate the constraints. When we apply constraints to the initial structures but allow free relaxation we are biasing the search, presumably towards structures which obey the initial constraints, but also perhaps in ways which we cannot predict. When we bias a search it is important to understand as well as possible which parts of the PES are being excluded or de-emphasised. This allows the user to assess the strengths and weaknesses of a search and, if required, to design further searches. It is therefore important that the effects of the "knobs" of the search (the parameters which can be varied) are as transparent as possible. We believe that the simplicity of our searching procedures results in a relatively small number of understandable and useful knobs.

7.5 Some technical aspects of the calculations

First-principles DFT calculations: DFT calculations are much more expensive than empirical potential ones and the number of structures whose energies may be evaluated is therefore greatly fewer. Many first-principles DFT codes are available, and we use the CASTEP package [25] which uses a plane wave basis set, periodic boundary conditions, and pseudopotentials. The code returns the total energy of a structure and the forces on the atoms and stresses on the unit cell. We use the forces and stresses to relax structures to the nearest local minimum in the PES. The second derivatives of the energy may also be calculated, but this is much more expensive and although very useful in checking for unstable phonons/elastic distortions and in calculating thermal effects in stable structures, it is far too expensive to be used routinely as part of the search strategy.

Pseudopotentials: Accurate results at very high pressures can be obtained using pseudopotentials, but they must be constructed with sufficiently small core radii and with the appropriate electrons treated explicitly. The pseudopotentials provided with standard codes may be inadequate at the high pressures we often work at. Lithium is an unusually difficult case. It is standard to treat all three electrons of lithium explicitly, but the pseudopotential core radii must still be small [26] in high-pressure studies. We use ultrasoft pseudopotentials [27] and find them to be accurate when the distance between neighbouring atoms is about equal to or greater than the sum of the core radii of the atoms. We recommend that pseudopotentials be tested for each application by generating them with different core radii and checking that energy differences are accurate for the shortest inter-atomic distances that will be encountered. For some of the applications described in Section 7.6 we have treated some core and semi-core states explicitly. For example, we used pseudopotentials with 11 electrons treated explicitly for our work on aluminium [28] and 16 electrons for iron [29].

k-point sampling: We use quite good Brillouin sampling and basis sets when searching because we find that poor quality calculations can lead to strong biases. We have come across modulated phases when searching in metals which went away when we relaxed them further with denser k-point sampling. We use Monkhorst-Pack (MP) meshes of k-points which are defined by choosing the smallest MP mesh where the smallest separation between k-points is less than some distance Δk. We often use $\Delta k = 2\pi \times 0.07$ Å^{-1} when searching and then perhaps $\Delta k = 2\pi \times 0.03$ Å^{-1} when refining the structures and their energetics. We deform the k-point mesh with the changes in the cell shape and occasionally recalculate the integer parameters of the MP mesh.

Predicting stability over a range of pressures: In our high-pressure studies we search at constant pressure, although one can just as easily search at constant volume. A search at pressure p_{s} may give many different structures. The structure with the lowest enthalpy $H(p_{\mathrm{s}})$ is the most stable at p_{s}, but different structures may be more stable at another pressure p. To investigate this we can use the thermodynamic relation

$$\begin{aligned} H(p) &\simeq H(p_{\mathrm{s}}) + (p - p_{\mathrm{s}}) \left.\frac{dH}{dp}\right|_{p_{\mathrm{s}}} + \frac{1}{2}(p - p_{\mathrm{s}})^2 \left.\frac{d^2H}{dp^2}\right|_{p_{\mathrm{s}}} && (3) \\ &= H(p_{\mathrm{s}}) + (p - p_{\mathrm{s}})V_{\mathrm{s}} - \frac{1}{2}(p - p_{\mathrm{s}})^2 \frac{V_{\mathrm{s}}}{B_{\mathrm{s}}} , && (4) \end{aligned}$$

where V_{s} and B_{s} are the volume and bulk modulus at p_{s}. Equation (4) can be used to approximate the enthalpy of each structure over a wide range of pressures. The simple linear approximation

$$H(p) \simeq H(p_{\mathrm{s}}) + (p - p_{\mathrm{s}})V_{\mathrm{s}} \qquad (5)$$

is particularly convenient because the quantities required ($H(p_{\mathrm{s}})$, p_{s}, V_{s}) are obtained directly from the search calculations. Suppose we apply equation (5) to two structures, A and B, found at p_{s}. Equation (5) tells us that if $V_{\mathrm{s}}^{\mathrm{A}} < V_{\mathrm{s}}^{\mathrm{B}}$ then structure A will become more favourable with respect to structure B at $p > p_{\mathrm{s}}$ and less favourable for $p < p_{\mathrm{s}}$. If B is more stable than A at p_{s} a phase transition from B to A could occur at some $p > p_{\mathrm{s}}$. It may be possible to use the quadratic form of equation (4) with an empirical relationship between the bulk modulus and volume, but we have not explored this further. We find, however, that the linear approximation is very useful for estimating the stability regions of different phases over a wide range of pressures, which gives the approach a “far sightedness”. Equations (4) and (5) can be used in both constant volume and constant pressure calculations, but we normally use a simple scatter-diagram representation in our constant pressure calculations, as explained in Fig. 5.

7.6 Brief survey of AIRSS calculations to date

Silane: In our first AIRSS paper we studied high pressure phases of silane (SiH_4) [31]. This group IVB hydride is a metastable compound under ambient conditions, but above about 50 GPa

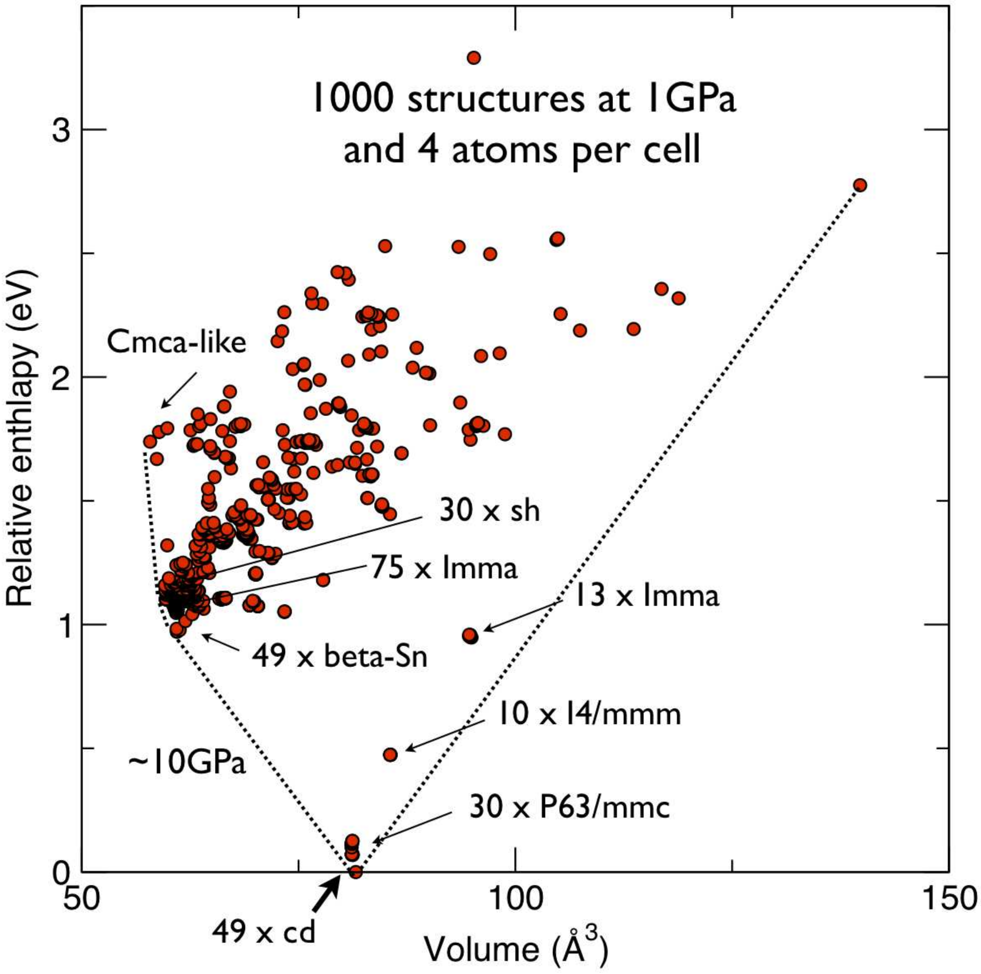

Figure 5: Scatter plot of the relative enthalpies against volume for a search at $p_{\rm s} = 1$ GPa with 4 silicon atoms per cell. The diamond structure (cd) is the most stable at this pressure and was found 49 times from a total of 1000 relaxed structures. The positions of the observed high-pressure phases [30], beta-Sn, *Imma*, sh (simple hexagonal) and *Cmca*-like, are also indicated on the figure. The hexagonal-close-packed (hcp) and face-centred-cubic (fcc) phases which are observed in experiments at pressures beyond the *Cmca* phase [30] were not found in the searches and we presume they are mechanically unstable at 1 GPa. Equation (5) shows that the stable phases can be found by drawing lines underneath the data points as shown in the figure. The stable phases at pressures greater than 1 GPa can then be read off the figure as those through which the dotted lines pass, and it can be seen that these are the experimentally observed ones at positive pressures where the dotted line has a negative slope. The slope of the line joining the cd and beta-Sn phases corresponds to a pressure of about 10 GPa, which is similar to the coexistence pressure [30]. The phases above the dotted lines are not the most stable at any pressure. The $P6_3/mmc$ phase differs from cd only in the stacking of layers

it becomes stable against decomposition into its elements. Our work was motivated by a theoretical study [32] which used chemical intuition to predict interesting high pressure non-molecular phases of silane. We found more-stable phases, most notably an insulating phase of $I4_1/a$ symmetry, shown in Fig. 6, which was the most-stable structure from about 50 GPa to over 200 GPa.

Each Si atom is bonded to eight H atoms which form bridges between neighbouring Si atoms. Each of the Si and H sites are equivalent in this high-symmetry structure. All of the bonds are electron-deficient three-centre-two-electron “banana” bonds, similar to those linking the boron atoms in diborane (B_2H_6). Interestingly, Feng *et al* [32] predicted structures with some Si-H-Si banana bonds, and their chemical intuition was essentially correct, but our structure is totally bananas. The $I4_1/a$ phase has subsequently been observed in x-ray diffraction studies [33] and its insulating behaviour was verified. We also found a slightly-less-stable phase of $I\bar{4}2d$ symmetry only 0.1 eV per SiH_4 unit above $I4_1/a$ at 100 GPa. The $I\bar{4}2d$ phase of silane has also been identified in experiments by Degtyareva *et al* [34]. An impressive debut for AIRSS!

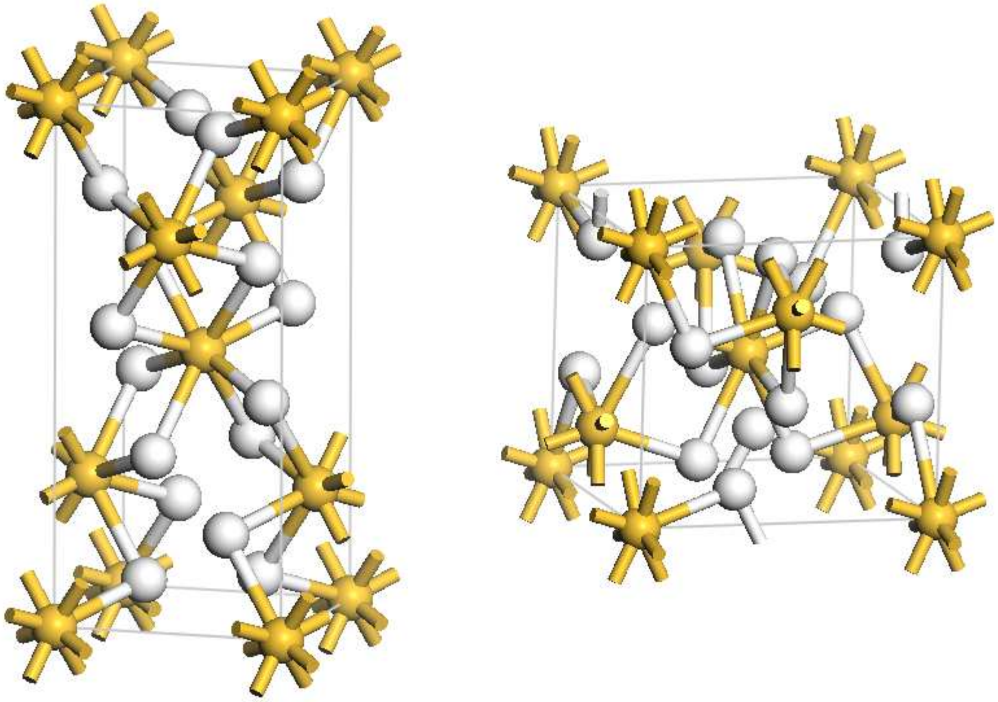

Figure 6: The $I4_1/a$ structure of silane (left) and the slightly less stable $I\bar{4}2d$ structure (right). Silicon atoms are shown in gold and hydrogen atoms are in white. All of the bonds in $I4_1/a$ and $I\bar{4}2d$ are of the Si–H–Si type. Both phases were subsequently found experimentally

Aluminium hydride: The silane studies were motivated by the quest for metallic hydrogen. Although metallic hydrogen has been formed fleetingly in shock wave experiments and must exist within planets such as Jupiter, it has not been produced in static compression experiments, where it could be studied in detail. Hydrides have been thought of as containing “chemically pre-compressed” hydrogen which might become metallic at pressures achievable in diamond anvil cells and might exhibit phonon-mediated high-temperature superconductivity [35]. The group IVB hydrides contain 80% hydrogen atoms, but the group IIIB hydrides contain nearly as much (75%). We studied aluminium hydride (AlH_3) and predicted the stability of a metallic $Pm\bar{3}n$ phase at pressures readily achievable in diamond anvil cells [36]. The structure of the $Pm\bar{3}n$ phase is illustrated in Fig. 7. Hydrogen atoms are considerably more electronegative than aluminium ones, so the electron density on the hydrogen atoms is large, which suggests that the high-frequency hydrogen-derived phonon modes could provide substantial electron-phonon coupling and promote superconductivity. However, the $Pm\bar{3}n$ phase of AlH_3 is a semimetal at the transition pressure with a relatively small electronic density of states at the Fermi energy, which strongly militates against superconductivity. $Pm\bar{3}n$ develops a band gap on further compression but, on the other hand, reducing the pressure increases the density of states at the Fermi energy which would promote superconductivity. The semi-metallic $Pm\bar{3}n$ phase was subsequently observed in high-pressure x-ray diffraction experiments [37], but it was not found to be a superconductor.

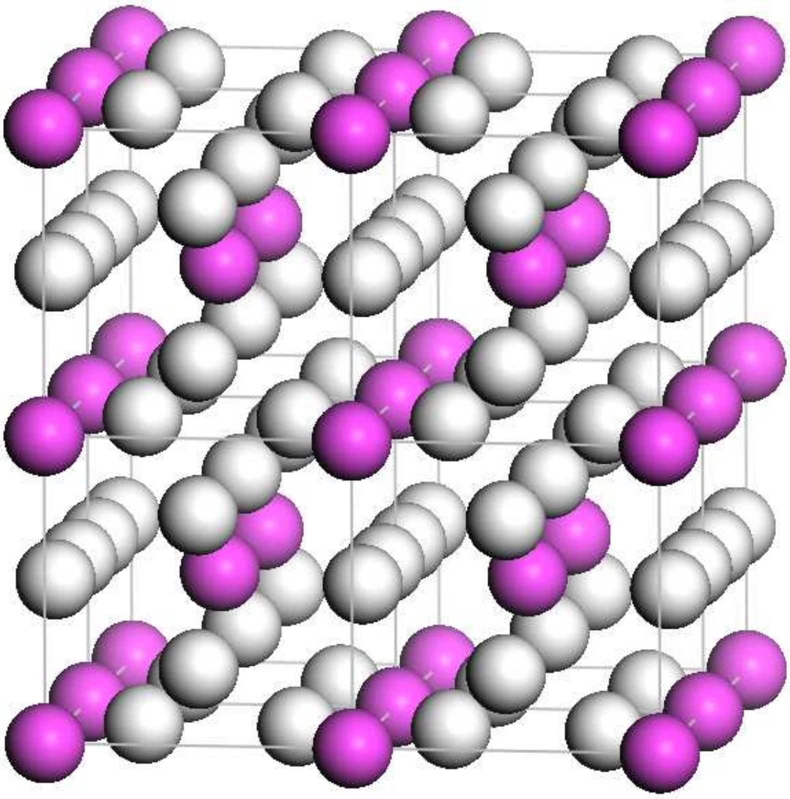

Figure 7: The $Pm\bar{3}n$ phase of aluminium hydride. The Al cations are shown in purple and the H anions are in white. The linear chains of H atoms can clearly be seen. This structure is also adopted by niobium stannide (Nb_3Sn) which is a superconductor used in high magnetic field applications

Hydrogen: Pure hydrogen has been compressed to over 300 GPa in a diamond anvil cell [38], but it stubbornly remains insulating. It is expected that a non-molecular and presumably metallic phase will become stable somewhere in the range 400-500 GPa [39], and such pressures will probably be achieved in static experiments in the near future. The metallic phase is expected to be a high-temperature superconductor, perhaps even a room-temperature superconductor. The structure of the low-pressure phase I of solid molecular hydrogen is well established [40]. Phase II is stable above 110 GPa, and probably consists of molecules arranged on a distorted close-packed lattice, and a molecular phase III of unknown structure appears above 150 GPa. Our AIRSS studies [41, 42] have shown there to be several candidate structures for phase II consisting of packings of molecules on distorted hexagonal-close-packed lattices. These structures are almost degenerate in enthalpy and quantum motion of the protons could mean that several significantly different local molecular configurations contribute to the overall structure of phase

II. Prior to our work, the DFT phase diagram showed a transition to a metallic phase below 200 GPa, in strong disagreement with experiment. We predicted new insulating molecular phases which are stable up to pressures well above 300 GPa. In particular, the predicted vibrational properties of our $C2/c$ molecular phase (which has 24 atoms in the primitive unit cell and is shown in Fig. 8) agree with the available experimental data for phase III [41].

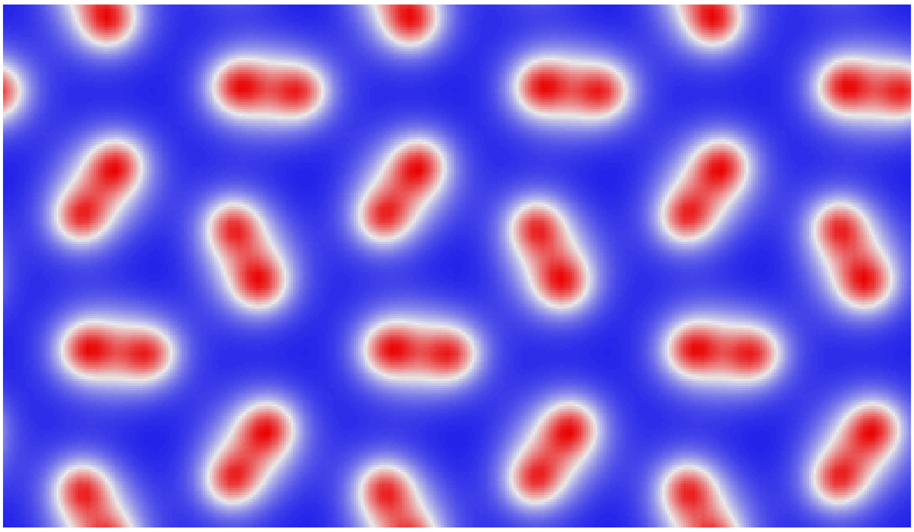

Figure 8: A slice through the charge density of a layer of the $C2/c$ molecular hydrogen phase which we predicted to be the most stable in the pressure range 105–270 GPa [41]. Note that the two ends of the molecules are inequivalent so they have dipole moments and the crystal has infra-red (IR) active vibron modes. The calculations show intense IR vibron activity with strong absorption peaks which are close in frequency and would appear as a single peak in experiments [41]. The IR activity of the strong IR active vibrons in $C2/c$ increases with pressure, as is observed in phase III [43]. The variation with pressure of the strong IR peak and the Raman active vibron frequency of $C2/c$ are in good agreement with experiment [44]

Nitrogen: The phase diagram of nitrogen has been much studied, with a number of apparently stable and metastable molecular phases having been reported [45–47], although their structures are mostly unknown. We found a new class of molecular structures which we predicted to be more stable than previously suggested ones over a wide range of pressures [48]. The dissociation energy of a nitrogen molecule is more than twice that of a hydrogen molecule, and yet nitrogen molecules dissociate at far lower pressures [49]. The reason for this is simply that nitrogen atoms can form up to three covalent bonds so that molecular, polymeric and dense framework structures are possible, whereas a hydrogen atom can form only one covalent bond. "Polymeric" nitrogen can in fact be recovered to ambient conditions as a metastable high-energy-density material [50]. The structure of the high-pressure singly-bonded "cubic gauche" phase formed on molecular dissociation was in fact predicted using DFT calculations [51] over a decade before it was observed experimentally [50], a triumph for chemical intuition. Computational searches for the phases beyond cubic gauche have also been performed [48, 52]. Ma *et al* [52] used DFT and a genetic algorithm to predict the phase beyond cubic gauche to be a singly-bonded layered structure of $Pba2$ symmetry with 16 atoms in the primitive unit cell. This structure is slightly more favourable than the very similar $P\bar{4}2_1m$ structure we found with 8 atoms. Unfortunately we did not perform searches with more than 12 atoms, so we could not have found the $Pba2$ phase. This serves as a warning to all searchers - there could always be a better structure in a larger unit cell.

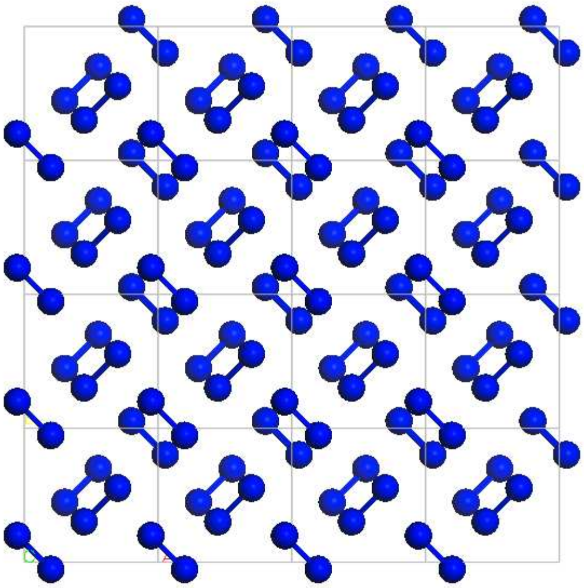

Figure 9: The $P4_12_12$ molecular phase of nitrogen which we predict to be the most stable from ∼9.5 GPa up to molecular dissociation at about 56 GPa [48]

Water: Our work on structures of H_2O [19] was motivated by an experimental study [67] in which a new metastable form of H_2O was synthesised. Mao *et al* subjected water to an applied pressure of about 20 GPa and 10 keV x-ray radiation for many hours within a diamond anvil cell, producing a crystalline phase which does not consist of water molecules. Mao *et al* [67] concluded that they had synthesised an alloy of O_2 and H_2 molecules. We performed a AIRSS study at 20 GPa, finding that the structures obtained consisted almost entirely of weakly bonded H_2O, H_3O, H_2O_2, $H_2OH\cdots OH$, H_2, and O_2 species. O–H bonds are the most energetically favourable at 20 GPa, so that the most stable phases consist of H_2O molecules and the highest enthalpy metastable phases consist of an “alloy” of H_2 and O_2 molecules (rocket fuel!). We argued [19] that the experimental x-ray diffraction, energy loss, Raman spectroscopy and other data were best rationalised not by an H_2/O_2 alloy but by a much more stable mixture of H_3O, O_2 and H_2 species, no doubt containing amounts of the other low-enthalpy species.

Ammonia: Compressed ammonia (NH_3) plays a significant role in planetary science. Ammonia forms hydrogen-bonded solids at low pressures, but we predict that at high pressures it will form ammonium amide ionic solids [53]. These structures, consisting of alternate layers of ammonium cations (NH_4^+) and amide (NH_2^-) anions are expected to be stable over a wide range of pressures readily obtainable in diamond anvil cells, although experimental verification of our prediction is still lacking. The ionic $Pma2$ phase, which is illustrated in Fig. 10, is predicted to be stable above 90 GPa. The driving force for the proton transfer reaction is that the ionic solid is substantially denser than the molecular one. The proton transfer costs energy under ambient conditions, but at high pressures the cost is overcome by the lower value of the pV term in the enthalpy. A proton transfer between water molecules, forming OH^- and H_3O^+ ions, costs more energy than in ammonia and water molecules pack better than ammonia molecules, so that proton transfer is not predicted to occur in compressed water. Proton transfer is even more favourable in water/ammonia mixtures which are expected to form OH^- and NH_4^+ ions at moderate pressures [54].

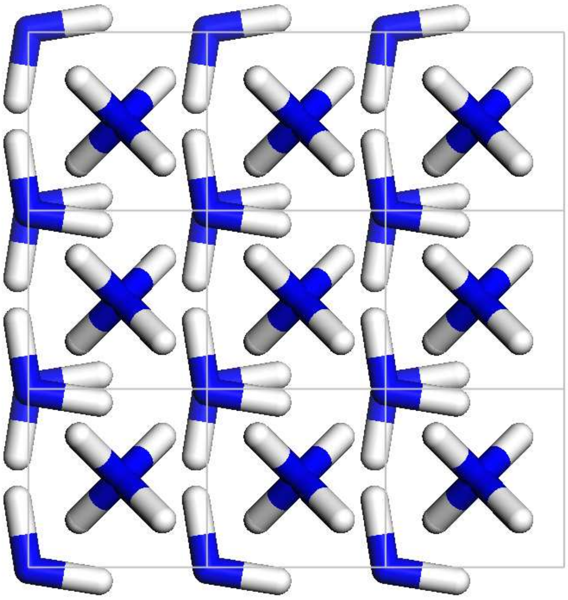

Figure 10: The ionic $Pma2$ phase of ammonia is predicted to be stable above 90 GPa and consists of alternate layers of NH_4^+ and NH_2^- ions. This view shows the three layers of the crystal structure. The top layer consists of NH_2^- ions with orientation $\llcorner$, the second layer consists of tetrahedrally bonded NH_4^+ ions and bottom layer consists of NH_2^- ions with orientation $\ulcorner$

Ammonia monohydrate: The properties of compressed ammonia monohydrate ($NH_3 \cdot H_2O$) are of direct relevance to models of the formation of Titan, Saturn's largest moon. Fortes and coworkers performed neutron diffraction experiments under pressure which yielded the unit-cell parameters and the candidate space groups (*Pcca*, *Pnca* and *Pbca*) of phase II of ammonia monohydrate, which is formed at pressures of a few tenths of a GPa [55,56]. The cell parameters indicated that the unit cell contains 16 $NH_3 \cdot H_2O$ formula units, giving a total of 112 atoms. We performed AIRSS calculations using the experimental unit cell with the further assumption that the crystal consisted of weakly hydrogen-bonded NH_3 and H_2O molecules. Each of the candidate space-groups contains eight symmetry operations, so the asymmetric unit contains two formula units. The initial structures were generated by inserting two $H_2NH \cdots OH_2$ units at random, generating the rest of the structure using the symmetry operations and rejecting initial configurations in which the molecules overlapped strongly. Searches were performed using each of the three candidate space groups, and the lowest enthalpy structure was obtained with space group *Pbca*, which allowed a refinement based on the original data to be performed. These results motivated new experiments which yielded diffraction data which, with additional insights from our predicted structure, were of sufficient quality to allow a full structural determination. A structure of space group *Pbca* was determined whose hydrogen bonding network is almost identical to that of the computationally-derived structure [55,56]. Subsequent DFT calculations have shown that the experimentally determined structure is about 0.01 eV per seven-atom formula unit lower in enthalpy than the theoretically predicted one [57]. This project shows the power of constrained searches. The size of the parameter space was enormously reduced by using the cell parameters and candidate space groups from experiment and the $H_2NH \cdots OH_2$ unit assumed on chemical grounds. One can never be sure when it is safe to stop searching, and in this case the search was terminated before the correct structure was found. It would certainly have been possible to carry out many more searches in which the correct structure might well have been found, but the experimental determination made this redundant. This project is a nice example of synergy between experimental and computational structure determination.

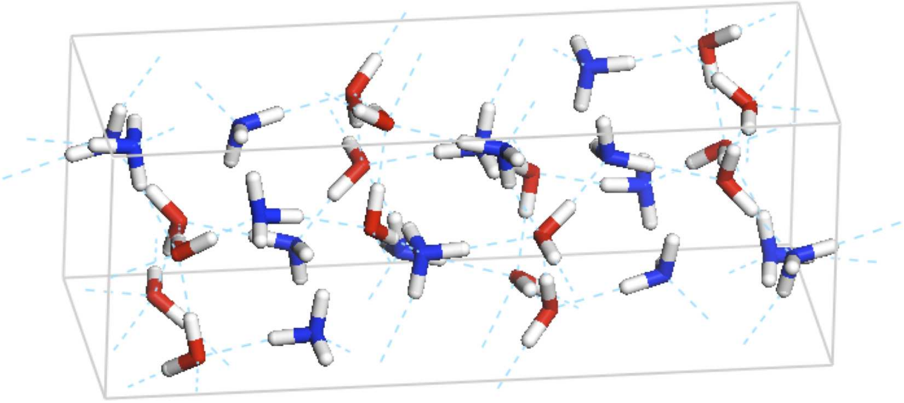

Figure 11: The structure of phase II of ammonia monohydrate predicted using AIRSS. Oxygen atoms are shown in red, nitrogen atoms in blue, and hydrogen in white. The dashed lines indicate close contacts between the molecules. The structure illustrated above and the structure obtained from the neutron diffraction data are very similar and both have *Pbca* symmetry, but they have slightly different proton orderings

Graphite intercalation compounds: Superconductivity was observed in some graphite intercalation compounds (GICs) in the 1960s. Interest in GICs was rekindled by the discovery of substantial superconducting transition temperatures in C_6Ca and C_6Yb which increase with pressure [58, 59]. The occupation of an inter-layer state is correlated with the occurrence of superconductivity [60]. Csányi *et al* [61] searched for low-enthalpy structures of C_6Ca under pressure. Energetically competitive structures were found at low pressures in which the six-membered rings of the graphene sheets buckle to accommodate Ca atoms within the troughs. Stone-Wales bond rotations [62] within the graphene sheets become favourable at higher pressures, leading to structures with five-, six-, seven- and eight-membered rings, with the Ca atoms sitting within the larger-diameter rings, see Fig. 12. The occurrence of large rings accommodating the intercalate atoms might be a general features of highly-compressed GICs, and suggests a route to synthesising novel layered carbon structures.

Hypothetical group IVB clathrate: AIRSS produces many structures and the metastable ones are often interesting. Looking at the results of a search on carbon we noticed a low-density high-symmetry sp^3-bonded structure which was unfamiliar to us [63]. This structure (Fig. 13) has a six-atom primitive unit cell with all atoms equivalent, and it is chiral, so that it cannot be superimposed on its mirror image. We have named this the “chiral framework structure” (CFS). It is only 112 meV per atom higher in energy than carbon diamond, while in silicon it is 53 meV per atom higher in energy than the diamond structure [63]. Further investigation revealed

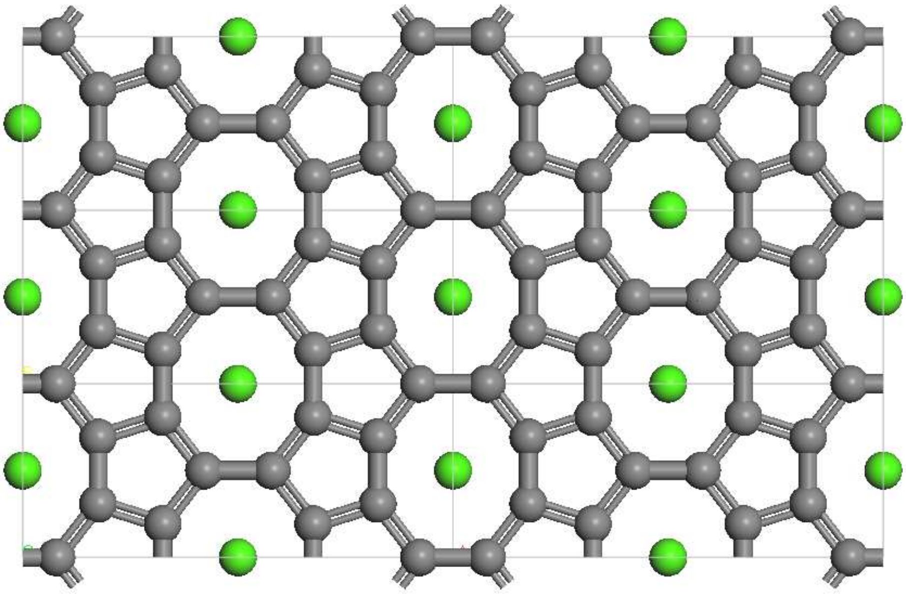

Figure 12: A CaC_6 graphite intercalation compound of *Cmmm* symmetry. The carbon atoms are shown in grey and the calcium atoms in green. In the *Cmmm* structure the hexagonal rings of the graphene sheets are replaced by five- and eight-membered carbon rings. This phase is very favourable at high pressures because the cost of the Stone-Wales bond rotations is offset by a large volume reduction as the metal ions are accommodated within the larger rings [61]

it to be the elemental analogue of a zeolite-type structure and it is also related to clathrate structures. Clathrate structures of several different types have been synthesised consisting of silicon, germanium and tin (but not carbon) [64, 65]. The synthesis can only be performed by including "guest" atoms such as Na, K, Rb, Cs or Ba, which act as templates for the self-assembly of the nano cages forming the structures, although in some cases the guest atoms can largely be removed. The clathrate II structures of silicon and carbon are calculated to be about 52 meV per silicon and 72 meV per carbon atom higher in energy than the corresponding diamond structures. Considering that the silicon clathrate II structure has been synthesised [66], might it be possible to synthesise the silicon CFS? A suitable template would have to be found, but it is an intriguing possibility.

Tellurium dioxide: Metal dioxides with large cation radii often form cotunnite phases under high pressures, and presumably these transform to post-cotunnite structures at higher pressures. Tellurium dioxide (TeO_2) is apparently the only dioxide in which a post-cotunnite phase has been observed [68], and it is therefore a candidate for the post-cotunnite structure of other metal dioxides. Unfortunately the quality of the x-ray diffraction data obtained by Sato *et al* for post-cotunnite TeO_2 was insufficient to allow a structural determination, although it was possible to eliminate the known post-cotunnite structures of dihalides [68]. Our AIRSS study [69] found a transition to a post-cotunnite phase of TeO_2 at 130 GPa, which is a little higher than the experimental transition pressure of 80-100 GPa. The calculated x-ray diffraction data for the predicted phase of $P2_1/m$ symmetry is in reasonable agreement with experiment. Interestingly we found that the cotunnite phase shows re-entrant behaviour, becoming more stable than

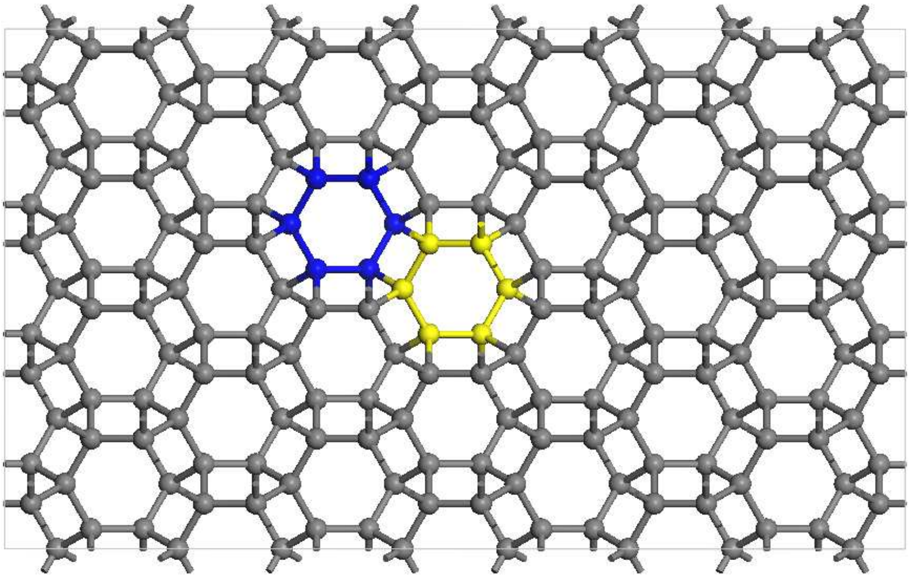

Figure 13: View of the "chiral framework structure" (CFS) along the axis of the helices [63]. The CFS is a low-energy hypothetical structure of group IVB elements which is only a little higher in energy than the diamond structure. The CFS has six atoms per primitive unit cell which are all equivalent by symmetry. The atoms are arranged in five-membered rings and are four-fold coordinated. The CFS has three bond angles slightly smaller than the perfect tetrahedral angle of 109.5° and one bond angle of about 125°. The structure consists of a hexagonal packing of helices which are crosslinked to satisfy four-fold coordination. The helices all twist either to the left or right, so that the crystal is chiral and cannot be superimposed on its mirror image

$P2_1/m$ again above 260 GPa. We tried our $P2_1/m$ structure in other metal dioxides but it was never the most stable phase [69]. Higher quality x-ray diffraction data are required to test our identification of the $P2_1/m$ structure as post-cotunnite TeO_2.

Lithium-beryllium alloys: Feng *et al* [70] used random structure searching to explore lithium-beryllium (Li-Be) alloys under pressure. These elements are immiscible under ambient conditions, but the calculations show they can react under pressure, with $LiBe_2$ becoming more stable than the separated elements above about 15 GPa, and Li_3Be, LiBe and $LiBe_4$ having regions of stability at higher pressures. The electronic structure of the most stable LiBe compound shows two-dimensional character, with a characteristic step-like feature at the bottom of the valence band. The changes in the electronic structure which allow the formation of Li-Be alloys under compression arise from overlap of the Li 1*s* core electrons which leads to charge transfer towards the Be atoms. In this work [70] the relative stabilities of the different stoichiometries was displayed using a "convex hull" diagram. An example of a convex hull diagram constructed using data obtained from our random searches for the Li-H system is shown in Fig. 14.

Lithium: One of the surprises in high pressure physics in recent years has been the discovery that *sp*-bonded elements often adopt complex non-close-packed structures under sufficient compression. The ionic cores take up a larger fraction of the total volume under pressure and some of the valence charge is pushed away from the atoms and into interstitial regions forming

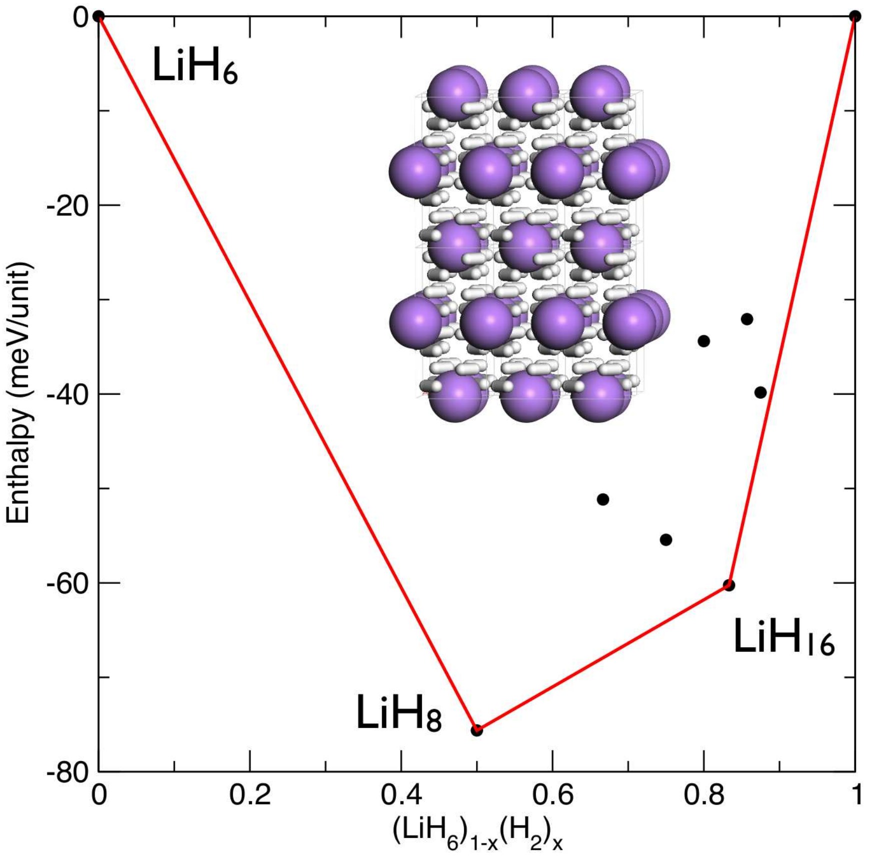

Figure 14: Zurek *et al* have found that “a little bit of lithium does a lot for hydrogen” [71]. In more extensive variable stoichiometry searches we find that even less lithium will do the trick of “metallising hydrogen”. We determined the low enthalpy structures of LiH_{2n} for $n = 3 - 10$ at 100 GPa using AIRSS, displaying the results on a convex hull. LiH_{16} (shown) is stable against decomposition into LiH_8 and H_2. It is metallic and is based on a body-centred-tetragonal (bct) packing of lithium atoms “coated” in H_2 molecules

“blobs” which are rather isolated from one another. The resulting structure can be thought of as an “electride” in which the interstitial electrons are the anions. The valence electronic energy bands consequently become narrower than the free-electron bands [72, 73]. Lithium (Li) adopts the fcc structure under ambient conditions, but it transforms to a three-fold coordinated structure at about 40 GPa [74]. We searched for structures of Li at high pressures, finding two new candidate phases of *Pbca* and *Aba*2 symmetry which are predicted to have small regions of stability around 100 GPa [26] and are distortions of the *Cmca*-24 structure found in a previous theoretical study [75]. All of these structures have substantial dips in their electronic densities of states (e-DOS) around the Fermi level. This is consistent with, but does not fully explain, the significant increase in electrical resistivity and change in its temperature dependence near 80 GPa observed by Matsuoka and Shimizu [76]. The occupied valence bandwidths of the *Pbca*, *Aba*2 and *Cmca*-24 phases are substantially narrower than the corresponding free-electron values, demonstrating their electride nature. The low (three-fold) coordination number of these structures arises from Jahn-Teller-like distortions which lower the e-DOS around the Fermi level, and we predicted that the coordination will increase to four-fold above about 450 GPa [26], with the diamond structure, see Fig. 15, becoming stable above ∼500 GPa. A first-principles study was also performed by Yao *et al* [77], who found similar results using random structure searching and an evolutionary algorithm. Overall we are, however, left with the impression that there are many nearly-degenerate structures around 100 GPa, and more twists in the story of compressed Li are likely.

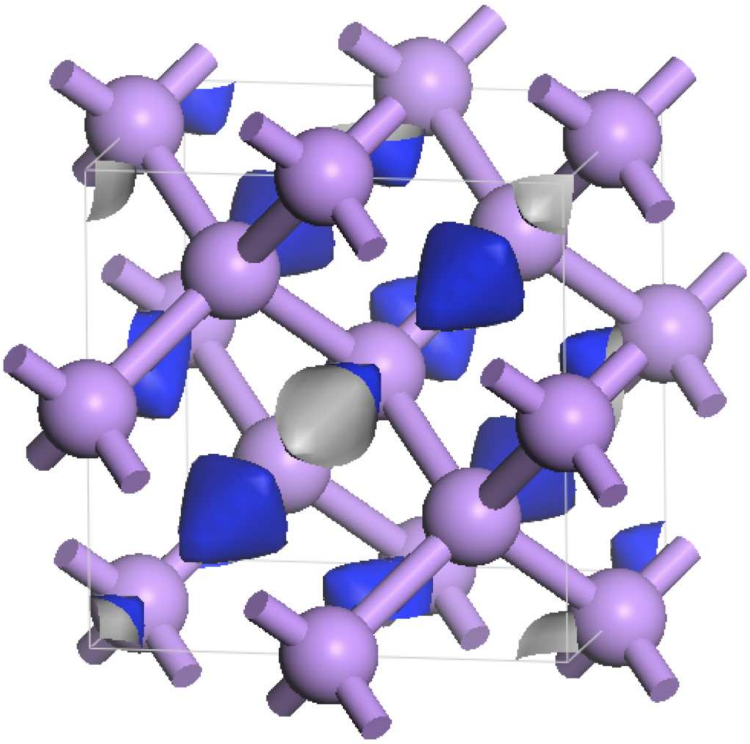

Figure 15: The diamond-structure electride phase of Li, which is predicted to be stable above 483 GPa. The Li atoms are shown as purple balls and nearest neighbour contacts are shown as sticks. The charge isosurface in blue shows electrons also located on a diamond lattice, in the voids between the lithium ions

Aluminium: Aluminium is used as a standard material in shock wave experiments, for which purpose an accurate equation of state must be available. Aluminium adopts the fcc structure under ambient conditions and transforms to hcp at 0.217 terapascals (TPa) [78], and a further transition to a body-centred-cubic (bcc) structure has been predicted at 0.38 TPa using DFT methods [79]. Our searches have identified a transformation from bcc to the Ba-IV non-close-packed incommensurate host-guest structure at 3.2 TPa and a further transition to a simple hexagonal structure at 8.8 TPa [28]. The non-close-packed structures have smaller volumes than bcc and their occurrence significantly alters the high-pressure equation of state. An important feature of our searches was that we studied cells containing 2, 4 and 8–21 atoms. Such a systematic search can yield interesting results and we found commensurate analogues of the host-guest structures in cells of 11, 16, and 21 atoms. The physics behind the occurrence of non-close-packed structures in highly compressed aluminium is similar to that described above for lithium at much lower pressures. The simple hexagonal structure consists of alternate layers of aluminium ions and electrons. There are two "blobs" of electronic charge for every ion and, considering the aluminium ions as the cations and the electron blobs as the anions, the structure is that of magnesium diboride (MgB_2), which is well known in ionic compounds of AB_2 stoichiometry. We described the stability of the different structures under pressure using empirical inter-atomic potentials to describe the aluminium ions and electron blobs. The potential parameters were tuned to stabilise the host-guest structure, and it then gave the bcc structure at lower pressures and the simple hexagonal structure at higher pressures. We also found a duality between the Ba-IV structure and the other incommensurate host-guest structure found in the elements, the Rb-IV structure, as explained in Fig. 16.

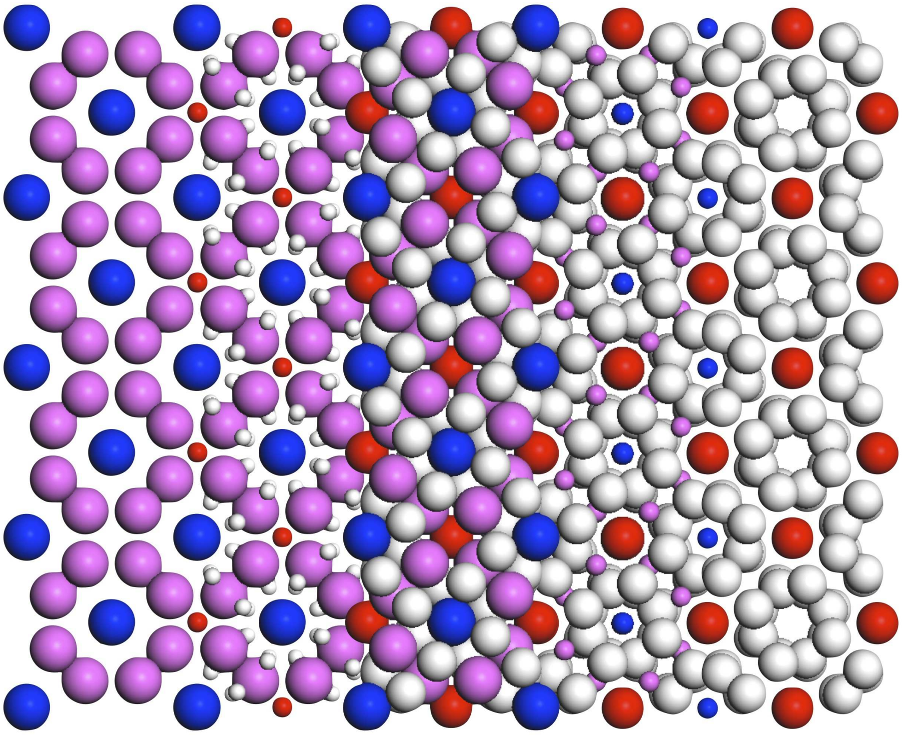

Figure 16: A representation of the Ba-IV incommensurate host-guest structure is shown on the left, with the host atoms in purple and the guest atoms in blue. The Ba-IV structure is also found in compressed Sr, Sc, As, Sb and Bi, and we predict it to be stable in aluminium in the range 3.2–8.8 TPa. A representation of the Rb-IV incommensurate host-guest structure is shown on the right with the guest atoms in red and the host atoms in white. The Rb-IV structure is found in Rb, K and Na at high pressures. Both structures consist of positively charged ions and negatively charged electron blobs located within interstitial regions. The Ba-IV and Rb-IV structures show a remarkable duality. The electron blobs in the Ba-IV structure occupy the atomic positions of the Rb-IV structure, while in the Rb-IV structure the electron blobs occupy the atomic positions of the Ba-IV structure [28]. The figure shows a view along the axis of the guest chains. As we scan the picture from left to right the structure changes from Ba-IV to Rb-IV

Iron: The Earth's core is largely composed of iron. Other planets, including many of the recently-discovered extrasolar planets (or exoplanets), are expected to possess iron-rich cores. Pressures similar to those at the centre of the Earth have been achieved in static diamond anvil cell experiments, but the multi-terapascal (TPa) pressures expected at the centres of more massive planets can currently be achieved only in shock-wave experiments, which give very limited structural information. Indeed, there are no materials whose structures have been determined experimentally at pressures of 1 TPa or more. At low pressures the electronic configuration of the iron atoms can be described as $3d^64s^2$, but the more extended $4s$ orbitals are pushed up in energy with respect to the $3d$ orbitals under compression and the $4s$ charge slowly drains into the $3d$ orbitals, leading to a $3d^84s^0$ configuration at multi-TPa pressures. AIRSS showed that only the standard close-packed phases are energetically competitive at multi-TPa pressures [29], see Fig. 17. The bcc structure is stabilised at low pressures by its ferromagnetic spin ordering, but it transforms to a hcp structure at pressures well below 100 GPa. We found a transition from hcp to fcc and back to hcp at TPa pressures (see Fig. 17), although these structures have similar enthalpies in the range 5–30 TPa. The most outstanding result was our prediction that the bcc phase, and a small bct distortion of it, become much more stable than hcp and fcc at extremely high pressures [29]. The reason for this is that the density of bct/bcc is about 0.6 % higher than hcp at the phase transition, which amounts to a very large enthalpy gain at pressures of around 30 TPa. We also studied harmonic phonon modes and the effects of electronic excitations at finite temperatures, but the overall effect on the relative stabilities of the phases is not large [29].

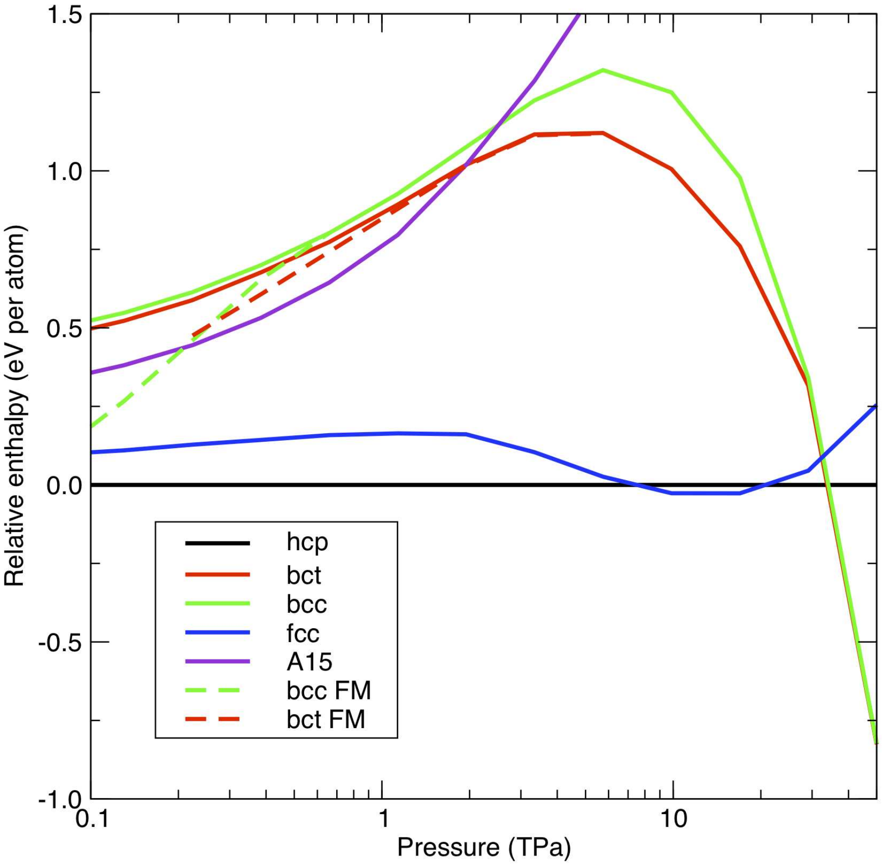

Figure 17: Variation with pressure of the enthalpies of various phases of iron with respect to the hcp phase. The dashed lines indicate ferromagnetic (FM) phases and the solid lines indicate non-magnetic phases

Defects in silicon: We have used AIRSS to study defect complexes in Si consisting of combinations of H, N, and O impurity atoms and Si self-interstitials and vacancies [80, 81]. Most of the searches were performed with 32-atom supercells, although we used larger cells for a few searches. We embedded the most interesting defects in larger cells and relaxed them with a higher energy cutoff and better k-point sampling. We found almost all of the previously-known point defects containing these impurity atoms, and we also found a number of new lowest-energy defects for some stoichiometries, such as $\{I, \mathrm{H}\}$ (an interstitial Si atom and a H atom) [80], and $\{3\mathrm{O}\}$ (three interstitial O atoms) [81]. It is possible to automate the search procedure so that one needs specify only the host crystal, the impurity atoms to be included and the size and location of the "hole" in the host compound into which the impurity atoms are placed. The number of different combinations of impurity atoms need not be excessive. For example, using three different types of impurity atom and a total number of impurity atoms of ≤ 4 requires searching over only 34 possible cell contents, and using five different types of impurity atom and a total number of impurity atoms of ≤ 4 requires searching over only 125. We estimate that if we were presented with the crystalline structure of a new material containing up to, say, three atomic species and we took into account three possible impurity species (H, N, and O, for example), we could determine the important point defects and their physical and electronic structures within a few weeks. Of course we could also have predicted the structure of the host material.

7.7 Conclusions

The different searching methods which have been used in conjunction with DFT methods should be judged by the results obtained. We believe that the AIRSS results presented here are impressive and that they make a strong case for the method. Our approach is pragmatic, we start from the most random method for generating structures that we can think of and introduce biases based on chemical, experimental and/or symmetry grounds. The starting structures are then relaxed while preserving the experimental and symmetry constraints. Sometimes we perform shaking and/or phonon calculations on the relaxed structures to look for energy lowering distortions.

We like the simplicity of this approach, it is easy to understand what the various "knobs" of the method do, which makes it easier to decide which knobs to turn and how far to turn them. We concentrate our computational efforts on relaxing a very wide variety of initial structures, which means that our stopping criterion of obtaining the same lowest-energy structure several times gives a good chance of finding the global minimum of the PES.

Our searching strategy will work very well on the petascale computers which are becoming available now and the exascale computers which will be available in a few years time. Such computing resources will be able to generate enormous databases of structures which will be useful for many purposes, such as fitting and testing empirical force fields, determining structures from diffraction data and determining structures using data mining [82]. The efficient handling and analysis of the huge amounts of data produced by structure searches will pose challenges for the electronic structure community.

Searching for structures with first-principles electronic structure methods has already made an impact in various branches of science and we imagine that it will become an integral part of materials design and discovery. Indeed it is reasonable to suppose that it will become important in all fields in which it is relevant to know the relative positions of atoms.

7.8 Acknowledgements

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A Summary of other computational searching methods

Although this article only deals with the AIRSS approach in detail, it is appropriate to mention other techniques which have been used to predict structures described by empirical or first-principles inter-atomic forces. There are many excellent reviews which describe structure prediction methods for clusters and solids [24, 83–87].

Simulated Annealing (SA) is a Monte Carlo technique devised by Kirkpatrick *et al* [88]. The name derives from an analogy with annealing in metallurgy, in which heating and cooling is used to remove defects from a metal. In this method the current approximate solution or state is replaced by a randomly chosen nearby state. The probability of accepting the new state is 1 if it is lower in energy than the initial state, and $e^{-\Delta E/T}$ if it is higher, where ΔE is the energy of the final state minus the initial state. If the temperature T is chosen to be zero then only states of lower energy than the current state are accessible and the algorithm normally becomes trapped in a local minimum. To avoid this, the temperature T is gradually reduced during the simulation and, if the cooling is slow enough, the system will eventually find the lowest energy state. SA with $T > 0$ allows the system to jump out of local minima. However, the basic algorithm is normally inefficient as it often gets stuck in local minima and many variants of it have been devised and tested in the quest for higher efficiency. There is considerable freedom to alter the proposed moves and the form of the acceptance probability, and to use more complicated "annealing schedules" in which the temperature is sometimes raised during the run.

SA requires only the energies of different configurations of the system, energy derivatives (forces and stresses) are not required. It is, however, straightforward to calculate energy derivatives using empirical potentials and, with a little more effort, within first-principles methods. Energy derivatives can be used to replace the Monte Carlo algorithm by classical molecular dynamics (MD). The most widespread use of energy derivatives in structure searching is to relax a structure to the minimum of its basin of attraction.

Methods have also been devised which evolve ensembles of structures rather than evolving a single structure. The simplest such idea is to run entirely separate searches with different starting points. Ensemble SA methods have been developed in which an adaptive annealing schedule is controlled by ensemble averages of thermodynamic information [89]. Another idea is to use parallel runs at different temperatures, such as in the parallel tempering algorithm which derives from the work of Swendsen and Wang [90, 91]. The particle swarm method was inspired by the collective behaviour of a flock of birds [92]. In this MD-based method each member of the ensemble or swarm is accelerated towards its own previous "best solution" and towards the swarm's previous "best solution".

Locating the global minimum is difficult because the energy surface contains many basins which may be separated by high barriers. One approach is to transform the energy surface to one which is easier to search. Perhaps the simplest such idea is to increase the range of the inter-atomic potential [93] which has the effect of removing many local minima [94]. Such an unphysical potential may of course have a significantly different global minimum. Consider instead a transformed energy surface obtained by setting the energy throughout each basin of attraction to the minimum energy of the basin. Obviously this transformation does not affect the relative energies of the minima. We now have to search the transformed energy surface. A simple Monte Carlo procedure known as "basin hopping" [22–24] is to start at a random position, relax to the basin minimum, propose a random move and relax to the new minimum. The move is accepted if the energy is lowered and accepted with probability $e^{-\Delta E/T}$ if the energy is raised. The simplest version of the algorithm has two parameters, the length of the move which may be adjusted to give a reasonable acceptance ratio, and the temperature T. The minima hopping method [95] is related to basin hopping.

Evolutionary algorithms (EA) are optimisation techniques inspired by biological evolution, involving concepts such as reproduction, mutation and recombination, fitness and selection [96]. Genetic algorithms (GAs) are a subset of EA in which a genetic representation of approximate solutions (structures) is used, normally a bit array [97]. An ensemble or population of structures is generated and each member is assigned a "fitness" which, for our purposes, is its energy or enthalpy. A fraction of the population is selected for reproduction, with a bias towards the fittest, and they are paired up for "recombination", the splicing together of the parental genes. A "mutation" step may also be performed. The new population is then subjected to selection and the whole process is repeated. When using GAs for structure searching it is standard to relax structures to the minimum of their basin of attraction before reproduction, so that the inheritance might be described as Lamarckian rather than Darwinian. GAs have been applied to many optimisation problems, and a review of the design and use of GAs for determining the structures of atomic clusters described by empirical potentials is given by Johnston [83].

The set of algorithms for predicting structures described above is of course far from complete and interesting alternatives have been pursued. For example, crystalline network structures, such as zeolites and carbon polymorphs, have been enumerated systematically using graph theory [98–100]. Faken *et al* [101] have sought high-dimensional barrier-less pathways between local minima in the physical three-dimensional space, and methods using quantum delocalisation have also been investigated [102–104]. Metadynamics is a powerful sampling technique for reconstructing the free-energy surface as a function of a set of collective variables, and this method can be used to study phase transitions at finite temperatures [105, 106].

Some of the strategies described above can clearly be combined, and many additional refinements have been suggested. There is often a substantial overlap between the various different methods, and it can be difficult to determine where one method ends and the next begins. On reading the description of our AIRSS approach in Section 7.3, the reader will recognise elements from the searching methods described in this appendix.

Almost all of the methods described above were first used in searching for structures with empirical potentials, although they have since been used with first-principles methods. Jones and coworkers used molecular dynamics simulated annealing with first-principles DFT to study the structures of numerous clusters from the late 1980s [107, 108]. Deaven and Ho searched for cluster geometries using a GA and a tight-binding model [109], and this work was important in bringing the possibilities of such methods to the attention of the "first-principles" community. Predicting crystal structures with first-principles methods is growing in popularity. Schön, Jansen and coworkers have used Hartree-Fock theory and DFT to search for stable structures and study the PES of various crystals [87, 110]. Zunger and coworkers [111, 112] and Oganov and coworkers [113, 114] have used GAs to search for crystal structures with DFT methods.

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