Ψ_k Newsletter

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

Number 102 December 2010

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Sponsored by: UK's CCP9
and Psi-k

Contents

1 Editorial

We start this December issue of the Psi-k Newsletter with a short write up by Paul J. Durham (STFC, UK) and Balazs L. Gyorffy (Bristol, UK) on Walter Temmerman on the occasion of his recent 60th birthday. Walter, together with Volker Heine, has been one of the leading figures in the history of Psi-k Network and is also the inventor of its name. We believe that he fully deserves to have his accomplishments documented in this Psi-k Newsletter.

On the whole, the present newsletter is dominated by reports on various workshops/meetings/summer schools sponsored or co-sponsored by Psi-k. In addition we have also some announcements and abstracts included in this issue.

The scientific highlight of this issue is by Jonathan R. Yates (Oxford), Chris J. Pickard (London) and Davide Ceresoli (Oxford) on "First principles calculations of Solid-State NMR parameters".

For further details on this newsletter please check its table of contents.

Since this is the last newsletter of 2010, we would like to take this opportunity and thank all of you for contributing to and reading our Psi-k newsletters. Also, we wish you all a very Merry Christmas and all the best in the New Year 2011.

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**

Dzidka Szotek, Martin Lüders and Walter Temmerman
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2 General News

2.1 From CCP9 to Psi-k: Celebrating Walter Temmerman's 60th Birthday

The 27 November 2010 was Walter Temmerman's 60th birthday. All those who know Walter will want to mark this special occasion in this Newsletter of the Psi-k Network which he has done so much to establish and nurture.

Career sketch

Walter studied mathematics in his home town of Gent and, after a year in Utrecht, came to the H H Wills Physics Laboratory in Bristol in 1974 to do a PhD (with Balazs Gyorffy) on a scholarship funded by the British Council. That excellent organisation must have thought Walter was a good bet, but they couldn't have known how important a role he was to play in the condensed matter physics community first in Britain and later in Europe as a whole. He did a spectacular PhD project: he set up and performed the first complete KKR-CPA calculations to describe realistically from first principles the electronic structure of a disordered system, a random substitutional alloy (PRL **41**, 339 (1978)). In the process, working closely with Malcolm Stocks, he became one of the first people in the UK whom one could call a practitioner of computational science, the emerging discipline that some regarded with suspicion, and he did a great deal to establish its credibility in condensed matter research. A little while later he was hired by John Pendry to join the Theory Group at Daresbury Laboratory, then part of the Science Research Council, at a very exciting time for the Lab - the building of the Synchrotron Radiation Source (SRS) was being completed and the Cray 1s had just arrived. His job then was to support the newly formed Collaborative Computational Project on the Electronic Structure of Solids - CCP9. As a result, he was one of the first in the UK to do self-consistent DFT calculations, and subsequently did an enormous amount of research on the band structures of transition metals and alloys (spin-polarised and/or relativistic when necessary), high T_c superconductors, f-band materials and much more. He has been one of the pioneers, with Dzidka Szotek, of the implementation and application of the self-interaction correction to strongly correlated systems. By the 1990's it was clear that the future of our field lay in European collaboration and the Psi-k Network was set up, through the European Human Capital and Mobility network, with Walter as its coordinator, also inventing the Psi-k as the brand name for it. He was the first leader of the Band Theory Group in Daresbury's Computational Science and Engineering Department, and, after many promotions, became an STFC Senior Fellow - the highest position a scientist can attain in our organisation. He is now the Director of Daresbury's CECAM node and a visiting professor at the University of Sheffield.

Story of CCP9 and Psi-k

Working in the UK Research Council system means that you have to interact with the whole UK research community rather than simply pursue your own research career. When Walter arrived at Daresbury the key tasks for the Theory Group were to support the synchrotron radiation science programme and to establish the portfolio of collaborative computational projects - the CCPs. Walter worked on both, but CCP9 was always his focus. After long efforts by Balazs Gyorffy and Malcolm Stocks and others to set up a national "band theory project", their idea took root in the formation of CCP9 with Balazs as the first Chairman and Walter as the post-doc supporting it. The first task was to import and adopt O K Andersen's LMTO code as the CCP9 "workhorse" for self-consistent band calculations. Walter struck up a productive collaboration with Ole and his group, who were marvellously generous to CCP9, and the project got off to a flying start, a flying start that was in itself a European effort. Over the years, CCP9 has been a key resource for the UK condensed matter research community, both theoretical and experimental - Volker Heine once referred to the CCPs as "the jewel in the crown" of the UK Research Councils. Of course, CCP9, although a UK initiative, always had many colleagues and collaborators from outside the UK and, as we mentioned above, it had a European aspect from its inception. Many of us in the UK came to feel that the collaborative approach embodied in CCP9 would work best on a European scale, and after much discussion with European colleagues, the Psi-k Network was born, initially as part of the European Commission's Human Capital and Mobility Programme (with Walter as its coordinator). Volker Heine, always a tremendous champion of European science, was the first Chairman of Psi-k, and Walter was its first scientific secretary with Dzidka taking the lead on the Newsletter. This team worked with tremendous dedication and enthusiasm, and quickly established what really felt like a "European family" in electronic structure research. We don't need to document the history of Psi-k here - it will be familiar to most readers - but we can all agree that it has been a great success. Just think of the progress of the big Psi-k conferences held every 5 years or so. The first three, organised at Schwäbisch Gmünd by the Andersen group in Stuttgart, second by Walter and the Daresbury group and third by Risto Nieminen and his group in Helsinki, grew steadily in scale and scope to the point where the fourth conference, organised in Berlin by Matthias Scheffler's group, welcomed over 1000 participants. Clearly, many people have contributed to this success story, but none more than Walter. As Volker Heine himself has recently remarked "... it has always been Walter who has been the true driving force behind Psi-k". It is an achievement of which he can be truly proud and the rest of us truly grateful.

Walter as a person

What has made Walter so important in these developments? First, he's an excellent scientist with a tremendous research record. People want to work with him because they know it will benefit their own research. Walter displays to a high degree the advantages of collaboration in research, and for his colleagues at Daresbury it has been a continual source of inspiration to see the stream of visiting scientists, young and old, who come from all over the world to work with him. This is what lends real credibility to his work in coordinating initiatives such as CCP9 and Psi-k. Moreover, Walter is a genuinely nice person and a delightful companion to those of us lucky enough to be his friends, and he and Dzidka are always wonderfully hospitable to their visitors. He is also one of those good 'housekeepers' no successful organization can do without. As such Walter worked tirelessly to establish Psi-k as a charity, with Peter Dederichs as its chairman and Walter vice-chairman, to carry it over from one ESF funding programme to another. He has a unique combination of scientific insight, common sense and Belgian bonhomie that would be impossible to replicate.

We wish him a very Happy 60th Birthday.

Paul J Durham and Balazs L Gyorffy

3 Psi-k Activities

"Towards Atomistic Materials Design"

3.1 Reports on the Workshops supported by Psi-k

3.1.1 Report on Workshop "Quantum Monte Carlo meets Quantum Chemistry: new approaches for electron correlation"

Lugano

June 15, 2010 to June 18, 2010

Cecam, Psi-K, Democritos, i2cam,

Ali Alavi, M. Casula and S. Sorella

http://www.cecam.org/workshop-466.html

Scope of Workshop

The aim of this workshop was to bring together two different communities who share a well-defined common interest, namely the ab-initio calculation of electron correlation problems (principally total energies, but touching other properties such magnetism, excitations, forces etc), using classes of methods alluded to in the title of the workshop. Despite the commonality of interests, these two communities do not regularly meet on the same conference circuit, and as a result, the interactions are not as strong as might be expected, nor indeed the awareness of techniques and methods which have been developed in the past few years. In addition, we believe that ideas taken from both quantum chemistry and quantum Monte Carlo (QMC) have the potential for synthesis into methods which actually exploit advantages of both types of computational algorithms. Therefore, time seemed ripe to organise a meeting on this topic.

In the event, we had an extremely good turnout, both of invited speakers (27) as well as non-supported participants (26), so that the workshop number (56) well-exceeded the initial target (40) and, after a careful selection, we have managed to limit this number well below the number of applications (71). From both communities, we had many of the foremost experts at this meeting.

Main Outcomes of key presentations

On the quantum chemistry (and, more generally, wave function-based methods) side, there were impressive talks in the use of wave function and density-matrix methods in treating both strong correlation systems, as well as large (going to bulk-periodic) systems. Kresse outlined new developments in VASP which moved towards more accurate description on correlation based on the random phase approximation (RPA), and coupled-cluster methods, showing applications to a broad range of wave function-based description of solids. Helgaker gave an intriguing talk on the possible use of Lieb's principle for constructing exact (universal) density functions. Mazziotti showed some progress on the use of reduced density-matrix optimisations, applied to some strong correlation problems. Chan presented some new ideas coming from quantum information theory to optimise density matrix renormalization group (DMRG)-type wave functions, Manby presented an impressive calculation on liquid water at ambient conditions, based on a very efficient implementation of the MP2 method . Alavi presented a new approach (dubbed full configuration interaction QMC or FCIQMC) which combines the FCI with QMC methods, and enables exact solutions to be obtained with a minute fraction of the effort employed to carry out exact diagonalization calculations.

On the quantum Monte Carlo side, many interesting applications were presented. In solids and weakly bounded systems containing few water molecules and Carbon based compounds, Alfe' showed that the standard Diffusion Monte Carlo (DMC) works quite accurately and provides always benchmark results compatible with experiments. On the other hand, wave functions containing a large number of determinants were used by Umrigar, Stich, Bressanini to describe faithfully static correlations in important chemical compounds, such as azobenzene, boranes, and azaboranes, and simple Carbon atom and Carbon dimer, as well as to compute excitations and structural properties of fluorescent and photosensitive compounds like the Green Fluorescent Protein (Filippi). Stella has reported an interesting result on the metal insulator transition in the one dimensional Hydrogen-chain, showing the importance of Resonating Valence Bond correlations near the transition point. Casula, on the other hand, has studied the metal-insulator structural transition in Silicon, showing that the lack of consistent pseudopotentials in Quantum Monte Carlo calculations may explain why the transition pressure, determined by QMC with Hartree-Fock (HF) and density functional theory (DFT) pseudopotentials, differs significantly from the experimental value. Finally, Moroni and Sorella reported some significant progress in the calculation of forces, which could open the way to accurate and large-scale geometry optimization and molecular dynamics in a correlated framework.

Report of Selected discussions

One of the issues to be debated is the reason for continuing scepticism on behalf of many practising quantum chemists to use QMC techniques. Some lively discussions took place on this. On the one hand, it is clear that the accuracy issue remains foremost on the quantum chemist's mind – whilst DMC can deliver in terms of absolute energies, it's performance is less satisfactory for relative energies (i.e. energy differences), owing to sometimes unfavourable error cancellation. On the other hand, the FCIQMC method of Alavi may provide the quantum chemists the sort of compromise that they feel comfortable to accept: i.e. sacrificing the continuum real-space methods of most QMC approaches (which however is replaced by a systematically improvable approximation by expanding the basis sets), while maintaining the key concept of DMC, namely to sample the configuration space. It is the belief of one of the organisers that this hybrid approach will prove successful in enticing the quantum chemists into stochastic frame of mind. On the other hand, quantum chemistry methods have so far appeared to be inadequate to describe qualitatively new phases of matter, missed at the HF level and not well described by post-HF methods. For instance, all chemists present in the discussion admitted that there is no reliable method to describe even simple superconductors within post-HF methods, whereas within QMC it is now possible to describe by means of a simple correlated wave function both Mott insulators and high temperature superconductors, and more generally qualitative new effects that go beyond simple mean field theories. The conclusion was that some of the ideas of QMC should be exported in quantum chemistry methods, while it is beneficial for certain QMC applications, like those aiming at studying excited states, to have as initial guess a multi-reference wave function, generated by state-of-the-art quantum chemistry approaches, like the complete active space (CAS) method.

The basic objective of the workshop was to invite leaders from two disciplines to be exposed to each other's methods and ideas, and to interact and debate on the pros and cons of the methods. Of course it will take some time before actual ideas are implemented into new methods and codes. However, we feel that a very useful interaction took place, with healthy and lively debates.

We believe the basic theme of the workshop is far from exhausted, and worthy of another workshop in three of four years time, where some of the above methods have had more time to develop.

Programme:

Day 1 - June, 15th 2010

Session I

09:00 to 09:10 - Welcome
09:10 to 10:00 - Martin Head-Gordon
Introduction to quantum chemistry methods
10:00 to 10:50 - David Ceperley
An Introduction to Quantum Monte Carlo
10:50 to 11:10 - Coffee Break
11:10 to 11:40 - Martin Head-Gordon
(Relatively) simple wave functions for describing strong electron correlations in molecules
11:40 to 12:30 - Michel Caffarel
Multi-Jastrow trial wavefunction for quantum Monte Carlo
12:30 to 14:00 - Lunch Break

Session II

14:00 to 14:30 - Discussion
14:30 to 15:20 - William Matthew Colwyn Foulkes
Finite-size errors in continuum quantum Monte Carlo calculations
15:20 to 16:10 - Ivan Stich
Electronic structure of lowest singlet states of azobenzene
16:10 to 17:00 - Dario Alfe
Recent quantum Monte Carlo calculations of weakly bound systems

17:00 to 17:20 - Coffee Break
17:20 to 17:40 - Dario Bressanini
QMC calculations on Boranes and Azaboranes
17:40 to 18:10 - Lorenzo Stella
Metal-insulator transition of one-dimension Hydrogen chains: a Variational Monte Carlo study
18:10 to 18:30 - Discussion
19:30 to 22:00 - Dinner

Day 2 - June, 16th 2010

Session III

08:50 to 09:40 - Fred Manby
Systematically improvable electronic structure calculations for solids and liquids
09:40 to 10:30 - Michele Casula
Diamond to betatin transition in Silicon: a playground for pseudopotentials.
10:30 to 10:50 - Coffee Break
10:50 to 11:40 - Beate Paulus
The method of increments - a wavefunction-based correlation methods for solids and surfaces
11:40 to 12:30 - Lorenzo Maschio
Local-correlation methods for the study of non conducting crystalline systems : the CRYSCOR program
12:30 to 14:00 - Lunch Break

Session IV

14:00 to 14:30 - Discussion
14:30 to 15:20 - Georg Kresse
Quantum chemistry methods for solids and surfaces: RPA and CCSD
15:20 to 16:10 - Saverio Moroni
Fixed-node calculation of force constants
16:10 to 16:30 - Coffee Break
16:30 to 17:20 - Cyrus Umrigar
Natural Orbital and Gauss-Slater Basis for Molecules
17:20 to 18:00 - Discussion

Day 3 - June, 17th 2010

Session V

08:50 to 09:40 - Lubos Mitas
Many-body nodal structures of ground and excited states, pairing effects and release node methods
09:40 to 10:30 - Ali Alavi
QMC in discrete spaces : a way to overcome the sign problem ?
10:30 to 10:50 - Coffee Break

10:50 to 11:40 - David Mazziotti
Two-electron Reduced-Density-Matrix mechanics : theory and applications
11:40 to 12:30 - Trygve Helgaker
The rigorous calculation of the universal density functional by the Lieb variation principle
12:30 to 14:00 - Lunch Break

Session VI

14:00 to 14:30 - Discussion
14:30 to 15:20 - Krzysztof Szalewicz
Calculations of interaction energies with micro to femtohartree accuracies
15:20 to 15:40 - Coffee Break
15:40 to 16:30 - Garnet Chan
New wavefunctions in quantum chemistry
16:30 to 17:20 - Claudia Filippi
Excitations in photosensitive biomolecules from quantum Monte Carlo

Session VII

17:20 to 18:30 - Poster Session

Day 4 - June, 18th 2010

Session VIII

08:50 to 09:40 - Laura Gagliardi
Recent developments in multiconfigurational quantum chemical methods and their application to water oxidation
09:40 to 10:30 - Shiwei Zhang
Auxiliary-field quantum Monte Carlo for quantum chemistry : recent progress and open issues
10:30 to 10:50 - Coffee Break
10:50 to 11:40 - Peter Knowles
The variatonal coupled cluster method and approximate pair functionals
11:40 to 12:30 - Discussion
12:30 to 14:00 - Lunch Break

Session IX

14:00 to 14:50 - Jeongnim Kim
QMC, hamessing computing powers of today and beyond
14:50 to 15:10 - Leonardo Guidoni
Stucture and harmonic frequencies of the water molecule by Quantum Monte Carlo
15:10 to 16:00 - Sandro Sorella
Algorithmic differentiation and the calculation of forces by quantum Monte Carlo methods
16:00 to 16:10 - Closing word

List of participants

1. Dario ALFE United Kingdom, University College London
2. Dario BRESSANINI Italy, Universita' dell'Insubria
3. Michel CAFFAREL France, University Paul Sabatier
4. David CEPERLEY USA
5. Garnet CHAN USA, Cornell University, Ithaca
6. Bryan CLARK USA, University of Illinois - Urbana Champain
7. Roberto DOVESI Italy, Dep. Chimica IFM -Univ. Torino
8. Kenneth ESLER USA, University of Illinois at Urbana-Champain
9. Claudia FILIPPI The Netherlands, Faculty of Science and ...
10. William Matthew Colwyn FOULKES United Kingdom, Imperial College London
11. Laura GAGLIARDI USA, University of Minnesota
12. Leonardo GUIDONI Italy, University of L'Aquila
13. Martin HEAD-GORDON USA, Department of Chemistry, University...
14. Trygve HELGAKER Norway, Centre for Theoretical and Compu...
15. Jeongnim KIM USA, NCSA
16. Peter KNOWLES United Kingdom, Cardiff University, UK
17. Georg KRESSE Austria, University of Vienna
18. Fred MANBY United Kingdom, University of Bristol
19. Lorenzo MASCHIO Italy, University of Torino
20. David MAZZIOTTI USA, Department of Chemistry and The Jam...
21. Lubos MITAS USA, North Carolina State University
22. Saverio MORONI Italy, DEMOCRITOS Trieste
23. Beate PAULUS Germany, Instititute of Chemistry and Bi...
24. Ivan STICH Slovakia, University of Bratislava
25. Krzysztof SZALEWICZ USA, University of Delaware
26. Cyrus UMRIGAR USA, Cornell University
27. Shiwei ZHANG USA, College of William and Mary

28. Roland ASSARAF France, University Pierre and Marie Curi...
29. Sam AZADI Italy, International school for advanced...
30. BRAIDA BENOîT France, Université Paris VI, laboratoire...
31. George BOOTH United Kingdom, University of Cambridge
32. Rodrigo CASASNOVAS Switzerland, ETH Zürich, Department of C...
33. Michele CERIOTTI Switzerland, Computational Science, Depa...
34. Deidre CLELAND United Kingdom, University of Cambridge
35. René DERIAN Slovakia, Institute of Physics, Slovak A...
36. Dominik DOMIN France, Laboratoire Chimie Theorique, Un...
37. Francesco FRACCHIA Italy, Università di Pisa
38. Mike GILLAN United Kingdom, Department of Physics an...
39. Rustam KHALIULLIN Switzerland, ETH Zürich, Department of C...
40. Konrad MARTI Switzerland, ETH Zürich
41. Giacomo MICELI Italy, Univ. Milano-Bicocca / ETH Zurich
42. Antonietta MIRA Switzerland, USI Lugano
43. Miguel MORALES USA, Rice University
44. Masayuki OCHI Japan, University of Tokyo
45. Noejung PARK South Korea, Dankook University, Seoul
46. Carlo PIERLEONI Italy, Physics Department, University of...
47. Brenda RUBENSTEIN USA, Columbia University
48. Anthony SCEMAMA France, CNRS
49. Gaetano SENATORE Italy, Universita" di Trieste
50. James SPENCER United Kingdom, Imperial College
51. Lorenzo STELLA Spain, Nano-Bio Spectroscopy Group and E...
52. Julien TOULOUSE France, University Pierre and Marie Curi...
53. Ching-Ming WEI Taiwan, Republic of China, Institute of ...

3.1.2 Report on Workshop “European School on Multiferroics” (ESMF2010)

L’Aquila, Italy

September 26th - October 1st 2010

Sponsors
Psi-k, ESF through Intelbiomat Network

Organizers
Silvia Picozzi, School director (*CNR-SPIN, IT)*
Manuel Bibes (*CNRS-Thales, FR)*
Jeroen van den Brink (*IFW Dresden, DE)*
Laurent Chapon (*ISIS, UK)*

http://www.casti.aquila.infn.it/homepages/bismuth/ESMF2010/index.html

The main goal of the school was to present a comprehensive overview in the exciting and fastly developing field of multiferroics (materials that combine spontaneous long-ranged magnetic and dipolar orders). ESMF2010 gathered 86 participants, in particular 68 students (mainly Europeans, but also including few participants from USA, Japan, South-Africa, etc) and 18 speakers (again, mostly Europeans with three coming from USA). The number of students was as large as previous editions (compared to same cases, even higher), showing that multiferroics continue to attract enormous interests all over the international scientific community. All the lessons were prepared in a way adequate to PhD students, most of the lectures showing first an introductory part with basic concepts and then moving to recent scientific results, in order to give to young participants a flavor of current research activities. In this respect, the lessons were interesting both for people new to the field as well as for participants with longstanding experience in the area. All the speakers were extremely qualified: plenty of examples were given, so as to make the general concepts clear to everybody when applied to specific materials, cases, mechanisms, etc. The schedule implied 4 lessons per day (90 minutes each + 15 minutes of discussions), excluding Wednesday (due to social excursion and dinner) and Friday (closing day) when two lectures only were held. A poster session, including a prize for the best poster presentation, was held on Tuesday September 28th. The organization of the school schedule was largely appreciated by most of the students.

The choice of the location of the ESMF school in 2010 had a somewhat special meaning, since L’Aquila was struck by a tremendous quake in April 2009 causing 300 casualties and about 60.000 evacuees. After 18 months, the situation was still rather severe in L’Aquila (for example, all the historical center, denoted as ’red zone’, was not accessible to people and nobody was - and still is - allowed to live there or even enter there). Despite many logistic problems that the local-organizer/director had to solve before the event, the school was held at the Faculty of Mathematical, Physical and Natural Sciences of the University of L’Aquila, with its building located in the peripheral area of L'Aquila. Being newer and recently constructed, in general less damages were caused by the quake in this area, so that the lesson room as well as the entire building was accessible and available. Moreover, several hotels could be found nearby and a shuttle-bus service connecting the hotels and the university was arranged for the participants.

After two introductory lectures on ferroelectrics (J. M. Triscone) and magnetic oxides (M. J. Coey) in the first day of the school, the talks were addressed into multiferroics and magneto-electric materials/phenomena and specifically focused on:

- the (co)-existence and cross-coupling between different long-range orders (magnetic, dipolar, ferroelastic, toroidal);
- the search for new materials showing strong magneto-electric coupling and multiferroicity, including handles [such as strain-engineering (K. Dörr) or materials design (C. Ederer)] to tune the relevant properties;
- the novel physical mechanisms at the basis of complex magnetic phase diagrams (S. W. Cheong), encompassing ferroelectricity (statically) induced by magnetic or charge order as well as dynamical magnetoelectric effects (including electromagnons and domain wall dynamics);
- advanced experimental techniques [neutrons (V. Simonet), X-ray magnetic scattering (A. Bombardi), piezo-force microscopy (S. Fusil), high-resolution transmission electron microscopy (M. Varela), etc] particularly suited for the analysis of multiferroics and magnetoelectrics
- examples of theoretical modelling of "electronic" multiferroics, with examples mainly of charge–ordered materials (J. van den Brink and D. Khomskii)
- the importance of symmetry analysis (L. Chapon) and Landau theory in this field, complemented by practical examples of well-known multiferroics
- perspectives for multifunctional applications (J. Fontcuberta, M. Bibes), including electrically controllable spintronic devices or tunnel electro-magnetic junctions

Systems of interest have ranged from bulk compounds [manganites (in their hexagonal and orthorhombic phases, under equilibrium or strained), nickelates, cobaltates, $BiFeO_3$, $EuTiO_3$, etc] to composites, from (strained) thin films to (hybrid) nanostructures (I. Mertig). A lesson given by Joel E. Moore on Topological insulators (TI, a topic currently attracting lots of interest), was included in the program, in particular focused on the connection between TI and orbital magnetoelectric responses.

The students actively participated in the lessons, with lively discussions lasting for all the allocated time (15 minutes for each lesson). They had also the opportunity, during the poster session, to present their own research activity; in particular, one award for the "best poster presentation of ESMF2010" was given to Pauline Rovillain, Univ. Paris 7, for her work on "Electric field effects on spin-modes in $BiFeO_3$ crystals".

Finally, we remark that a school website was created and continuously updated (in particular to upload all the presentations given by the speakers so that they could be publicly downloaded):

http://www.casti.aquila.infn.it/homepages/bismuth/ESMF2010/index.html

Programme:

Sunday Sept. 26th

18:00-19:30: Welcome Party

19:30: **Prof. Gianluca Ferrini**, *Univ. L'Aquila, Geology Dept.*, "L'Aquila earthquake on April 6^{th} 2009"

Monday Sept. 27th

9:00-9:30: **Silvia Picozzi, Ruggero Vaglio**, *CNR-SPIN (IT)*, "Opening"

9:30-11:15: **Jean Marc Triscone**, *University of Geneva (CH)*, "Ferroelectric materials: an introduction to the field and some examples of recent developments"

11:45-13:39: **Michael Coey**, *Trinity College Dublin (IE)*, "Magnetic Oxides; Introduction and New Directions"

15:00:16:45: **Claude Ederer**, *Trinity College Dublin (IE)*, "First principles studies of multiferroic materials"

17:15-19:00: **Joel Moore**, *Dept. of Physics, Univ. of California, Berkeley (US)*, "Topological insulators and orbital magnetoelectric coupling"

Tuesday Sept. 28th

9:00-10:45: **Katrin Dörr**, *IFW-Leibniz Institut Dresden (DE)*, "Strain effects in ferroic oxide films"

11:15-13:00: **Jeroen Van den Brink**, *IFW, Leibniz Institute for Solid State and Materials Research (DE)*, "Multiferroics: Hamiltonian modeling"

13:00-15:00: Poster session

15:00-16:45: **Alessandro Bombardi**, *Diamond Light Source Ltd, Rutherford Appleton Lab (UK)*, "An introduction to x-ray non-resonant and resonant scattering applied to multiferroics"

17:15-19:00: **Virginie Simonet**, *Institut Néel CNRS Grénoble (FR)*, "Neutron scattering a probe for multiferroics and magnetoelectrics"

Wednesday Sept. 29th

9:00-10:45: **Maria Varela**, *Oak Ridge National Lab, TN (USA)*, "An atomic resolution view at complex oxides: progress challenges and applications"

11:15-13:00: **Stéphane Fusil**, *Unité Mixte de Physique CNRS-Thales (FR)*, "BiFeO3 or the Guinea pig of multiferroics under the magnifier of piezoresponse force microscopy"

15:00-23:00: Social excursion + dinner

Thursday Sept. 30th

9:00-10:45: **Manuel Bibes**, *Unité Mixte de Physique CNRS-Thales (FR)*, “Ferroic and multiferroic tunnel junctions”

11:15-13:00: **Sang-Wook Cheong**, *Rutgers University, NJ (USA)*, “Multiferroic Vortices”

14:30-16:15: **Ingrid Mertig**, *MPI für Mikrostrukturphysik Halle and Martin-Luther-Universität Halle-Wittenberg (DE)*, “Magnetoelectric coupling at multiferroic interfaces”

16:45-18:30: **Laurent Chapon**, *ISIS, Rutherford Appleton Lab (UK)*, “Symmetry applied to magnetoelectrics and multiferroics”

Friday Oct. 1st

9:00-10:45: **Daniel Khomskii**, *Univ. Koeln (DE)*, “Multiferroics and beyond”

11:15-13:00: **Josep Fontcuberta**, *Institut de Ciencia de Materials (ICMAB) - CSIC, Barcelona (ES)*, “Electric and magnetic control of magnetization and polarization in multiferroic heterostructures and devices”

13:00-13:15: Closing

List of participants:

1. Sebastian Albiez, University of Cologne, Germany
2. Sergey Artyukhin, Univ. Groningen, The Netherland
3. Carmine Autieri, Univ. Salerno, Italy
4. Jaita Banerjee, Bose Natl Center for Basic Sciences, IN
5. José Barbosa, Universidade do Minho, Portugal
6. Paolo Barone, CNR-SPIN L’Aquila, Italy
7. Carsten Becher, University of Bonn, Germany
8. Manuel Bibes, Unité Mixte de Physique CNRS/Thales, France
9. Federico Bisti, University of L’Aquila, Italy
10. Alessandro Bombardi, Diamond Light Source Ltd., Rutherford Appleton Lab, United Kingdom
11. Emilie Bruyer, UCCS Artois, France
12. Nuala Caffrey, Trinity College Dublin, Ireland

13. Teresa Carvalho, Universidade de Trs-os-Montese Alto Douro, Portugal
14. Laurent Chapon, ISIS, Rutherford Appleton Lab, United Kingdom
15. Sang-Wook Cheong, Rutgers University, New York, United States
16. Michael Coey, Trinity College Dublin, Ireland
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19. Lavinia-Petronela Curecheriu, University Alexandru Ioan Cuza, Romania
20. Hena Das, Bose Natl. Center, India
21. Gabriella Maria De Luca, CNR-SPIN, Italy
22. Nitin Deepak, Tyndall National Institute, India
23. Kris Delaney, Univ. California Santa Barbara, USA
24. Flavia Viola Di Girolamo, Federico II University, Naples, Italy
25. Domenico Di Sante, Univ. L'Aquila, Italy
26. Kathrin Dörr, IFW-Leibniz Institut Dresden, Germany
27. Luca D'Ortenzi, University of L'Aquila, Italy
28. Claude Ederer, Trinity College Dublin, Ireland
29. Marta Elzo Aizarna, Institut Néel CNRS (Grenoble), France
30. Saeedeh Farokhipoor, Zernike Institute (Rug university), Netherland
31. Josep Fontcuberta, Institut de ciencia de Materials, (ICMAB)-CSIC Spain
32. Daniel Fritsch, Trinity College Dublin, Ireland
33. Tetsuya Fukushima, CNR-SPIN L'Aquila, Italy
34. Stéphane Fusil, Unité Mixte de Physique, CNRS/Thales, France
35. Livia Giordano, UniveristaÕ Di Milano-Bicocca, Italy
36. Joo (Nuno Santos) Gonalves, Universidade de Aveiro, Portugal
37. Christoph Gruber, TU Vienna, Austria
38. Gisele Gruener, LEMA / Faculté des Sciences, France
39. Alexander Hearmon, University of Oxford, United Kingdom
40. Johan Hellsvik, Uppsala University, Sweden
41. Jeroen Heuver, Zernike institute for advanced materials, Netherland

42. Yuji Hiraoka, Osaka University, Japan
43. Tim Hoffmann, University of Bonn, Germany
44. Jiawang Hong, Rutgers Univ., USA
45. Tanveer Hussain, Univ. Uppsala, Sweden
46. Diana Iusan, Univ. Uppsala, Sweden
47. Adam Jacobsson, Forschungszentrum Juelich, Germany
48. Daniel Khomskii, Universitaet zu Koeln, Germany
49. Marjana Lezaic, Forschungszentrum Juelich, Germany
50. Jia Liu, North Carolina State Univ., USA
51. Giorgia Maria Lopez, Univ. of Cagliari and Cnr-Iom, Cagliari, Italy
52. Luca Matteo Martini, Universitá degli Studi di Trento, Italy
53. Shlomi Matityahu, University of the Negev, Israel
54. Ingrid Mertig, MPI für Mikrostrukturphysik Halle and M. Luther Universität Halle- Wittemberg, Germany
55. Francesco Mezzadri, Universitá degli Studi di Parma, Italy
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57. Elise Pachoud, Laboratoire CRISMAT, France
58. Krisztian Palotas, Univ. Budapest, Hungary
59. Jonathan Peace, University of Warwick, United Kingdom
60. Silvia Picozzi, CNR-SPIN L'Aquila, Italy
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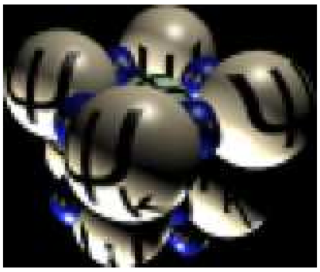

3.1.3 Report on the CAMD Summer School 2010 on the Electronic Structure theory & Materials Design

Sponsors:

The Lundbeck Foundation, Psi-k, C:O:N:T

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Karsten W. Jacobsen, Department of Physics, DTU
Kristian S. Thygesen, Department of Physics, DTU
Jan Rossmeisl, Department of Physics, DTU
Tejs Vegge, Materials Research Division, Risø National Lab
Thomas Bligaard, Department of Physics, DTU

Administrative organizers:
Marianne Ærsøe, Head of Administration

Webpage:
`http://www.camd.dtu.dk/English/Events/CAMD\_Summer\_School\_2010.aspx`

In brief

The Psi-k sponsored “CAMD Summer School 2010 Electronic Structure Theory and Materials Design” was held in the week August 14-20, 2010 at the Technical University of Denmark in Lyngby. Thanks to the 70 attentive summer school students and the 12 very helpful invited lecturers the school was the nice success that we had hoped for.

Motivation

The motivation for the school was that the era of cheap fossil fuels over the next few decades is expected to come to an end. Arguably making the development of sustainable energy solutions the most important scientific and technical challenge of our time. In order to address these and other technical challenges, we must in the future present a significantly improved capability to rationally design new materials. Computational design of new materials has been demonstrated in a few test cases, but in order to carry out systematic computational design of new materials for e.g. energy storage, fuel synthesis, and light harvesting, a number of methodological improvements are needed. Methods dealing with the description of electron transfer processes at surfaces in solid or liquid electrolytes, for photo-absorption and charge separation in extended solids, and for electronic localization in insulators have to be improved. Developing better handles on the errors in the electronic structure description (e.g. through Bayesian Error Estimation methods) may also prove critical. In order to begin addressing these challenges, the summer school focused on the fundamental concepts and the current status of the areas of DFT, and DFT implementations, TDDFT, excited states, thermodynamic properties derived from electronic structure calculations, modern xc-functionals, properties of surfaces and electron transfer at these, energy materials, error estimation, catalysis, electro-catalysis, and materials design strategies.

Purpose

The summer school aimed to teach the students how electronic structure theory can be used for materials design. An introduction to density functional theory with particular emphasis on practical methodology and implementation aspects was given and extensions beyond the standard DFT formalism were discussed. A significant focus was on the methodology applied "on-top" of electronic structure calculations to enable the search after new functional materials.

The summer school was a combination of lectures given by experts in the field and exercises giving hands-on-experience with the Atomic Simulation Environment (ASE) supervised by expert users. The ASE is a general purpose open source simulation environment that can be used to setup, control, and analyze electronic structure simulations carried out in a variety of electronic structure codes, e.g. including GPAW, Dacapo, VASP, Octopus, AbInit, ASAP, Siesta, and others.

Subjects

The subjects covered in lectures were more specifically:

- The fundamentals of Density Functional Theory
- Strategies for solving the Kohn-Sham equations
- Projector Augmented Wave Implementation
- Exchange-correlation functionals beyond GGA

- Error estimation in Density Functional Theory
- Time-dependent DFT
- Many-body approaches to the electronic structure problem
- Van der Waals descriptions
- Superconductivity with DFT
- Quantum electron transport theory
- Spectroscopy from DFT
- Thermodynamic properties and kinetics from DFT
- Energy Materials
- Chemistry at surfaces/Heterogeneous Catalysis
- Electrochemistry
- Materials Informatics

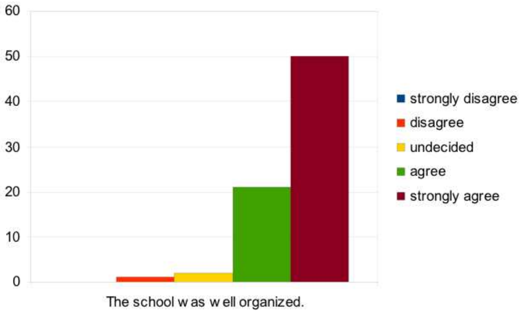
Lecturers

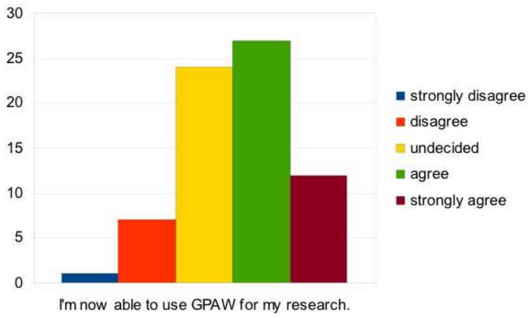
The Invited Lecturers were:
Peter Blöchl, TU Clausthal
Kieron Burke, UC Irvine
Mike J. Gillan, UC London
E.K.U. Gross, Freie Universität Berlin
Martin Head-Gordon, UC Berkeley
Hannes Jónsson, University of Iceland
John Kitchin, Carnegie Mellon University
Bengt Lundqvist, Chalmers Technical University
Manos Mavrikakis, UW Madison
Lucia Reining, École Polytechnique
Lars G. M. Pettersson, Stockholm University
Jens K. Nørskov, Stanford University
who gave presentations on their respective fields of expertise. In addition talks were presented by the local scientific organizing committee.

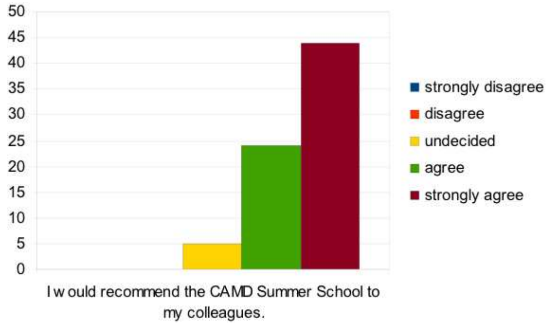
The participants and their evaluation

The participants were primarily PhD-students (more than 60) but there was also a few post docs. Most had a background in physics (44), but there were also some chemists (23) and some with a background in Chemical engineering and materials science. More than 50 of the participants were DFT users.

After the termination of the summer school, the participants were asked to evaluate a number of criteria, and generally we were quite happy with the outcome of the evaluation. In the figures some of the responses from the students has been shown. The students seemed to find that the administrational organization of the school was quite satisfactory, and somewhat to the surprise of the organizers, many of the summer school students, who did not know the electronic structure code GPAW before the school, actually learned it so well, that they now feel that they can use it directly in their research. We were very happy that a good fraction of the participants would recommend another CAMD Summer School to their colleagues.







Programme

Saturday, August 14, 2010:

14:00-19:00 Arrival to the guest houses on the DTU campus
19:00 Welcome reception (Chinese dinner) at NanoDTU

Sunday, August 15, 2010:

08:45-09:30 Breakfast
09:30-10:45 Fundamentals of DFT 1 (Kieron Burke)
10:45-11:15 Coffee break
11:15-12:30 Fundamentals of DFT 2 (Kieron Burke)
12:30-14:00 Lunch

14:00-15:00 Path techniques and reaction rates in DFT (Hannes Jónsson)
15:00-15:30 Coffee break
15:30-16:30 Van der Waals in DFT (Bengt Lundqvist)
16:30-16:45 Short break (with coffee)
16:45-17:15 Description of the data bar system (Jens Jørgen Mortensen)
17:15-18:30 Getting set to go in the data bar, etc. (Jens Jørgen + The entire team)

Monday, August 16, 2010:
08:45-09:30 Breakfast
09:30-10:30 Strategies for solving the Kohn-Sham equations (Peter Blöchl)
10:30-11:00 Coffee
11:00-12:00 Projector Augmented Wave Implementation (Peter Blöchl)
12:00-13:30 Lunch
13:30-14:15 Adsorbate-surface interactions (Jens Nørskov)
14:15-14:30 Short break (with coffee)
14:30-15:15 Concepts and trends in surface reactivity (Jens Nørskov)
15:15-18:00 Exercises (ASE)
18:00-20:00 Poster session and refreshments

Tuesday, August 17, 2010:
08:45-09:30 Breakfast
09:30-10:15 Exchange-correlation functionals beyond GGA (Martin Head-Gordon)
10:15-10:30 Short break (with coffee)
10:30-11:15 Excited states in extended systems (Martin Head-Gordon)
11:15-11:45 Coffee break
11:45-12:30 Error estimation in DFT (Karsten Jacobsen)
12:30-14:00 Lunch
14:00-14:45 Catalysis from DFT (Manos Mavrikakis)
14:45-15:15 Coffee break
15:15-16:00 Adsorbate-adsorbate interactions (John Kitchin)
16:00-16:30 Presentation of the CAMD Linux-cluster technology (Ole H. Nielsen)
16:30-18:30 Exercises (GPAW) + Tour to computer room for those who are interested

Wednesday, August 18, 2010:
08:45-09:30 Breakfast
09:30-10:15 Time Dependent DFT (Hardy Gross)
10:15-10:30 Short break (with coffee)
10:30-11:15 Superconductivity in DFT (Hardy Gross)
11:15-11:45 Coffee break
11:45-12:30 Quantum electron transport (Kristian Thygesen)
12:30-13:30 Lunch

13:30-15:00 Exercises (GPAW)
15:15- Departure by bus from building 311 -
Excursion to the Planetarium in Copenhagen followed by dinner at Brasserie Nimb, Tivoli. After dinner you can visit Tivoli on your own as you like.

Thursday, August 19, 2010:
08:45-09:30 Breakfast
09:30-10:30 Spectroscopy from DFT (Lars G.M. Pettersson)
10:30-11:00 Coffee break
11:00-12:00 Many-body approaches (Lucia Reining)
12:00-13:30 Lunch
13:30-14:15 Electro-catalytic reactions (Jan Rossmeisl)
(*14:15-19:00 ASE/GPAW install session on personal laptops (Marcin + Jens Jørgen)*)
14:15-18:00 Exercises (GPAW)
Afternoon coffee and cake will be available in Building 311

Friday, August 20, 2010:
Check out and handing in keys to your rooms to Marianne before 09:30.
08:45-09:30 Breakfast
09:30-10:15 Thermodynamic Properties from DFT 1 (Mike J. Gillan)
10:15-10:30 Short break (with coffee)
10:30-11:15 Thermodynamic Properties from DFT 2 (Mike J. Gillan)
11:15-11:45 Coffee break
11:45-12:30 Energy materials (Tejs Vegge)
12:30-14:00 Lunch
14:00-14:45 Catalysis Informatics (Thomas Bligaard)
14:45-15:00 Closing remarks (Karsten Jacobsen)
15:00-16:00 Afternoon cake and diffusion
16:00 Summer School closed - departure

More information about the lectures can be found on the homepage.

List of participants

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3.1.4 Report on Spring College on Computational Nanoscience

Trieste, Italy

May 17-28, 2010

Psi-k, CECAM, ICTP

A. Foster, N. Marzari, S. Scandolo

http://cdsagenda5.ictp.trieste.it/full_display.php?smr=2145

More than 150 participants (out of more than 500 applications) attended the College on Computational Nanoscience that was held in Trieste on May 17-28, 2010. The College started with an historical perspective of computational nanoscience given by R. Martin, and ended with a topical session on simulations in nanobiology. In between, twenty-five lecturers gave an overview of the field by focusing on aspects such as Electronic structure, Chemistry, Optical properties, Transport, Mechanical properties and Assembly, and Biological applications. The lectures were complemented by two hands-on sessions based on the SIESTA and Quantum-Espresso codes. Four keynote speakers gave the students the perspective from the experimental side. Lecture notes are available on the College web site. In addition, all lectures have been videorecorded and are available at the web site http://www.ictp.tv/eya/smr2145.php

Programme
Venue: Leonardo da Vinci Building Main Lecture Hall, ICTP

17 May 2010

08:30 - 09:45 Registration and Administrative Matters
09:45 - 10:00 Professor Fernando QUEVEDO / ICTP Director
Opening Remarks
10:00 - 11:00 R.M. MARTIN / Univ. of Illinois at Urbana Champaign, USA
Electronic structure: Yesterday, Today and Tomorrow
11:00 - 11:30 --- Coffee/tea break ---
11:30 - 12:30 R. NIEMINEN / Helsinki Univ. of Technology, Espoo, Finland
Computational science as nanotechnology pillar
12:30 - 14:00 --- Lunch break ---
14:00 - 15:00 S. BLUEGEL / Quantum Theory of Materials, IFF, Juelich, Germany
Magnetism at the nanoscale - Part I
15:00 - 16:00 R.M. MARTIN / Univ. of Illinois at Urbana Champaign, USA
Examples of electronic properties DFT and TD-DFT calculations.
Explicit many-body methods.
16:00 - 16:30 --- Coffee/tea break ---
16:30 - 17:30 S. BARONI / SISSA & DEMOCRITOS, Trieste, Italy

Variational principles, the Hellmann-Feynman theorem, density functional theory

18 May 2010

09:00 - 10:00 H. HAKKINEN / Nanoscience Center, Univ. Jyvaskyla, Finland
Stability of metal nanoclusters - shells of atoms and electrons
10:00 - 11:00 G. PACCHIONI / Material Sciences, Univ. Milano-Bicocca, Italy
From supported clusters to nanocatalysis - Part I
11:00 - 11:30 --- Coffee/tea break ---
11:30 - 12:30 F. BESENBACHER / iNANO, Univ. Aarhus, Denmark
Dynamics of nanoclusters on surfaces studied by fast scanning STM
12:30 - 14:00 --- Lunch break ---
14:00 - 15:00 H. HAKKINEN / Nanoscience Center, Univ. Jyvaskyla, Finland
Chemically passivated gold nanoclusters - building blocks of nano-matter?
15:00 - 16:00 G. PACCHIONI / Material Sciences, Univ. Milano-Bicocca, Italy
From supported clusters to nanocatalysis - Part II
16:00 - 16:30 --- Coffee/tea break ---
16:30 - 17:30 R.M. MARTIN / Univ. of Illinois at Urbana Champaign, USA
Calculation of mechanical and electro-mechanical properties of materials.
19:00 - 20:30 Welcome Reception Cafeteria Terrace Leonardo Building

18 May 2010

09:00 - 10:00 E. TOSATTI / SISSA, Trieste, Italy
Metal nanocontacts: Physics, theory, simulation
10:00 - 11:00 D. TOMANEK / Physics & Astronomy, Michigan State Univ, USA
Control and assembly of nanoscale structures
11:00 - 11:30 --- Coffee/tea break ---
11:30 - 12:30 E. TOSATTI / SISSA, Trieste, Italy
Nanofriction: Physics, theory, simulation
12:30 - 14:00 --- Lunch break ---
14:00 - 15:00 D. TOMANEK / Physics & Astronomy, Michigan State Univ., USA
Control and assembly of nanoscale structures - Part II
15:30 - 16:30 (Room: Adriatico Guest House Informatics Laboratories)
P. ORDEJON and J.A. TORRES / CIN2 Barcelona / Univ. Madrid, Spain
SIESTA TUTORIAL
16:30 - 16:45 --- Coffee break ---
16:45 - 18:30 (Room: Adriatico Guest House Informatics Laboratories)
P. ORDEJON and J.A. TORRES / CIN2 Barcelona / Univ. Madrid, Spain
continuation of SIESTA TUTORIAL

19 May 2010

09:00 - 10:00 G. GALLI / Univ. of California at Davis,
Chemistry, CA, USA

Dielectric properties of materials, solids and nanostructures from
first principles - Part I
10:00 - 11:00 R. NIEMINEN / Helsinki Univ. of Technology, Espoo, Finland
Nanostructured carbon and complex oxides
11:00 - 11:30 --- Coffee/tea break ---
11:30 - 12:30 M. STRANO / MIT, Chemical Engg., Cambridge, MA, USA
New concepts in molecular and energy transport within carbon nanotubes:
thermopower waves, stochastically resonant ion channels, and single molecule
biosensors
12:30 - 14:00 --- Lunch break ---
14:00 - 15:00 S. BLUEGEL / Quantum Theory of Materials, IFF, Juelich, Germany
Magnetism at the nanoscale - Part II
15:00 - 16:00 G. GALLI / Univ. California at Davis,
Chemistry, Davis, CA, USA
Dielectric properties of materials, solids and nanostructures
from first principles - Part II
16:00 - 16:30 --- Coffee/tea break ---
16:30 - 17:30 S. BARONI / SISSA & DEMOCRITOS, Trieste, Italy
Response functions and lattice vibrations from density-functional perturbation
theory
17:30 - 18:30 POSTER SESSION

20 May 2010

09:00 - 10:00 M. SCHEFFLER / Theory Department, FHI, Berlin, Germany
Get Real! Multi-scale modeling from first principles of materials
properties and function
10:00 - 11:00 G. PACCHIONI / Material Sciences, Univ. Milano-Bicocca, Italy
From supported clusters to nanocatalysis - Part III
11:00 - 11:30 --- Coffee/tea break ---
11:30 - 12:30 H. HAKKINEN / Nanoscience Center, Univ. Jyvaskyla, Finland
Catalytic properties of nanoscale gold
12:30 - 14:00 --- Lunch break ---
14:00 - 14:10 F. QUEVEDO / ICTP Director
DIRAC MEDAL CEREMONY
Welcome Address
14:10 - 14:30 E. TOSATTI / SISSA, Trieste, Italy
DIRAC MEDAL CEREMONY
Introductory Remarks
14:30 - 15:15 Roberto CAR / Princeton Univ., Princeton, U.S.A.
Dirac Medal
Quantum mechanics in a glass of water
15:15 - 16:00 Michele PARRINELLO / ETH, Zurich, Switzerland
Dirac Medal
Coloring the noise or cheating one's way to quantum effects

23 May 2010

09:00 - 10:00 P. UMARI / DEMOCRITOS, Trieste, Italy
Applications of GW
10:00 - 11:00 S. JOHNSON / MIT, Applied Mathematics, Cambridge, MA, USA
Computational Photonics: Band structures and dispersion relations
11:00 - 11:30 --- Coffee/tea break ---
11:30 - 12:30 R. GEBAUER / ICTP, Trieste, and Democritos, Trieste, Italy
Time-dependent density functional theory and its applications to linear and non-linear optical properties
12:30 - 14:00 --- Lunch break ---
14:00 - 15:00 S. JOHNSON / MIT, Applied Mathematics, Cambridge, MA, USA
Computational Photonics: Cavities and resonant devices
15:00 - 16:00 L. MARTIN-SAMOS / DEMOCRITOS, Trieste, Italy
Theory of GW
16:00 - 16:30 --- Coffee/tea break ---
16:30 - 17:30 M. SCHEFFLER / Theory Department, FHI, Berlin, Germany
At the fifth rung of Jacob's ladder: A discussion of exact exchange plus local- and nonlocal-density approximations to the correlation functional

24 May 2010

09:00 - 10:00 N. MARZARI / MIT, Cambridge, USA and Univ. of Oxford, UK
Electronic-structure and transport in nanostructures based on Wannier functions
10:00 - 11:00 S. JOHNSON / MIT, Applied Mathematics, Cambridge, MA, USA
Computational Photonics: Forces and quantum fluctuations
11:00 - 11:30 --- Coffee/tea break ---
11:30 - 12:30 F. MAURI / IMPMC, Univ. Pierre et Marie Curie, Paris, France
Electric transport in carbon nanotubes and graphene at high field - Parti I
12:30 - 14:00 --- Lunch break ---
14:00 - 15:00 R. GEBAUER / ICTP, Trieste and Democritos, Trieste, Italy
A computationally efficient approach to the computation of TDDFT spectra in complex systems
15:30 - 16:30 (Room: Adriatico Guest House Informatics Laboratories)
R. GEBAUER and P. UMARI / ICTP, Trieste and Democritos, Trieste, Italy
QE TUTORIAL
16:30 - 16:45 --- Coffee/tea break ---
16:45 - 17:45 (Room: Adriatico Guest House Informatics Laboratories)
R. GEBAUER and P. UMARI / ICTP, Trieste and Democritos, Trieste, Italy
continuation of QE TUTORIAL

25 May 2010

09:00 - 10:00 A.-P. JAUHO / DTU Nanotech, Micro-and Nanotechnology,
Lyngby, Denmark
Nanowires and nanopatterned graphene - Computational methods and
physical phenomena - Part I
10:00 - 11:00 F. MAURI / IMPMC, Univ. Pierre et Marie Curie, Paris, France
Electric transport in carbon nanotubes and graphene at high field - Part II
11:00 - 11:30 --- Coffee/tea break ---
11:30 - 12:30 L. VENKATARAMAN / Applied Physics & Mathematics,
Columbia Univ., New York, USA
Electronics and mechanics of single molecule circuits
12:30 - 14:00 --- Lunch break ---
14:00 - 15:00 A.-P. JAUHO / DTU Nanotech, Micro-and Nanotechnology,
Lyngby, Denmark
Nanowires and nanopatterned graphene - Computational methods and
physical phenomena - Part II
15:00 - 16:00 Ph. KIM / Physics, Columbia Univ., New York, USA
Electric transport in carbon nanotubes and graphene
16:00 - 16:30 --- Coffee/tea break ---
16:30 - 17:30 A.-P. JAUHO / DTU Nanotech, Micro-and Nanotechnology,
Lyngby, Denmark
Nanowires and nanopatterned graphene - Computational methods and
physical phenomena - Part I
17:30 - 18:30 Poster Session

26 May 2010

09:00 - 10:00 P. GUMBSCH / Fraunhofer-Institut fuer Werkstoffmechanik
IWM, Freiburg, Germany
Mechanical properties at the nanoscale - Part I (tentative)
10:00 - 11:00 D. FRENKEL / Univ. Cambridge, Chemistry, U.K.
Self-assembly at the nanoscale - Part I (tentative)
11:00 - 11:30 --- Coffee/tea break ---
11:30 - 12:30 G. SCOLES / SISSA, Trieste, Italy
Self-assembly of thiols on the (111) surface of gold: From structure
determination to medical applications
12:30 - 14:00 --- Lunch break ---
14:00 - 15:00 D. FRENKEL / Univ. Cambridge, Chemistry, U.K.
Self-assembly at the nanoscale - Part II (tentative)
15:00 - 16:00 P. GUMBSCH / Fraunhofer-Institut fuer Werkstoffmechanik
IWM, Freiburg, Germany
Mechanical properties at the nanoscale - Part II (tentative)
16:00 - 16:30 --- Coffee/tea break ---
16:30 - 17:30 D. FRENKEL / Univ. Cambridge, Chemistry, U.K.
Self-assembly at the nanoscale - Part III (tentative)
19:00 - 20:15 --- Performance by the Choir of the Trieste Conservatory

"G.Tartini" ---

27 May 2010

09:00 - 10:00 M. VENDRUSCOLO / Univ. Cambridge, Chemistry, U.K.
Computational methods for the determination of protein structure and dynamics - Part I
10:00 - 11:00 D. ESTRIN / CONICET, INQUIMAE, Buenos Aires, Argentina
QM and hybrid QM-MM simulation of biomolecules - Part I
11:00 - 11:30 --- Coffee/tea break ---
11:30 - 12:30 D. ESTRIN / CONICET, INQUIMAE, Buenos Aires, Argentina
QM and hybrid QM-MM simulation of biomolecules - Part II
12:30 - 14:00 --- Lunch break ---
14:00 - 15:00 D. ESTRIN / CONICET, INQUIMAE, Buenos Aires, Argentina
QM and hybrid QM-MM simulation of biomolecules - Part III
15:00 - 16:00 M. VENDRUSCOLO / Univ. Cambridge, Chemistry, U.K.
Computational methods for the determination of protein structure and dynamics - Part II
16:00 - 16:30 --- Coffee/tea break ---
16:30 - 17:30 M. VENDRUSCOLO / Univ. Cambridge, Chemistry, U.K.
Computational methods for the determination of protein structure and dynamics - Part III
17:30 - 18:00 CLOSING REMARKS

The list of participants (total=181 participants), the Abstracts of the poster presentations and the lecture notes of the lecturers are available on the College web site.

4 General Job Announcements

Postdoctoral Position

RMIT University, Melbourne, Australia

"THE ELECTRONIC BEHAVIOUR OF GRAPHENE NANOSTRUCTURES UNDER REALISTIC CONDITIONS"

Ian Snook (RMIT University) and Amanda Barnard (CSIRO)

A postdoctoral research fellowship supported by the Australian Research Council Discovery Grant DP110101362 is available at RMIT University, Melbourne, Australia.

Project Description

This project will use a range of quantum mechanical methods e.g. DFT and DFTB to explore theoretically the effect of heating, electrically charging and of adsorption of molecules on graphene. This will provide an extensive theoretical study of how the important properties of graphene vary with its structure under realistic working conditions. This project is to be carried out in the Applied Physics Department, RMIT University (in downtown Melbourne) and at the CSIRO, Virtual Nanoscience Laboratory, Clayton, Victoria, adjacent to Monash University. Computer facilities for this work are a dedicated 40 processor cluster at RMIT, the VPAC Supercomputer facility in Melbourne and the NCI, Supercomputer Facility in Canberra.

Personal Specification

Applicants should, by the start date, hold a doctoral degree (or equivalent) in chemistry, physics, computational or materials science, or a related discipline and must have demonstrated experience in the use of quantum mechanical density functional theory (DFT). Experience in applying DFT to carbon based or similar nano-structures would be an advantage. They should have a proven track record of publishing in high quality journals and excellent presentation skills, be self-motivated and ready to work with and guide other team members.

More information about this project and details of the position are available from Professor Ian Snook, ian.snook@rmit.edu.au.

The aim is for a start date in early to mid, 2011 and the appointment will be initially for 2 years with possible extension for another year at the end of this time.

5 Abstracts

Rare Earth Monopnictides and Monochalcogenides from First Principles: Towards an Electronic Phase Diagram of Strongly Correlated Materials

L. Petit[1,2], R. Tyer[2], Z. Szotek[2], W.M. Temmerman[2], A. Svane[1]
[1]*Department of Physics and Astronomy, Aarhus University,*
DK-8000 Aarhus C, Denmark
[2]*Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK*

Abstract

We present results of an ab-initio study of the electronic structure of 140 rare earth compounds. Specifically we predict an electronic phase diagram of the entire range of rare earth monopnictides and monochalcogenides, composed of metallic, semiconducting and heavy fermion-like regions, and exhibiting valency transitions brought about by a complex interplay between ligand chemistry and lanthanide contraction. The calculations exploit the combined effect of a first-principles methodology, which can adequately describe the dual character of electrons, itinerant vs. localized, and high throughput computing made possible by the increasing available computational power. Our findings, including the predicted "intermediate valent" compounds SmO and TmSe, are in overall excellent agreement with the available experimental data. The accuracy of the approach, proven e.g. through the lattice parameters calculated to within ∼1.5% of the experimental values, and its ability to describe localization phenomena in solids, makes it a competitive atomistic simulation approach in the search for and design of new materials with specific physical properties and possible technological applications.

(New Journal of Physics **12**, 113041 (2010))

Contact person: leon.petit@stfc.ac.uk

Semiconductor-half metal transition at the Fe_3O_4(001) surface upon hydrogen adsorption

Gareth S. Parkinson[1,2], Narasimham Mulakaluri[3,4],
Yaroslav Losovyj[5], Peter Jacobson[1,2], Rossitza Pentcheva[3], Ulrike Diebold[1,2]
[1]*Department of Physics,*
Tulane University, New Orleans, LA, 70118, USA
[2]*Institute of Applied Physics,*
Vienna University of Technology, Vienna, Austria
[3]*Dept. of Earth and Environmental Sciences,*
University of Munich, Theresienstr. 41, 80333 Munich, Germany
[4]*Fritz-Haber-Institut der Max-Planck-Gesellschaft,*
Faradayweg 4-6, D-14195 Berlin, Germany
[5]*Center for Advanced Microstructures and Devices,*
Louisiana State University,
6980 Jefferson Highway, Baton Rouge, LA 70806, USA

Abstract

The adsorption of H on the magnetite (001) surface was studied with photoemission spectroscopies, scanning tunneling microscopy, and density functional theory. At saturation coverage the insulating $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction is lifted and the surface undergoes a semiconductor - half metal transition. This transition involves subtle changes of the local geometric structure linked to an enrichment of Fe^{2+} cations at the surface. The ability to manipulate the electronic properties by surface engineering has important implications for magnetite based spintronic devices.

(Phy. Rev B. **82**, 125413 (2010))

Contact persons: Rossitza.Pentcheva@lrz.uni-muenchen.de,
mulakaluri.narasimham@lrz.uni-muenchen.de

Parallel solution of partial symmetric eigenvalue problems from electronic structure calculations

Thomas Auckenthaler[1], Volker Blum[2], Hans-Joachim Bungartz[1],
Thomas Huckle[1], Rainer Johanni[3], Lukas Krämer[4],
Bruno Lang[4], Hermann Lederer[3], Paul R. Willems[4]
[1] *Fakultät für Informatik, Technische Universität München,*
D-85748 Garching, Germany
[2] *Fritz-Haber-Institut der Max-Planck-Gesellschaft,*
Faradayweg 4–6, 14195 Berlin, Germany
[3] *Rechenzentrum Garching der Max-Planck-Gesellschaft*
am Max-Planck-Institut für Plasmaphysik,
D-85748 Garching, Germany
[4] *Fachbereich C, Bergische Universität Wuppertal,*
D-42097 Wuppertal, Germany

Abstract

The computation of selected eigenvalues and eigenvectors of a symmetric (Hermitian) matrix is an important subtask in many contexts, for example in electronic structure calculations. If a significant portion of the eigensystem is required then typically direct eigensolvers are used. The central three steps are: Reduce the matrix to tridiagonal form, compute the eigenpairs of the tridiagonal matrix, and transform the eigenvectors back. To better utilize memory hierarchies, the reduction may be effected in two stages: full to banded, and banded to tridiagonal. Then the back transformation of the eigenvectors also involves two stages. For large problems, the eigensystem calculations often are the computational bottleneck, in particular with large numbers of processors. In this paper we discuss variants of the tridiagonal-to-banded back transformation, improving the parallel efficiency for large numbers of processors as well as the per-processor utilization. We also modify the divide-and-conquer algorithm for symmetric tridiagonal matrices such that it can compute a subset of the eigenpairs at reduced cost. The effectiveness of our modifications is demonstrated with numerical experiments.

(Submitted to: Parallel Computing (2010).)

Contact person: Volker Blum (blum@fhi-berlin.mpg.de)

Beyond the Random Phase Approximation for the Electron Correlation Energy: The Importance of Single Excitations

Xinguo Ren, Patrick Rinke, Alexandre Tkatchenko, Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4–6, 14195 Berlin, Germany

Abstract

The random phase approximation (RPA) for the electron correlation energy, combined with the exact-exchange energy, represents the state-of-the-art exchange-correlation functional within density-functional theory (DFT). However, the standard RPA practice – evaluating both the exact-exchange and the RPA correlation energy using local or semilocal Kohn-Sham (KS) orbitals – leads to a systematic underbinding of molecules and solids. Here we demonstrate that this behavior is largely corrected by adding a ”single excitation” (SE) contribution, so far not included in the standard RPA scheme. A similar improvement can also be achieved by replacing the non-self-consistent exact-exchange total energy by the corresponding self-consistent Hartree-Fock total energy, while retaining the RPA correlation energy evaluated using Kohn-Sham orbitals. Both schemes achieve chemical accuracy for a standard benchmark set of non-covalent intermolecular interactions.

(Submitted to: Phys. Rev. Lett. (2010).)

Contact person: Xinguo Ren (ren@fhi-berlin.mpg.de)

Role of Non-Local Correlations for the Cohesive Properties of the Coinage Metals

Lorenz Romaner[1], Xinguo Ren[2], Claudia Ambrosch-Draxl[1], and Matthias Scheffler[2]
[1] *Chair of Atomistic Modeling and Design of Materials, University of Leoben,*
Franz-Josef-Straße 18, A-8700 Leoben, Austria
[2] *Fritz-Haber-Institut der Max-Planck-Gesellschaft,*
Faradayweg 4–6, 14195 Berlin, Germany

Abstract

Cohesion in the coinage metals originates from covalent, metallic, and van der Waals interactions. Density-functional theory in its exact form includes all of them. In practice, however, several popular choices of approximations give rise to substantially different descriptions of the cohesive properties. Using different exchange-correlation functionals, in particular exact-exchange together with the random phase approximation for correlation, and decomposition of the cohesive energy into its parts, we identify non-local correlations as a dominant contribution to cohesion.

(Submitted to: Phys. Rev. Lett. (2010).)

Contact person: Xinguo Ren (ren@fhi-berlin.mpg.de)

6 SCIENTIFIC HIGHLIGHT OF THE MONTH: "First principles calculation of Solid-State NMR parameters"

First principles calculation of Solid-State NMR parameters

Jonathan R. Yates[1], Chris J. Pickard[2], Davide Ceresoli[1]

1- Materials Modelling Laboratory, Department of Materials, University of Oxford, UK

2- Department of Physics, University College London, UK

Abstract

The past decade has seen significant advances in the technique of nuclear magnetic resonance as applied to condensed phase systems. This progress has been driven by the development of sophisticated radio-frequency pulse sequences to manipulate nuclear spins, and by the availability of high-field spectrometers. During this period it has become possible to predict the major NMR observables using periodic first-principles techniques. Such calculations are now widely used in the solid-state NMR community. In this short article we aim to provide an overview of the capability and challenges of solid-state NMR. We summarise the key NMR parameters and how they may be calculated from first principles. Finally we outline the advantages of a joint experimental and computational approach to solid-state NMR.

1 Introduction

Nuclear Magnetic Resonance (NMR) is, as the name implies, a spectroscopy of the nuclei in given material. Some nuclei (eg ^{1}H, ^{13}C, ^{29}Si) are found to posses nuclear spin, and in the presence of a magnetic field exhibit small splittings in their nuclear spin states due to the Zeeman effect. Transitions between these levels are very much smaller than electronic excitations in the system and can be probed with radio-wave frequency pulses. At a first thought this might appear to only provide us with information about the nuclei; however, the precise splitting of the levels is found to be influenced by the surrounding electronic structure. This make NMR a highly sensitive probe of local atomic structure and dynamics.

For the case of a spin 1/2 nucleus the splitting is given by $E = -\gamma \hbar B$ where γ is the gyromagnetic ratio of the nucleus. To give a feel for the numbers involved we take the case of a hydrogen atom (for obvious reasons referred to as a proton by NMR spectroscopists) in the field of a typical NMR spectrometer (9.4 T). The separation of the nuclear spin levels is 2.65x10^{-25}J. At room temperature the ratio of the occupancies of the upper and lower levels as given by Boltzmann statistics is 0.999935. This immediately tells us that NMR is a relatively insensitive technique: we could not hope to see the signal from a single site, rather we observe the signal from an ensemble of sites. With current techniques 10 micro-litres of sample could be sufficient in very favourable conditions, but often sample volumes are of the order of micro-litres. Sensitivity

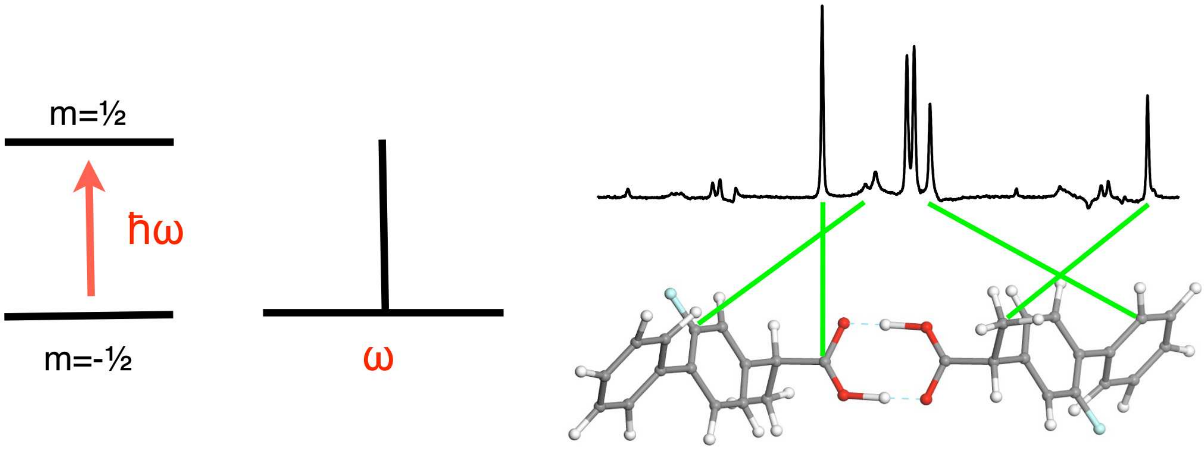

Figure 1: (right) ^{13}C CP-MAS spectrum of a molecular crystal (Flurbiprofen(1)). The effect of magnetic shielding causes nuclei in different chemical environments to resonate at slightly different frequencies

can be increased by using high magnetic fields and choosing nuclei with a large value of γ. The largest commercially available solid-state NMR spectrometers operate at a field of 23.5 T (giving a Larmor frequency for protons of 1 GHz). However, the nuclear constants are dictated by nature and some common isotopes such as ^{12}C or ^{16}O have no net spin, as will any nucleus with an even number of neutrons and protons. In many cases interesting and technologically significant elements have NMR active isotopes which are present in low abundance (eg Oxygen for which the NMR active ^{17}O is present at 0.037%) and/or have small γ (eg ^{47}Ti which has $\gamma(^{47}\mathrm{Ti})=0.06\gamma(^{1}\mathrm{H})$). It is only with the latest techniques and spectrometers that NMR studies on such challenging nuclei has become feasible.

1.1 Solid-State NMR

After its initial development in the 1940's NMR was rapidly adopted in the field of organic chemistry where is it now used as a routine analytic technique, illustrated by the fact that undergraduate students are taught to assign NMR spectra of organic compounds based on empirical rules. Advances in technique have enabled the study of protein structures and other complex bio-molecules. Given its application to such complex systems it may appear surprising that the use of NMR to study solid materials is still a developing research topic, and not yet a routine tool. To appreciate the difference between the solution state techniques of analytical chemistry and solid-state NMR it is important to understand that most interactions in NMR are anisotropic. In a simple way this means that the splitting of the nuclear spin states depend on the orientation of the sample with respect to the applied field. In solution, molecules tumble at a much faster rate than the Larmor frequency of the nuclei (which is typically between 50 and 1000 MHz). This means that nuclei will experience an average magnetic field, giving rise to a well defined transition frequency and sharp spectral lines. For a powdered solid the situation is different; instead of a time average we have an static average over all possible orientations. Rather than the sharp spectral lines observed in the solution-state a static NMR spectrum of a solid material will typically be a broad featureless distribution (see Figure 2). In a sense the problem is that NMR in the solid-state provides too much information. The experimentalist must work hard to remove the effects of these anisotropic interactions in order to obtain useful

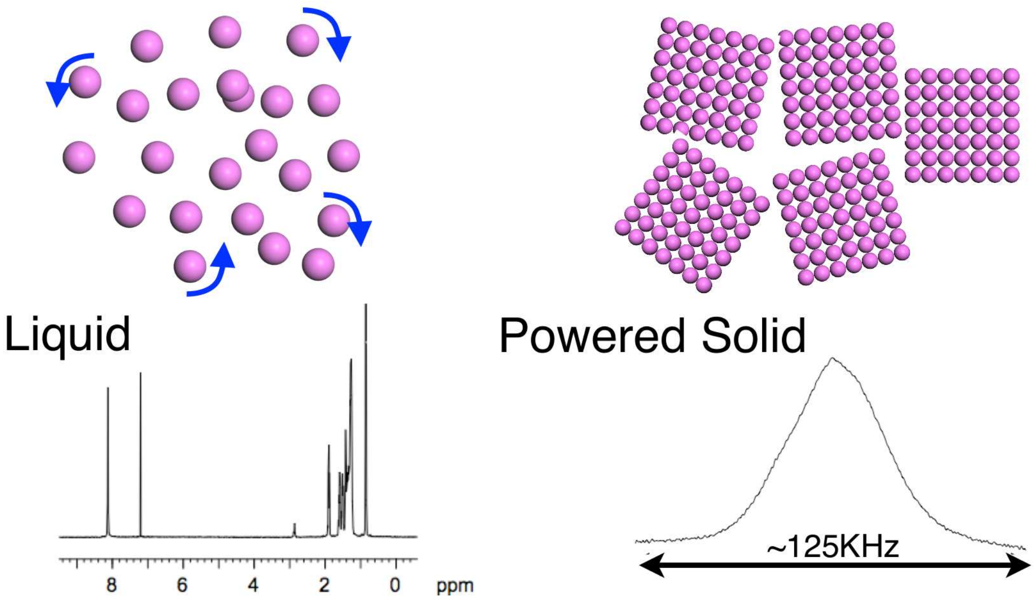

Figure 2: Schematic Representation of the difference between NMR on liquids and powered solids. In a solution the molecules tumble, leading to averaging of anisotropic interactions and sharp spectral lines. In a power the observed spectrum is now a superposition of all possible orientations, and anisotropic interactions lead to a broad spectrum.

information. On the other hand solid-state NMR has the potential to yield far more information than its solution-state counterpart. Anisotropic interactions can be selectively reintroduced into the experiment providing information on the principle components and orientations of the NMR tensors. The most widely used technique to reduce anisotropic broadening is Magic Angle Spinning (MAS). The magic angle, $\theta = 54.7°$, is a root of the second-order Legendre polynomial $(3\cos^2(\theta) - 1)$. For a sample spun in a rotor inclined at a fixed angle to the magnetic field, it can be shown that the anisotropic component of most NMR tensors when averaged over one rotor period, have a contribution which depends on the second-order Legendre polynomial. It follows that if the sample is spun about $\theta = 54.7°$ the anisotropic components will be averaged out (at least to first order). In practise this is achieved through the use of an air spin rotor, spinning speeds of 20kHz are common and the latest techniques allow for samples to be spun at up to 70kHz.

To summarise, a solid-state NMR spectrometer comprises of a superconducting magnet, encased in a large cooling bath (the part that is usually visible). A probe containing the sample is placed in a hole running though the centre of the magnet. The probe contains radio-frequency circuits to irradiate the sample, and also to collect the subsequent radio frequency emissions. In the case of solid-state NMR the probe also contains a device to rotate the sample. The probe may also be capable of heating or cooling the sample. Connected to the probe is a console which houses radio-frequency circuitry, amplifiers, digitisers and other pieces of electronics. To give some sample prices an 'entry level' 400MHz (9.4 T) solid-state NMR spectrometer would currently cost about 350,000 Euros, a more advanced spectrometer (600MHz 14.1 T) about 850,000 Euros, and the highest field spectrometers (1GHz 23.5 T) several millions of Euro.

2 NMR parameters

There are a large number of NMR experiments ranging in complexity from a simple (one-dimensional) spectrum of a spin one-half nucleus such as ^{13}C, to sophisticated multidimensional spectra involving the transfer of magnetism between nuclear sites. All experiments depend on careful excitation, manipulation and detection of the nuclear spins. Several pieces of software have been developed to test NMR excitation sequences and to extract NMR parameters from experimental results (eg SIMPSON(2), Dmfit(3)). The correct language to describe this is that of effective nuclear Hamiltonians (see e.g. (4)). In a conceptual sense a spin Hamiltonian can be obtained from the full crystal Hamiltonian by integrating over all degrees of freedom except for the nuclear spins and external fields. The effect of the electrons and positions of the nuclei are now incorporated into a small number of tensor properties which define the key interactions in NMR. It is these tensors which can be obtained from electronic-structure calculations and we now examine them in turn.

2.1 Magnetic Shielding

The interaction between a magnetic field, **B** and a spin 1/2 nucleus with spin angular momentum $\hbar\mathbf{I}_\mathrm{K}$ is given by

$$H = -\sum_\mathrm{K} \gamma_\mathrm{K} \mathbf{I}_\mathrm{K} \cdot \mathbf{B}. \tag{1}$$

If we consider **B** as the field at the nucleus due to presence of an externally applied field $\mathbf{B}_\mathrm{ext}$ we can express Eqn. 1 as

$$H = -\sum_\mathrm{K} \gamma_\mathrm{K} \mathbf{I}_\mathrm{K} (1 + \overleftrightarrow{\sigma}_\mathrm{k}) \mathbf{B}_\mathrm{ext}. \tag{2}$$

The first term is the interaction of the bare nucleus with the applied field while the second accounts for the response of the electronic structure to the field. The electronic response is characterised by the magnetic shielding tensor $\overleftrightarrow{\sigma}_\mathrm{K}$, which relates the induced field to the applied field

$$\mathbf{B}_\mathrm{in}(\mathbf{R}_\mathrm{K}) = -\overleftrightarrow{\sigma}_\mathrm{K} \mathbf{B}_\mathrm{ext}. \tag{3}$$

In a diamagnet the induced field arises solely from orbital currents $\mathbf{j}(\mathbf{r})$, induced by the applied field

$$\mathbf{B}_\mathrm{in}(\mathbf{r}) = \frac{1}{c} \int d^3r' \mathbf{j}(\mathbf{r}') \times \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3}. \tag{4}$$

The shielding tensor can equivalently be written as a second derivative of the electronic energy of the system

$$\overleftrightarrow{\sigma}_\mathrm{K} = \frac{\partial^2 E}{\partial \mathbf{m}_\mathrm{K} \partial \mathbf{B}} \tag{5}$$

In solution state NMR, or for powdered solids under MAS conditions we are mainly concerned with the isotropic part of the shielding tensor $\sigma_\mathrm{iso} = 1/3Tr[\overleftrightarrow{\sigma}]$. The magnetic shielding results in nuclei in different chemical environments resonating at frequencies that are slightly different to the Larmor frequency of the bare nucleus. Rather than report directly the change in resonant frequency (which would depend of the magnetic field of the spectrometer) a normalised chemical shift is reported in parts per million (ppm)

$$\delta = \frac{\nu_\mathrm{sample} - \nu_\mathrm{ref}}{\nu_\mathrm{ref}} (\times 10^6) \tag{6}$$

where ν_{ref} is the resonance frequency of a standard reference sample. The magnetic shielding and chemical shift are related by

$$\delta = \frac{\sigma_{\mathrm{ref}} - \sigma_{\mathrm{sample}}}{1 - \sigma_{\mathrm{ref}}}. \tag{7}$$

For all but very heavy elements $|\sigma_{\mathrm{ref}}| \ll 1$ and so

$$\delta = \sigma_{\mathrm{ref}} - \sigma_{\mathrm{sample}}. \tag{8}$$

Figure 1 shows a typical ^{13}C spectrum of a molecular crystal obtaining under MAS conditions. The spectrum consists of peaks at several different frequencies corresponding to carbon atoms in different chemical environments. The assignment has been provided by first-principles calculation of the magnetic shielding. Strategies for converting between calculated magnetic shielding and observed chemical shift have been discussed in Ref. (5).

Calculations of magnetic shieldings have been implemented in several local-orbitals quantum chemistry code; see Ref (6) for an overview. For crystalline systems the GIPAW approach for computing magnetic shieldings(7; 8) was initially implemented in the PARATEC code. This is no longer developed but implementations are available in the planewave pseudopotential codes CASTEP(9; 10) and Quantum-Espresso (11). A method using localised Wannier orbitals(12) has been implemented in the planewave CPMD code. The CP2K program has a recent implementation using the Gaussian and Augmented planewave method(13). In all these cases the shieldings are calculated using perturbation theory (linear response). Recently a method which avoids linear response, the so-called 'converse approach', have been developed (see Section3.2.2) and implemented in the Quantum-Espresso package.

2.2 Spin-spin coupling

In the previous section we considered the effect of the magnetic field at a nucleus resulting from an externally applied field. However, there may also be a contribution to the magnetic field at a nucleus arising from the magnetic moments of the other nuclei in the system. In an effective spin Hamiltonian we may associate this spin-spin coupling with a term of the form

$$H = \sum_{\mathrm{K}<\mathrm{L}} \mathbf{I}_{\mathrm{K}}(\mathbf{D}_{\mathrm{KL}} + \mathbf{J}_{\mathrm{KL}})\mathbf{I}_{\mathrm{L}}. \tag{9}$$

$\mathbf{D}_{\mathrm{KL}}$ is the direct dipolar coupling between the two nuclei and is a function of only the nuclear constants and the internuclear distance,

$$\mathrm{D}_{\mathrm{KL}} = -\frac{\hbar}{2\pi}\mu_0 4\pi\gamma_{\mathrm{K}}\gamma_{\mathrm{L}}\frac{3\mathbf{r}_{\mathrm{KL}}\mathbf{r}_{\mathrm{KL}} - \mathbf{1}r_{\mathrm{L}}^2}{r_{\mathrm{KL}}^5} \tag{10}$$

where $\mathbf{r}_{\mathrm{KL}} = \mathbf{R}_{\mathrm{K}} - \mathbf{R}_{\mathrm{L}}$ with $\mathbf{R}_{\mathrm{L}}$ the position of nucleus L. $\mathbf{D}_{\mathrm{KL}}$ is a traceless tensor and its effects will be averaged out under MAS. However, dipolar coupling can be reintroduced to obtain information on spatial proximities of nuclei. $\mathbf{J}_{\mathrm{KL}}$ is the indirect coupling and represents an interaction of nuclear spins mediated by the bonding electrons. J has an isotropic component and in solution-state NMR this leads to multiplet splitting of the resonances, see Figure 3. For light elements J is generally rather small (ie of the order of 100Hz for directly bonded carbon atoms, and often below 10Hz for atoms separated by more than one bond). This is less than the typical solid-state linewidth and so it is only with the very latest advances in experimental technique such as accurate setting of the magic angle, very high spinning speeds together with the

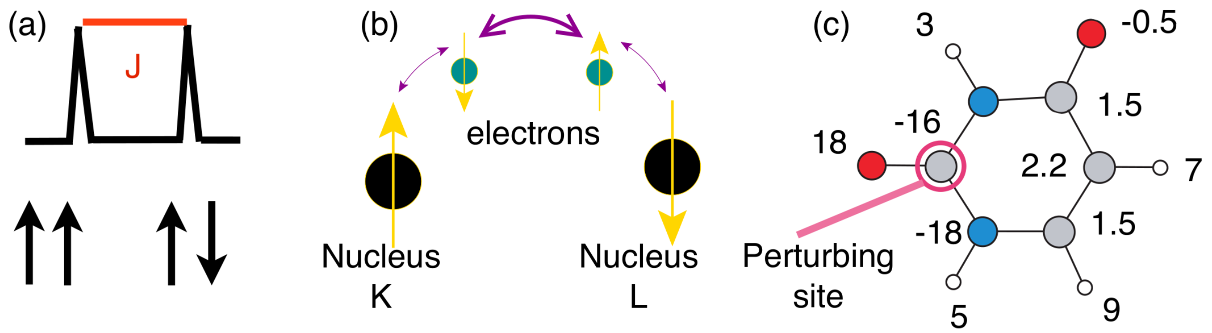

Figure 3: (a) Schematic representation of the effect of J coupling of two spin 1/2 nuclei on an NMR resonance. The peak is split by amount corresponding to the energy different between the spins being aligned parallel and antiparallel. (b) Schematic representation of the mechanism of transfer of J between nuclei. (c) Values of the J coupling (Hz) in Uracil (^{1}H- white, ^{13}C - grey, ^{15}N - blue, ^{17}O - red)

availability of high-field spectrometers that is has become possible to measure small J couplings (see Ref.(14) for a recent summary). Highlights have included the observation of two J couplings between a given spin pair(15), the measurement of distributions of J in amorphous materials(16), and reports of J as low as 1.5Hz(17)

The J-coupling is a small perturbation to the electronic ground-state of the system and we can identify it as a derivative of the total energy E, of the system

$$\mathbf{J}_{\mathrm{KL}} = \frac{\hbar\gamma_{\mathrm{K}}\gamma_{\mathrm{L}}}{2\pi}\frac{\partial^2 E}{\partial \mathbf{m}_{\mathrm{K}}\partial \mathbf{m}_{\mathrm{L}}} \tag{11}$$

An equivalent expression arises from considering one nuclear spin (L) as perturbation which creates a magnetic field at a second (receiving) nucleus (K)

$$\mathbf{B}^{(1)}_{\mathrm{in}}(\mathbf{R}_{\mathrm{K}}) = \frac{2\pi}{\hbar\gamma_{\mathrm{K}}\gamma_{\mathrm{L}}}\mathbf{J}_{\mathrm{KL}}\cdot\mathbf{m}_{\mathrm{L}}. \tag{12}$$

Eqn. 12 tells us that the question of computing J is essentially that of computing the magnetic field induced indirectly by a nuclear magnetic moment. The first complete analysis of this indirect coupling was provided by Ramsey(18; 19). When spin-orbit coupling is neglected we can consider the field as arising from two, essentially independent, mechanisms. Firstly, the magnetic moment can interact with electronic charge inducing an orbital current $\mathbf{j}(\mathbf{r})$, which in turn creates a magnetic field at the other nuclei in the system. This mechanism is similar to the case of magnetic shielding in insulators. The second mechanism arises from the interaction of the magnetic moment with the electronic spin, causing an electronic spin polarisation. The relavant terms in the electronic Hamiltonian are the Fermi-contact (FC),

$$\mathrm{H}_{\mathrm{FC}} = g\beta\frac{\mu_0}{4\pi}\frac{8\pi}{3}\mathbf{S}\cdot\boldsymbol{\mu}_{\mathrm{L}}\,\delta(\mathbf{r}_{\mathrm{L}}), \tag{13}$$

and the spin-dipolar (SD),

$$\mathrm{H}_{\mathrm{SD}} = g\beta\frac{\mu_0}{4\pi}\mathbf{S}\cdot\left(\frac{3\mathbf{r}_{\mathrm{L}}(\boldsymbol{\mu}_{\mathrm{L}}\cdot\mathbf{r}_{\mathrm{L}}) - r_{\mathrm{L}}^2\boldsymbol{\mu}_{\mathrm{L}}\mathbf{1}}{|r_{\mathrm{L}}|^5}\right). \tag{14}$$

Here $\mathbf{r}_{\mathrm{L}} = \mathbf{r} - \mathbf{R}_{\mathrm{L}}$ with $\mathbf{R}_{\mathrm{L}}$ the position of nucleus L, μ_0 is the permeability of a vacuum, δ is the Dirac delta function, $\mathbf{S}$ is the Pauli spin operator, g the Lande g-factor and β is the Bohr magneton. The resulting spin density $\mathbf{m}(\mathbf{r})$ creates a magnetic field through a second hyperfine interaction. By working to first order in these quantities we can write the magnetic field at atom K induced by the magnetic moment of atom L as

$$\begin{aligned}\mathbf{B}_{\text{in}}^{(1)}(\mathbf{R}_{\text{K}}) &= \frac{\mu_0}{4\pi}\int \mathbf{m}^{(1)}(\mathbf{r})\cdot\left[\frac{3\mathbf{r}_{\text{K}}\mathbf{r}_{\text{K}}-|\mathbf{r}_{\text{K}}|^2}{|\mathbf{r}_{\text{K}}|^5}\right]\mathrm{d}^3\mathbf{r}\\ &+ \frac{\mu_0}{4\pi}\frac{8\pi}{3}\int \mathbf{m}^{(1)}(\mathbf{r})\delta(\mathbf{r}_{\text{K}})\,\mathrm{d}^3\mathbf{r}\\ &+ \frac{\mu_0}{4\pi}\int \mathbf{j}^{(1)}(\mathbf{r})\times\frac{\mathbf{r}_{\text{K}}}{|\mathbf{r}_{\text{K}}|^3}\,\mathrm{d}^3\mathbf{r}.\end{aligned} \tag{15}$$

Several quantum chemistry packages provide the ability to compute J coupling tensors in molecular systems (see Ref. (20) for a review of methods). An approach to compute J tensors within the planewave-pseudopotential approach has recently been developed(21). Some examples are discussed in Section 4.3, and a review of applications is provided in Ref. (22).

2.3 Electric Field Gradients

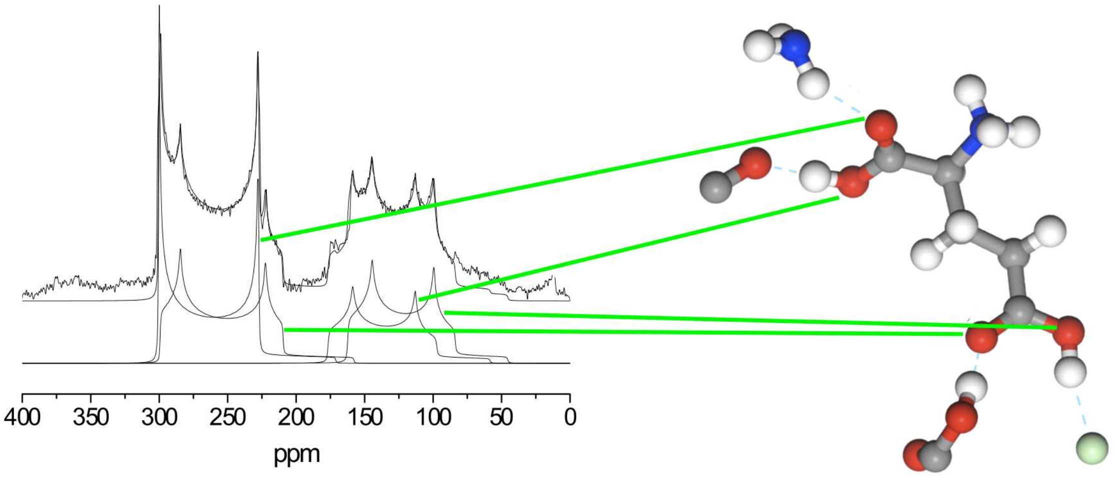

Figure 4: ^{17}O NMR spectrum of Glutamic acid obtained using MAS. The upper trace is the observed spectrum, below is the deconvolution into four quadrupolar line-shapes. The assignment to crystallographic sites is provided by first principles calculation(23)

For a nucleus with spin >1/2 the NMR response will include an interaction between the quadrupole moment of the nucleus, Q, and the electric field gradient (EFG) generated by the surrounding electronic structure. The EFG is a second rank, symmetric, traceless tensor $G(\mathbf{r})$ given by

$$G_{\alpha\beta}(\mathbf{r}) = \frac{\partial E_\alpha(\mathbf{r})}{\partial r_\beta} - \frac{1}{3}\delta_{\alpha\beta}\sum_\gamma \frac{\partial E_\gamma(\mathbf{r})}{\partial r_\gamma} \tag{16}$$

where α, β, γ denote the Cartesian coordinates x,y,z and $E_\alpha(\mathbf{r})$ is the local electric field at the position $\mathbf{r}$, which can be calculated from the charge density $n(\mathbf{r})$:

$$E_\alpha(\mathbf{r}) = \int d^3r \frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|^3}(r_\alpha - r'_\alpha). \tag{17}$$

The EFG tensor is then equal to

$$G_{\alpha\beta}(\mathbf{r}) = \int d^3r \frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|^3}\left[\delta_{\alpha\beta} - 3\frac{(r_\alpha - r'_\alpha)(r_\beta - r'_\beta)}{|\mathbf{r}-\mathbf{r}'|^2}\right]. \tag{18}$$

The computation of electric field gradient tensors is less demanding than either shielding or J-coupling tensors as it requires only knowledge of the electronic ground state. The LAPW approach in its implementation within the Wien series of codes(24) has been widely used and shown to reliably predict Electric Field Gradient (EFG) tensors(25). The equivalent formalism for the planewave/PAW approach is reported in Ref. (26).

The quadrupolar coupling constant, C_Q and the asymmetry parameter, η_Q can be obtained from the the diagonalized electric field gradient tensor whose eigenvalues are labelled V_{xx}, V_{yy}, V_{zz}, such that $|V_{zz}| > |V_{yy}| > |V_{xx}|$:

$$C_Q = \frac{eV_{zz}Q}{h}, \tag{19}$$

where h is Planck's constant and

$$\eta_Q = \frac{V_{xx} - V_{yy}}{V_{zz}}. \tag{20}$$

The effect of quadrupolar coupling is not completely removed under MAS, leading to lineshapes which can be very broad. Figure 4 shows a typical MAS spectrum for a spin 3/2 nucleus. The width of each peak is related to C_Q and the shape to η_Q. See Ref. (27) for recent review of NMR techniques for quadrupolar nuclei.

2.4 Paramagnetic Coupling

If a material contains an unpaired electron then this net electronic spin can create an additional magnetic field at a nucleus via Fermi contact and spin-dipolar mechanisms. Paramagnetism introduces several difficulties from the point of view of solid-state NMR, for example the resonances can exhibit significant broadening. However, NMR has been used to analyse local magnetic interactions, for example in manganites(28) and lithium battery materials(29). There are several reports of calculations of NMR parameters in paramagnetic systems for example paramagnetic shifts of ^{6}Li(30) and EFGs of layered vanadium phosphates(31). However, to the best of our knowledge, unlike the case of paramagnetic molecules(32) there is currently no methodology to predict all of the relavant interactions in paramagnetic solids at a consistent computational level.

In metallic systems the electronic spin also plays an important role as the external field will create a net spin density (Pauli susceptibility) which will in turn create a magnetic field at the nucleus. This additional contribution to the magnetic shielding is known as the Knight shift. The linear-response GIPAW approach has been extended(33) to compute the magnetic shielding and Knight-shift in metallic systems, although there have been few applications to date.

3 A first principles approach

In order to have a scheme for computing solid-state NMR properties with the planewave-pseudopotential implementation of DFT there are two major challenges. Firstly, how to deal with the fact that the pseudo-wavefunction does not have the correct nodal structure in the region of interest, ie the nucleus. Secondly, how to compute the response of the system to an applied field. We examine these in turn.

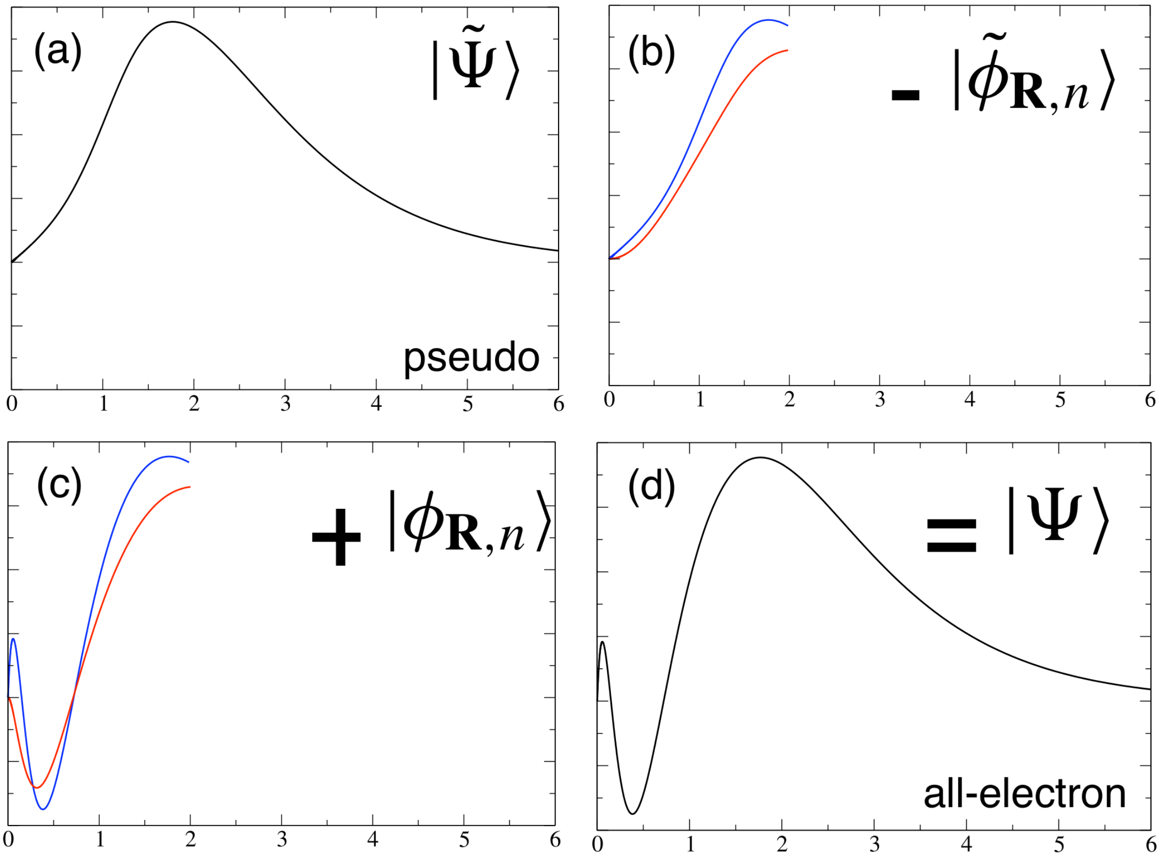

Figure 5: Schematic representation of the PAW transformation in Eqn. 21 using two projectors. The x-axis represents radial distance from a nucleus. (a) representation of the pseudowavefunction (b) two pseudo-atomic like states (c) two corresponding all-electron atomic-like states (d) all-electron wavefunction.

3.1 Pseudopotentials

The combination of pseudopotentials and a planewave basis has proved to give a reliable description of many material properties, such as vibrational spectra and dielectric response(10; 34), but properties which depend critically on the wavefunction close to the nucleus, such as NMR tensors require careful treatment. The now standard approach to computing such properties is the projector augmented wave method (PAW) introduced by Blöchl(35) which provides a formalism to reconstruct the all-electron wavefunction from its pseudo counterpart, and hence obtain all-electron properties from calculations based on the use of pseudopotentials.

The PAW scheme proposes a linear transformation from the pseudo-wavefunction $|\tilde{\Psi}\rangle$, to the true all-electron wavefunction $|\Psi\rangle$, ie $|\Psi\rangle = \mathbf{T}|\tilde{\Psi}\rangle$, where

$$\mathbf{T} = \mathbf{1} + \sum_{\mathbf{R},n} [|\phi_{\mathbf{R},n}\rangle - |\tilde{\phi}_{\mathbf{R},n}\rangle] \langle \tilde{p}_{\mathbf{R},n}| \tag{21}$$

$|\phi_{\mathbf{R},n}\rangle$ is a localised atomic state (say 3p) and $|\widetilde{\phi}_{\mathbf{R},n}\rangle$ is its pseudized counter part. $|\widetilde{p}_{\mathbf{R},n}\rangle$ are a set of functions which project out the atomic like contributions from $|\tilde{\Psi}\rangle$. This equation is represented pictorially in Figure 5. For an all-electron local or semi-local operator O, the corresponding pseudo-operator, $\widetilde{O}$, is given by

$$\widetilde{O} = O + \sum_{\mathbf{R},n,m} |\widetilde{p}_{\mathbf{R},n}\rangle \left[\langle \phi_{\mathbf{R},n}|O|\phi_{\mathbf{R},m}\rangle - \langle \widetilde{\phi}_{\mathbf{R},n}|O|\widetilde{\phi}_{\mathbf{R},m}\rangle \right] \langle \widetilde{p}_{\mathbf{R},m}|. \tag{22}$$

As constructed in Eqn. 22 the pseudo-operator $\widetilde{O}$ acting on pseudo-wavefunctions will give the same matrix elements as the all-electron operator O acting on all-electron wavefunctions. Pseudo operators for the operators relavant for magnetic shielding are reported in Ref. (7; 8), for electric field gradients in Ref. (26) and for J coupling in Ref. (21). Pseudo-operators for magnetic shielding including relativistic effects at the ZORA level are given in Ref. (36)

For a system under a uniform magnetic field PAW alone is not a computationally realistic solution. In a uniform magnetic field a rigid translation of all the atoms in the system by a vector $\mathbf{t}$ causes the wavefunctions to pick up an additional field dependent phase factor, which can we written as, using the symmetric gauge for the vector potential, $\mathbf{A}(\mathbf{r}) = 1/2\mathbf{B} \times \mathbf{r}$,

$$\langle \mathbf{r}|\Psi'_n\rangle = e^{\frac{i}{2c}\mathbf{r}\cdot\mathbf{t}\times\mathbf{B}}\langle \mathbf{r}-\mathbf{t}|\Psi_n\rangle. \tag{23}$$

In short Eqn. 22 will require a large number of projectors to describe the oscillations in the wavefunctions due to this phase. In using a set of localized functions we have introduced the gauge-origin problem well known in quantum chemical calculations of magnetic shieldings(6). To address this problem Pickard and Mauri introduced a field dependent transformation operator $\mathcal{T}_{\mathbf{B}}$, which, by construction, imposes the translational invariance exactly:

$$\mathcal{T}_{\mathbf{B}} = \mathbf{1} + \sum_{\mathbf{R},n} e^{\frac{i}{2c}\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}[|\phi_{\mathbf{R},n}\rangle - |\tilde{\phi}_{\mathbf{R},n}\rangle]\langle\tilde{p}_{\mathbf{R},n}|e^{-\frac{i}{2c}\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}. \tag{24}$$

The resulting approach is known as the Gauge Including Projector Augmented Wave (GIPAW) method.

(GI)PAW techniques allow us to reconstruct the valence wavefunction in the core region, however the pseudopotential approach is usually coupled with a frozen-core approximation. A careful study of all-electron calculations on small molecules(37) has shown that this is a valid approximation for the calculation of magnetic shielding; the contribution of the core electrons to the magnetic shielding is not chemically sensitive and can be computed from a calculation on a free atom. Figure 6 shows shieldings computed using pseudopotentials and the GIPAW scheme, together with large Gaussian basis-set quantum-chemical calculations. For shieldings in these isolated molecules the agreement is essentially perfect. However, in practise it is not alway straight forward to partition states into core and valence. This is highlighted by the calculation of electric field gradients in 3d and 4d elements such as V and Nb. Here a major contribution to the electric field gradient arises from the small distortion of the highest occupied p states, and it is essential to include these states as valence for accurate NMR parameters (2p for V, 3p for Nb). The use of ultrasoft potentials has proved to be essential to constructing efficient pseudopotentials with these semi-core state in valence. Figure 6 shows the comparison of pseudopotential+PAW calculations with those using the Wien2k code(38). The agreement between the two approaches is very good. Other examples include the study of ^{95}Mo NMR parameters.(39)

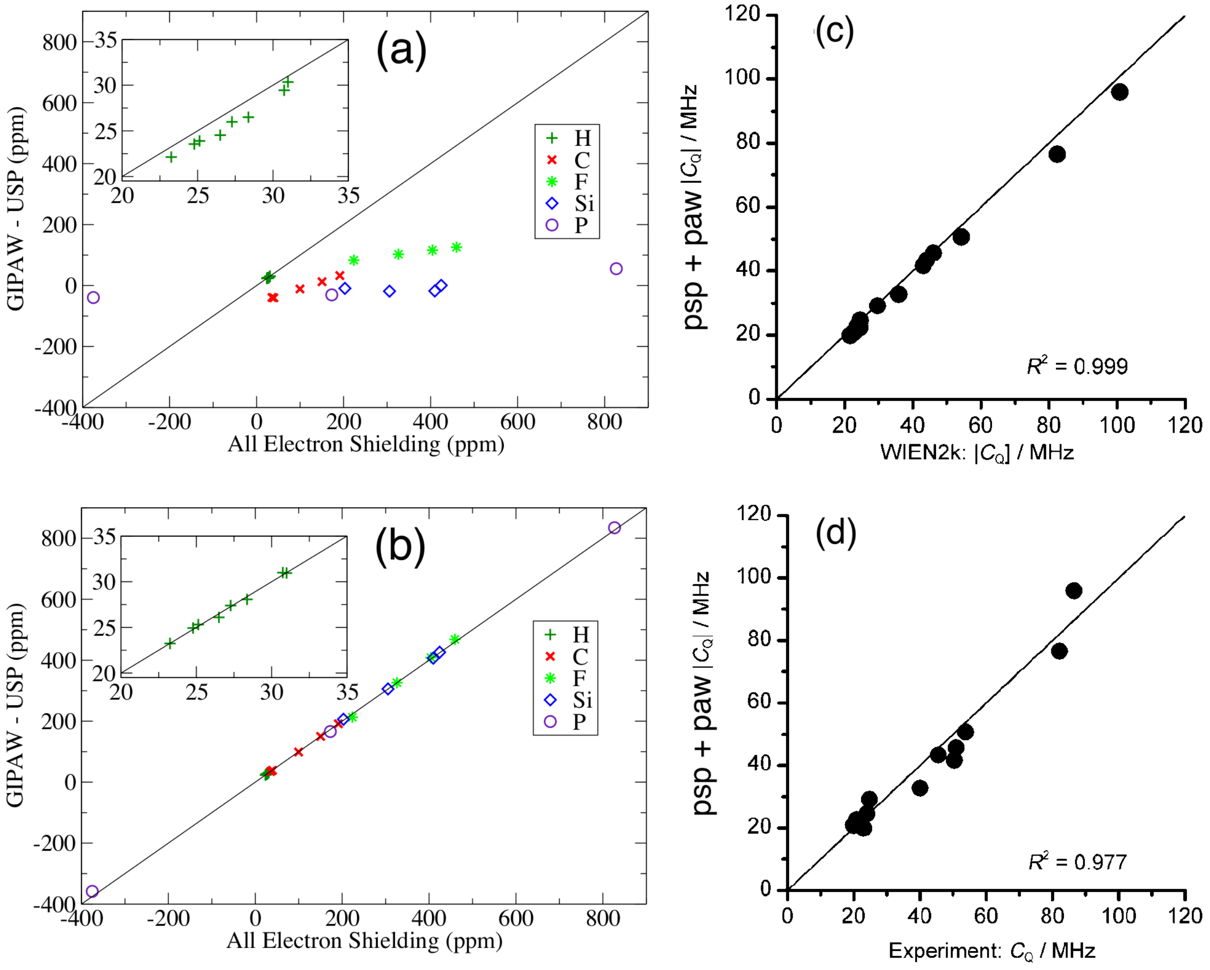

Figure 6: Comparison of all-electron and pseudopotential (with frozen core) calculations of NMR parameters. (a) Comparison of chemical shieldings for a range of small molecules computed using Guassian basis sets and those from pseudopotential calculations without the GIPAW augmentation (b) as previous but using the GIPAW augmentation (c) Comparison of ^{93}Nb Quadrupolar Couplings computed using peudopotentials and PAW with results from an LAPW+lo code (d) Results from previous as compared to experiment

3.2 Magnetic Response

3.2.1 Linear Response

As discussed in Section 2 one route to obtaining the magnetic shielding is to compute the induced orbital current, $\mathbf{j}^{(1)}(\mathbf{r})$ using perturbation theory,

$$\mathbf{j}^{(1)}(\mathbf{r}') = 4\sum_{o} Re\left[\langle\Psi_o^{(0)}|\mathbf{J}^{\mathrm{p}}(\mathbf{r}')|\Psi_o^{(1)}\rangle\right] + 2\sum_{o}\langle\Psi_o^{(0)}|\mathbf{J}^{\mathrm{d}}(\mathbf{r}')|\Psi_o^{(0)}\rangle. \tag{25}$$

The current operator, $\mathbf{J}(\mathbf{r}')$ is obtained from the quantum mechanical probability current, replacing linear with canonical momentum. It can be written as the sum of diamagnetic and paramagnetic terms,

$$\begin{aligned}
\mathbf{J}(\mathbf{r}') &= \mathbf{J}^{\mathrm{d}}(\mathbf{r}') + \mathbf{J}^{\mathrm{p}}(\mathbf{r}'), && (26)\\
\mathbf{J}^{\mathrm{d}}(\mathbf{r}') &= \frac{1}{c}\mathbf{A}(\mathbf{r}')|\mathbf{r}'\rangle\langle\mathbf{r}'|, && (27)\\
\mathbf{J}^{\mathrm{p}}(\mathbf{r}') &= -\frac{\mathbf{p}|\mathbf{r}'\rangle\langle\mathbf{r}'| + |\mathbf{r}'\rangle\langle\mathbf{r}'|\mathbf{p}}{2}. && (28)
\end{aligned}$$

The first-order change in the wavefunction $|\Psi_o^{(1)}\rangle$, is given by

$$|\Psi_o^{(1)}\rangle = \sum_e \frac{|\Psi_e^{(0)}\rangle\langle\Psi_e^{(0)}|}{\varepsilon - \varepsilon_e} H^{(1)}|\Psi_o^{(0)}\rangle = \mathcal{G}(\varepsilon_o^{(0)}) H^{(1)}|\Psi_o^{(0)}\rangle, \tag{29}$$

where $H^{(1)} = \mathbf{p}\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{p}$. Using the symmetric gauge for the vector potential, $\mathbf{A}(\mathbf{r}) = (1/2)\mathbf{B}\times\mathbf{r}$, we arrive at the following expression for the induced current,

$$\mathbf{j}^{(1)}(\mathbf{r}') = 4\sum_o \mathrm{Re}\left[\langle\Psi_o^{(0)}|\mathbf{J}^{\mathrm{p}}(\mathbf{r}')\mathcal{G}(\varepsilon_o^{(0)})\mathbf{r}\times\mathbf{p}|\Psi_o^{(0)}\rangle\right] - \frac{1}{2c}\rho(\mathbf{r}')\mathbf{B}\times\mathbf{r}' \tag{30}$$

where $\rho(\mathbf{r}') = 2\sum_o \langle\Psi_o^{(0)}|\mathbf{r}'\rangle\langle\mathbf{r}'|\Psi_o^{(0)}\rangle$. For a finite system there is in principle no problem in computing the induced current directly from Eqn. 30. However, for an extended system there is an obvious problem with the second (diamagnetic) term of Eqn. 30; the presence of the position operator $\mathbf{r}$ will generate a large contribution far away from $\mathbf{r} = 0$, and the term will diverge in an infinite system. The situation is saved by recognising that an equal but opposite divergence occurs in the first (paramagnetic) term of Eqn. 30, and so only the sum of the two terms is well defined. Through the use of a sum-rule(7; 8; 40) we arrive at an alternative expression for the current

$$\mathbf{j}^{(1)}(\mathbf{r}') = 4\sum_o \mathrm{Re}\left[\langle\Psi_o^{(0)}|\mathbf{J}^{\mathrm{p}}(\mathbf{r}')\mathcal{G}(\varepsilon_o^{(0)})(\mathbf{r}-\mathbf{r}')\times\mathbf{p}|\Psi_o^{(0)}\rangle\right]. \tag{31}$$

In an insulator the Green function $\mathcal{G}(\varepsilon_o^{(0)})$ is localized and so $\mathbf{j}^{(1)}(\mathbf{r}')$ remains finite at large values of $(\mathbf{r}-\mathbf{r}')$. At this point there still remains the question of the practical computation of the current, which for reasons of efficiency it is desirable to work with just the cell periodic part of the Bloch function. Eqn. 31 is not suitable for such a calculation as the position operator cannot be expressed as a cell periodic function. One solution to this problem(40) is to consider the response to a magnetic field with a finite wavelength i.e. $\mathbf{B} = sin(\mathbf{q}\cdot\mathbf{r})\hat{\mathbf{q}}$. In the limit that $q \rightarrow 0$ the uniform field result is recovered. For a practical calculation this enables one to work with cell periodic functions, at the cost that a calculation at a point in the Brillouin Zone $\mathbf{k}$ will require knowledge of the wavefunctions at $\mathbf{k}\pm\mathbf{q}$ (ie six extra calculations for the full tensors for all atomic sites). A complete derivation was presented in Refs. (7; 40) leading to the final result for the current,

$$\mathbf{j}^{(1)}(\mathbf{r}') = \lim_{q\rightarrow 0}\frac{1}{2q}\left[\mathbf{S}(\mathbf{r}',q) - \mathbf{S}(\mathbf{r}',-q)\right] \tag{32}$$

where

$$\mathbf{S}(\mathbf{r}',q) = \frac{2}{cN_{\mathrm{k}}}\sum_{i=x,y,z}\sum_{o,\mathbf{k}}\mathrm{Re}\left[\frac{1}{i}\langle u_{o,\mathbf{k}}^{(0)}|\mathbf{J}^{\mathrm{p}}_{\mathbf{k},\mathbf{k}+\mathbf{q}_i}(\mathbf{r}')\mathcal{G}_{\mathbf{k}+\mathbf{q}_i}(\varepsilon_{o,\mathbf{k}})\mathbf{B}\times\hat{\mathbf{u}}_i\cdot(\mathbf{p}+\mathbf{k})|\bar{u}_{o,\mathbf{k}}^{(0)}\rangle\right],$$

$\mathbf{q}_i = q\hat{\mathbf{u}}_i$, N_{k} is the number of $\mathbf{k}$-points included in the summation and

$$\mathbf{J}^{\mathrm{p}}_{\mathbf{k},\mathbf{k}+\mathbf{q}_i} = -\frac{(\mathbf{p}+\mathbf{k})|\mathbf{r}'\rangle\langle\mathbf{r}'| + |\mathbf{r}'\rangle\langle\mathbf{r}'|(\mathbf{p}+\mathbf{k}+\mathbf{q}_i)}{2}. \tag{33}$$

Equivalent expressions valid when using separable norm-conserving pseudopotentials are given in Ref. (7), and for ultrasoft potentials in Ref. (8).

3.2.2 Converse Approach

The problem of computing NMR shielding tensors can be reformulated so that the need for a linear-response framework is circumvented. In this way the NMR shifts are obtained from the macroscopic magnetization induced by magnetic point dipoles placed at the nuclear sites of interest. This method shall be referred to as *converse* (41; 42) as opposed to *direct* approaches, based on linear-response, in which a magnetic field is applied and the induced field at the nucleus is computed.

The converse approach is made possible by the recent developments that have led to the *Modern Theory of Orbital Magnetization* (43–47), which provides an explicit quantum-mechanical expression for the orbital magnetization of periodic systems in terms of the Bloch wave functions and Hamiltonian, in absence of any external magnetic field.

The converse and linear response approaches should give the same shielding tensors if the same electronic structure method is used (eg the LDA). The main advantage of the converse approach is that it can be coupled easily to advanced electronic structure methods and situations where a linear-response formulation is cumbersome or unfeasible. For example in the case of DFT+U (48) or hybrid functionals, the converse method should provide a convenient shortcut from the point of view of program coding. It is possible that in the case of high-level correlated approaches like multi-configuration (49; 50) and quantum Monte Carlo, the converse method will also provide a convenient route to calculate NMR chemical shifts.

Let us start by considering a sample to which a constant external magnetic field $\boldsymbol{B}^{\text{ext}}$ is applied. The field induces a current that, in turn, induces a magnetic field $\boldsymbol{B}^{\text{ind}}(\boldsymbol{r})$ such that the total magnetic field is $\boldsymbol{B}(\boldsymbol{r}) = \boldsymbol{B}^{\text{ext}} + \boldsymbol{B}^{\text{ind}}(\boldsymbol{r})$. In NMR experiments the applied fields are small compared to the typical electronic scales; the absolute chemical shielding tensor $\overleftrightarrow{\sigma}$ is then defined via the linear relationship

$$\boldsymbol{B}^{\text{ind}}_s = -\overleftrightarrow{\sigma}_s \cdot \boldsymbol{B}^{\text{ext}}, \quad \sigma_{s,\alpha\beta} = -\frac{\partial B^{\text{ind}}_{s,\alpha}}{\partial B^{\text{ext}}_{\beta}}. \tag{34}$$

The index s indicates that the corresponding quantity is to be taken at position $\boldsymbol{r}_s$, i.e., the site of nucleus s.

Instead of determining the current response to a magnetic field, we derive chemical shifts from the orbital magnetization induced by a magnetic dipole. Using $B_{s,\alpha} = B^{\text{ext}}_{\alpha} + B^{\text{ind}}_{s,\alpha}$, Eq. (34) becomes $\delta_{\alpha\beta} - \sigma_{s,\alpha\beta} = \partial B_{s,\alpha}/\partial B^{\text{ext}}_{\beta}$. The numerator may be written as $B_{s,\alpha} = -\partial E/\partial m_{s,\alpha}$, where E is the energy of a virtual magnetic dipole $\boldsymbol{m}_s$ at the nuclear position $\boldsymbol{r}_s$ in the field $\boldsymbol{B}$. Then, writing the macroscopic magnetization as $M_\beta = -\Omega^{-1}\,\partial E/\partial B_\beta$ (where Ω is the cell volume), we obtain

$$\delta_{\alpha\beta} - \sigma_{s,\alpha\beta} = -\frac{\partial}{\partial B_\beta}\frac{\partial E}{\partial m_{s,\alpha}} = -\frac{\partial}{\partial m_{s,\alpha}}\frac{\partial E}{\partial B_\beta} = \Omega\frac{\partial M_\beta}{\partial m_{s,\alpha}}\;. \tag{35}$$

Thus, $\overleftrightarrow{\sigma}_s$ accounts for the shielding contribution to the macroscopic magnetization induced by a magnetic point dipole $\boldsymbol{m}_s$ sitting at nucleus $\boldsymbol{r}_s$ and all of its periodic replicas. In other words, instead of applying a constant (or long-wavelength) field $\boldsymbol{B}^{\text{ext}}$ to an infinite periodic system and calculating the induced field at all equivalent nuclei s, we apply an infinite array of magnetic dipoles to all equivalent sites s and calculate the change in orbital magnetization (47). Since the perturbation is now periodic, it can easily be computed using finite differences of ground-state calculations. Note that $\boldsymbol{M} = \boldsymbol{m}_s/\Omega + \boldsymbol{M}^{\text{ind}}$, where the first term is present merely because we have included magnetic dipoles by hand. It follows that the shielding is related to the true induced magnetization via $\sigma_{s,\alpha\beta} = -\Omega\,\partial M^{\text{ind}}_{\beta}/\partial m_{s,\alpha}$.

In order to calculate the shielding tensor of nucleus s using eq. (35), it is necessary to calculate the induced orbital magnetization due to the presence of an array of point magnetic dipoles $\boldsymbol{m}_s$ at all equivalent sites $\boldsymbol{r}_s$. The vector potential of a single dipole in Gaussian units is given by

$$\boldsymbol{A}_s(\boldsymbol{r}) = \frac{\boldsymbol{m}_s \times (\boldsymbol{r} - \boldsymbol{r}_s)}{|\boldsymbol{r} - \boldsymbol{r}_s|^3}. \tag{36}$$

For an array of magnetic dipoles $\boldsymbol{A}(\boldsymbol{r}) = \sum_{\boldsymbol{R}} \boldsymbol{A}_s(\boldsymbol{r} - \boldsymbol{R})$, where $\boldsymbol{R}$ is a lattice vector. Since $\boldsymbol{A}$ is periodic, the average of its magnetic field $\nabla \times \boldsymbol{A}$ over the unit cell vanishes; thus, the eigenstates of the Hamiltonian remain Bloch-representable. The periodic vector potential $\boldsymbol{A}(\boldsymbol{r})$ can now be included in the Hamiltonian with the usual substitution for the momentum operator $\boldsymbol{p} \rightarrow \boldsymbol{p} - \frac{e}{c}\boldsymbol{A}$, where m_e is the electronic mass and c is the speed of light. Because of the lattice periodicity of the vector potential, the magnetic dipole interacts with all its images in neighboring cells. However, due to the $1/r^3$ decay of the dipole-dipole interaction, the chemical shifts are found to converge very fast with respect to super-cell size.

In practice, we can calculate the full shielding tensor by performing three SCF ground state calculations. In each SCF calculation, we place a virtual magnetic dipole $\boldsymbol{m}_s$ (eq. (36)) aligned along one of the Cartesian directions and we calculate the resulting change in orbital magnetization.

The main disadvantage of the converse method is requires a set of three calculations for every atom we are interested in, as opposed to linear-response, which yield all the shielding tensors at once. This disadvantage can be partly mitigated by distributing every set of calculations on a large number of CPUs and machines. Of course, if we are interested on in a subset of atomic sites or atomic species, the converse method can be efficient as the linear-response approach.

In the case of a pseudopotential code the situation is complicated due to nonlocal projectors usually used in the Kleinman-Bylander separable form. However, by using the GIPAW formalism, the converse method has recently been generalized such that it can be used in conjunction with norm-conserving, non-local pseudopotentials, to calculate the NMR chemical shifts (51) and the EPR g-tensor (52).

The converse method has been recently implemented in Quantum-Espresso (11), VASP (53) and ADF-BAND (54).

4 Uses of Computations

4.1 NMR Crystallography

Diffraction based techniques are the traditional route to obtaining information on the structure of crystalline solids. Diffraction certainly provides information on long-range order and atomic positions. However, it is less sensitive to local disorder whether that be positional or compositional. In systems such as microporous framework materials (layered hydroxides, zeolites) this local disorder plays a key role in determining the macroscopic physico-chemical properties. As solid-state NMR is a local probe it can be used to provide insight on such local defects as a complement to the information provided by diffraction. Moving to amorphous materials, while diffraction studies provide information on first-nearest neighbour distributions, NMR can provide complimentary information about second nearest neighbours and hence bond angles. In many supramolecular systems and organic compounds it is often not possible to obtain large single crystals. In such cases diffraction studies often provide only limited information eg just the unit cell parameters. However, the corresponding solid-state NMR spectra can show sharp peaks demonstrating that the material is locally well ordered. Here the challenge is to go directly from NMR data to the crystal structure. NMR can also be used to probe dynamics in crystalline materials; a range of NMR experiments can be used to examine motion on different timescales(55). In all cases the ability to compute NMR observables from first-principles essential in order to provide the link between structure and spectra.

We examine some recent studies which highlight the interplay between diffraction, solid-state NMR and computations. An extensive list of applications of planewave/pseudopotential calculations of NMR parameters can be found at http://www.gipaw.net.

4.1.1 Clinohumite - local disorder

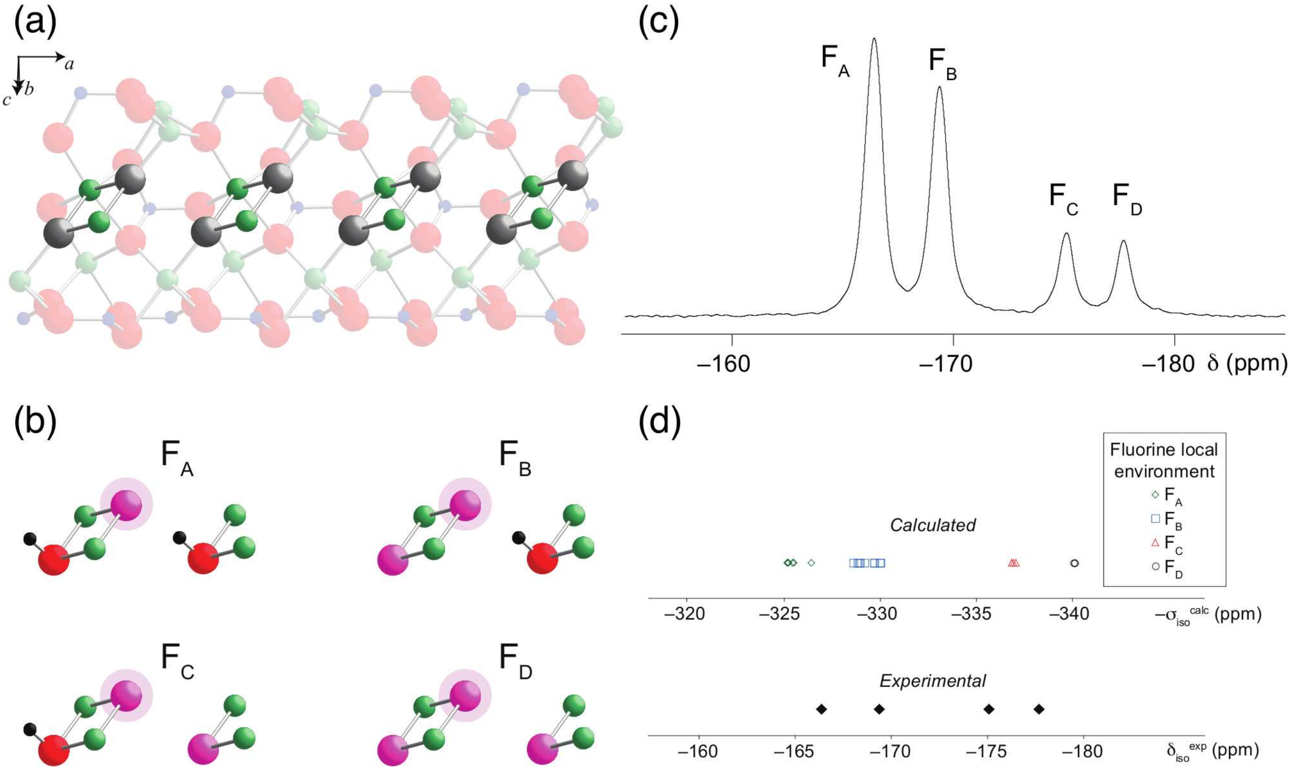

Figure 7: (a) Crystal structure of Clinohumite showing the staggered arrangement of F/OH sites (grey). Atom colours are: Si (blue), Mg (green), O(red). (b) ^{19}F MAS NMR spectrum of 50% fluorinated clinohumite. (c) Four possible local fluorine environments (d) Comparison of calculated ^{19}F shielding and experimental shifts.

First-principles calculations and solid-state NMR have recently been used to study disorder in the fluorine substituted hydrous magnesium silicate clinohumite ($4Mg_2SiO_4{\cdot}Mg(F,OH)_2$). This mineral is of considerable interest as model for the incorporation of water within the Earth's upper mantle. Diffraction provides the overall crystal structure but gives no information on the ordering of the F^-/OH^- ions. As shown in Figure 7 the ^{19}F NMR spectrum reveals 4 distinct fluorine environments. Griffin *et al* performed first-principles calculations(56) on a series of supercells of clinohumite using F and OH substitutions to generate all possible local fluorine environments. From these it was found that the computed ^{19}F NMR parameters were clustered into four distinct ranges depending on their immediate neighbours. The ranges correspond well to the observed peaks providing an assignment of the spectrum. Interestingly further experiments revealed the presence of ^{19}F-^{19}F J-couplings despite the fact that there is no formal bond between fluorine atoms. The magnitude of these coupling was reproduced by first-principles calculations, suggesting that there is a 'though-space' component to these J-couplings.

4.1.2 $\mathrm{Ge_xSe_{1-x}}$ glasses

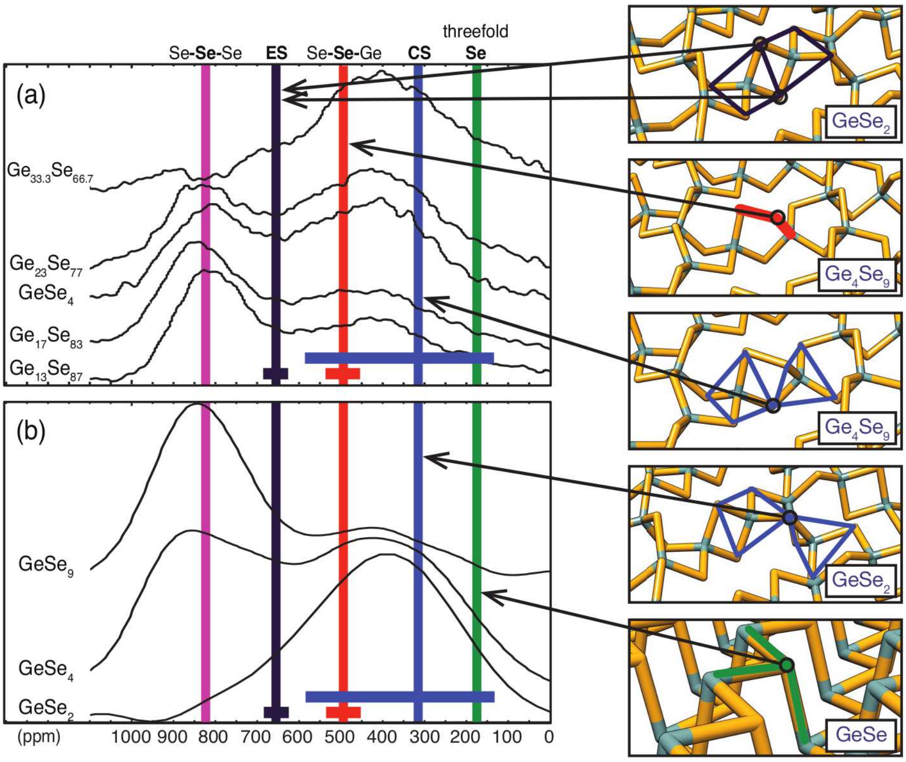

Figure 8: Average (vertical lines) and range (horizontal lines) of ^{77}Se chemical shifts as found for various Se sites in several crystalline precursors of Germanium Selenide glasses, together with experimental ^{77}Se MAS spectra for $\mathrm{Ge_xSe_{1-x}}$ glasses.

Conventional diffraction studies do not provide sufficient information to determine the short range order in Chalcogenide $\mathrm{Ge_xSe_{1-x}}$ glasses, which can include corner-sharing, and edge-sharing, tetrahedral arrangements, under-coordinated and over-coordinated atoms, and homopolar bonds. Recent ^{77}Se NMR studies obtained under MAS have shown two large, but rather broad peaks (as shown in Figure 8). Two conflicting interpretations have been suggested: the first consists of a model of two weakly linked phases, one characterised by Se-Se-Se sites, the other Se-Ge-Se. The second model assumes a fully bonded structure with the contributions from Ge-Se-Se and Ge-Se-Ge linkages overlapping. To answer this question Kibalchenko *et al*(57) carried out first-principles calculations on several crystalline precursors of Germanium Selenide glasses (GeSe$_2$, Ge$_4$Se$_9$ and GeSe) to establish the range of chemical shifts associated with each type of Se site. The results are summarised in Figure 8. This connection between local structure and observed NMR parameters provides a reliable interpretation of the ^{77}Se spectra of $\mathrm{Ge_xSe_{1-x}}$ glasses, ruling out the presence of a bimodal phase and supporting a fully bonded structure.

Charpentier and co-workers have used a combination of Monte Carlo and molecular dynamics simulations together with first-principles calculations of NMR parameters in order to parameterise the relationship between local atomic structure and NMR observables. This methodology has been applied to interpret the NMR spectra of several amorphous materials including vitreous silica(58), calcium silicate glasses(59), lithium and sodium tetrasilicate glasses(60).

4.1.3 Structure Solution

A challenge for solid-state NMR is the idea of 'NMR Crystallography': the ability to go directly from an observed NMR spectrum to the crystal structure(61). Early work by Facelli and Grant(62) combined calculation of ^{13}C magnetic shieldings with single crystal NMR studies. More recently proton-proton spin diffusion (PSD) experiments have been shown to provide three dimensional crystal structures which can be successfully used as input into a scheme for crystal structure determination. In Ref. (63) PSD measurements were combined with subsequent DFT geometry optimisations to give the crystal structure of the small molecule thymol in good agreement with diffraction data. There has been considerable effort to develop schemes based on molecular modelling to predict the lowest energy polymorphs of molecular crystals. At the present time the best schemes are able to reliable predict the naturally occurring structure amongst a set of 10-100 low energy structures. Recent work has shown that the combination of computational and experimental ^{1}H chemical shifts is sufficient to identify the experimental structure from amongst this set of candidate structures(64).

4.2 Dynamics and the role of temperature

NMR can be used to study motional processes in solids. One technique is the use of deuterium NMR. ^{2}H has spin I=2 and the magnitude of its quadrupolar coupling (typically 250kHz) makes it suitable to study motional processes on the micro and milli second timescale. Griffin *et al* (65) have used ^{2}H solid-state NMR to study the dynamic disorder of hydroxyl groups in hydroxyl-clinohumite. In this material the deuteron can exchange between two crystallographic sites. By combining first-principles calculations, a simple model of the effect of motion on the NMR line-broadening, and experimental ^{2}H NMR spectra it was possible to obtain the activation energy for the exchange processes.

NMR spectra are commonly obtained at room temperature. Given that first-principles calculations are typically use a static configuration of atoms (eg obtained from diffraction) this raises questions about the influence of thermal motion on NMR spectra, even if it is thought that there are no specific motional processes, such as exchange, involved.

Dumez and Pickard (66) have examined two ways of including motional effects: by averaging NMR parameters over snapshots taken from molecular dynamics simulations, and by averaging over vibrational modes (as previously used by Rossano *et al*(67) to study the effects of temperature on ^{17}O and ^{25}Mg NMR parameters in MgO). They found the effects of zero-point motion to be significant as well the influence of thermal effects on shielding anisotropies. An extreme example of the effect of temperature on NMR parameters is the case of silsesquioxanes (68). Zero Kelvin simulations strongly overestimate the observed room temperature shielding anisotropies of the ^{29}Si and ^{13}C sites. Good agreement between computation and experiment was obtained by averaging the computed NMR parameters over several orientations of the methyl and vinyl groups. In some cases it may be possible to quantify the effect of temperature experimentally. Webber *et al*(69) measured the change in ^{1}H and ^{13}C chemical shifts in the range 348 K to 248 K (by simply varying the temperature of the gas used inside the NMR probe). By extrapolating the results to 0K the change in ^{1}H shift for the hydroxyl protons with respect to room temperature was 0.5ppm. The change in the C-H ^{1}H shifts over the same range was less than 0.1ppm. The experimental shifts extrapolated to 0K were found to be in better agreement with first-principles calculation those those records at room temperature.

4.3 Experimental Design

The ability to predict NMR observables allows the experimentalist to examine the feasibility of a particular NMR experiment, or optimise its setup (of course this implies that the experimentalist should trust the accuracy of the calculations!). One such area is the measurement of J-coupling in condensed phases. Current experiments can hope to observe values of J in organic compounds that are above about 5Hz. There is little empirical knowledge about magnitude of J couplings in solids, and so calculations have been used to identify systems with measurable couplings. An initial application of the planewave/pseudopotential approach for computing J-couplings in solids(70) showed that calculations at the PBE level gave values for ^{15}N-^{15}N J-couplings across hydrogen bonds in very good agreement with experimental measurements (typically within the experimental errors). The same study predicted that ^{13}C-^{17}O and ^{15}N-^{17}O J-couplings should be of sufficient magnitude to be observed experimentally. This prompted new experimental work on labelled samples of glycine.HCl and uracil. Further calculations were required to interpret the data resulting in the first experimental determination of the biologically significant ^{13}C-^{17}O, ^{17}O-^{17}O and ^{15}N-^{17}O J-couplings in the solid-state(71).

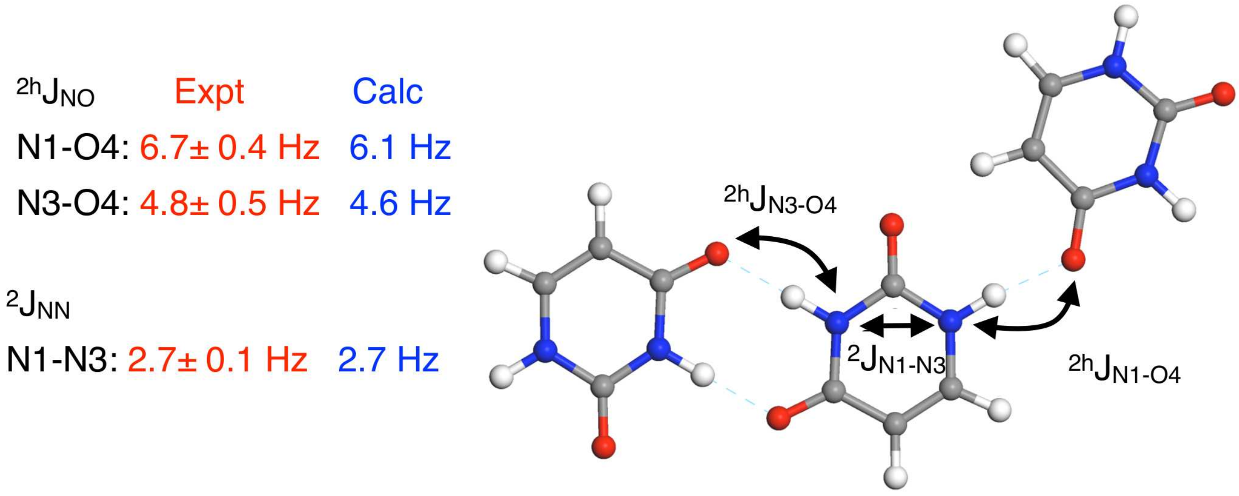

Figure 9: Calculated and Experimental J couplings in the crystalline form of Uracil

4.4 Improving First-principles methodologies

Finally, one can look at the situation in the reverse direction and ask how NMR spectroscopy can contribute to the development of electronic structure methods. For a given crystal structure solid-state NMR experiments provide range of tensor properties for each atomic site. Reproducing this data is a strict test of any first-principles methodology. In our experience, for a given geometry, both LDA and common GGA functionals (PBE, Wu-Cohen, PBEsol) give a very similar description of NMR parameters. Usually the agreement with experiment is reasonably good - a rough rule of thumb is that errors in the chemical shift are within 2-3% of the typical shift range for that element. There are, however, some notable exceptions: Several groups have shown(56; 72) that while present functionals can predict the trends in ^{19}F chemical shifts, a graph of experimental against calculated shifts has slope significantly less than 1. Another example is the calculation of ^{17}O chemical shifts (73) in calcium oxide and calcium aluminosilicates. There are significant errors in the ^{17}O shifts which arise due to the failure of GGA-PBE to treat the unoccupied Ca 3d states correctly. In Ref. (73) it was found that a simple empirical adjustment of the Ca 3d levels via the pseudopotential was sufficient to bring the ^{17}O chemical shifts into good agreement with experiment. However, in both cases it is clear that current GGAs do not describe all of the relavant physics. The converse approach to computing NMR parameters provides an easy route to including exact-exchange in the calculation of magnetic shielding, and it will be interesting to see if this can improve the treatment of these known difficult cases.

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