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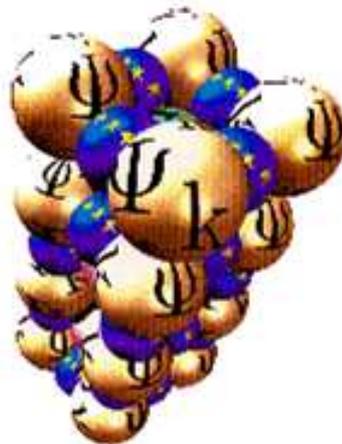
## AB INITIO (FROM ELECTRONIC STRUCTURE) CALCULATION OF COMPLEX PROCESSES IN MATERIALS

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Number 82

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Sponsored by: UK's CCP9  
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# 1 Editorial

In this newsletter we would like to turn readers attention to the message by the chairman of the ESF Psi-k Programme on the new Psi-k network and its funding beyond the end of 2007. Following this, there is also a call for proposals for workshops/meetings for 2008 to be funded from the budget of the newly established network.

Among other things worthwhile mentioning are a call for nominations for the "President of Ireland Young Researcher Award" and, following it, a very comprehensive and informative scientific highlight of this newsletter by Julie B. Staunton (Warwick University, UK) on "**Relativistic Effects and Disordered Local Moments in Magnets**".

For further details please check the tables of content of the newsletter.

The *Networks* have a home page on World Wide Web (WWW). Its *Uniform Resource Locator* (URL) is:

**<http://psi-k.dl.ac.uk/>**

The above contains information on the Psi-k 2007 workshops and hands-on courses (subject to funding).

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

The following email addresses, which remain in operation, are repeated for your convenience, and are the easiest way to contact us.

	<b>function</b>
<b>psik-coord@dl.ac.uk</b>	<b>messages to the coordinators, editor &amp; newsletter</b>
<b>psik-network@dl.ac.uk</b>	<b>messages to the whole <math>\Psi_k</math> community</b>

Dzidka Szotek, Martin Lüders and Walter Temmerman  
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## 2 News from the ESF Programme

### ”Towards Atomistic Materials Design”

#### 2.1 Chairman’s Information on a New Psi-k Network: ”Psi-k”

Dear All,

With this letter I would like to inform you about a new Psi-k Network in the form of a legally independent, non-profit company ”Psi-k”. As you know, the present ESF Psi-k Programme ”Towards Atomistic Materials Design” finishes at the end of 2007. The ESF has pointed out that we will not be able to get a renewal. There are several reasons for this. Firstly, this would be the third funding period, which naturally represents a big barrier for any funding agency. Secondly we are extremely large and scientifically very diversified, which is very different from the usual conception of a network. For this reason we also do not fit into the EU funding schemes either.

On the other hand the 10 years of ESF funding were very good for Psi-k. Our Network has strongly grown and was extremely successful. The large number of 20-25 workshop activities every year as well as the successful Large Psi-k 2005 Conference have shown that the European ab-initio community is worldwide leading. Therefore the Psi-k Steering Committee has decided that we have to help ourselves and form a legally independent, not-for-profit, science organisation ”Psi-k”. The problem of a basic funding will be partially solved by financial contributions (”Membership Fees”) of the largest and financially strongest Psi-k groups in Europe, each giving an annual contribution of about 5.000-10.000 Euro over a five year period. In this way the new ”Psi-k” will have a similar budget as the ESF-Psi-k budget in the last five years. The bottom-up funding of a Network from the budgets of its members is a novelty in Europe. It dramatically illustrates the success of our Network and that our members want to continue the Psi-k activities in the future. If also you and your institute can make a contribution, please let me know.

The goals and tasks of the new Psi-k Network will be very much the same as the well proven Psi-k Programme of the ESF. In particular, also the new Network will be open for all European scientists, who e.g. can participate at Psi-k Workshops or make applications for Psi-k activities. Also the organisation will be as lean as in the past; no staff positions will be involved. The management of the finances and the travel expenses will be handled by members of the Daresbury Laboratory. For this we are founding at present a non-profit ’Company limited by guarantee’ in the UK.

The call for proposals of workshops in 2008 within this new Psi-k Network is published separately in this newsletter.

With best regards

Peter

(Psi-k Chairman)

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## 2.2 Call for Psi-k Workshop Proposals for 2008

Herewith we ask for proposals for workshops, small conferences, hands-on tutorials and summer schools in the field of ab-initio calculations to be held in 2008 and to be partially funded by the new Psi-k network.

**The deadline of proposals is 30. Sept. 2007**

The 2008 year is the first year of the new Psi-k Network, being funded by financial contributions of the large European research groups in the ab-initio field. We all aim at excellent workshop activities and therefore we ask you to write a detailed and well founded proposal. Training activities like computer tutorials and summer schools will be given some preference, but we hope for a similar workshop program as in the past.

Submission of Psi-k Proposals: Instructions for submitting a proposal as well as a submission template will soon be available on the Psi-k website (<http://psi-k.dl.ac.uk>).

Collaboration with CECAM: As in the past years we strongly encourage joint CECAM/ Psi-k Workshops as well as joint tutorials about electronic structure calculations, the latter ones funded partially by the EU contract of the Molecular Simulation Network and the EU-Psi-k Training contract. The collaboration with CECAM is working very well and has effectively increased our funding substantially.

**The deadline for CECAM proposals is 1. October 2007**

As you know, CECAM likes very much discussion workshops on well focussed topics. Conferences will not be supported. Moreover, CECAM proposals have to be competitive. Thus, as for Psi-k, well founded proposals are required. The CECAM council has decided to upgrade CECAM and has published an open call for a (new) host institution. Thus in the planning of the proposals details about the future host are not yet known. However there will be a normal workshop program in 2008.

Funding for US participants: Very often the workshops have an American co-organizer, who can bring in additional support for US participants by funding from NSF or other agencies. As pointed out by Christian Elsaesser, European organizers can also apply for support of US participants from:

- U.S. Office of Naval Research Global (<http://www.onrglobal.navy.mil>)
- European Office of Aerospace Research and Development (<http://www.london.af.mil>)

With best regards,

Peter Dederichs and Walter Temmerman

(Chair and Vice-chair, Psi-k)

## 2.3 Workshop/Meeting Announcements of the ESF Psi-k Programme

### 2.3.1 Tutorial on “Use of the $O(N)$ DFT code CONQUEST”

CECAM, Lyon, France

7 - 8 September 2007

**Organisers: M. J. Gillan, D. R. Bowler and T. Miyazaki**

CONQUEST is a linear-scaling DFT code which operates efficiently on parallel computers having hundreds of processors. Demonstration calculations on Si/Ge nanostructures have recently been reported, in which structural relaxation is performed on systems of over 20,000 atoms. The code is currently on beta-release, but will soon be released under a GNU General Public License. A tutorial on the theory underlying the code and on its practical use, including hands-on sessions, will take place at CECAM, Lyon, 7 - 8 September 2007. This CONQUEST tutorial follows immediately after a CECAM workshop on “Linear-scaling *ab initio* calculations: Applications and future directions”, 3 - 6 September 2007. For further information about both the CONQUEST tutorial and the linear-scaling workshop, please go to the CECAM web pages at [www.cecama.fr](http://www.cecama.fr).

### 2.3.2 Workshop on Modern Concepts for Creating and Analyzing Surface and Nanoscale Materials

12 – 16 May 2008

Hotel Eden Roc, Sant Feliu de Guixols, Girona, Spain

This is a Marie Curie Training Workshop (support comes from Psi-k Training<sup>1</sup>, CECAM<sup>2</sup>, NSF<sup>3</sup>, AFOSR<sup>4</sup>, and IDECAT<sup>5</sup>). It is ideally suited for young researchers (graduate students, postdocs, junior faculty) from physics, chemistry, and materials sciences who seek to come abreast with the latest developments in the field and discuss their own research projects with peers and senior experts.

For details on the prominent invited speakers, the workshop program, venue, and application please see

<http://www.fhi-berlin.mpg.de/th/Meetings/MarieCuriePsik2008>

The conference fee is 620 Euro which covers all the conference activities, as well as accommodation, meals, transfer from Barcelona, and the outing event. All room reservations will be made directly by the organizers.

To apply, please submit the online application on the above website (or send an e-mail to one of the organizers with your brief statement of motivation, resume, and a preliminary title of your poster contribution). Please do so as soon as possible and before 31 January 2008.

Young attendees may receive some financial support, please indicate your needs and reasoning when applying. If you are from the U.S. you should apply for support from the MCC Travel Award Program

<http://www.mcc.uiuc.edu/travel/>

Organizers:

Kristen Fichthorn	<a href="mailto:fichthorn@psu.edu">fichthorn@psu.edu</a>
Matthias Scheffler	<a href="mailto:scheffler@fhi-berlin.mpg.de">scheffler@fhi-berlin.mpg.de</a>
Martin Fuchs	<a href="mailto:fuchs@fhi-berlin.mpg.de">fuchs@fhi-berlin.mpg.de</a> (preferred contact)

<sup>1</sup> Psi-k Training organizes a training program for young researchers in the field referred to as "ab-initio" or "first-principles" calculations. It is an EU-funded Marie Curie Action initiated by the Psi-k Network (<http://www.mc-psi-k-training.cecama.org>)

<sup>2</sup> CECAM (<http://www.cecama.org>)

<sup>3</sup> US National Science Foundation

<sup>4</sup> US Airforce Office of Scientific Research (pending)

<sup>5</sup> IDECAT Network of Excellence <http://www.idecat.org> (pending)

## 2.4 Reports on ESF Psi-k Programme Workshops/Conferences

### 2.4.1 Final Report for the Joint Psi-k/CECAM Workshop: Maximally Localized Wannier Functions: Concepts, Applications, and Beyond

Lyon, France, 27–29 June 2007

*with PWSCF/Wannier90 Tutorial on June 26.*

### Organizers:

#### Nicola Marzari

Massachusetts Institute of Technology  
Department of Materials Science and Engineering  
77 Massachusetts Avenue, MA 02139 Cambridge, United States

marzari@mit.edu

#### Alfredo Pasquarello

Institut de Théorie des Phénomènes Physiques (ITP)  
Ecole Polytechnique Fédérale de Lausanne (EPFL),  
CH-1015 Lausanne, Switzerland

Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA)  
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Berkeley, United States

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### Summary

Maximally localized Wannier functions (MLWFs) provide a representation of the electronic structure in terms of spatially localized functions which is both insightful and useful: Since their

introduction, they have found numerous applications in solid-state theory and in ab-initio simulations in physics, chemistry, and materials science. Also, MLWFs have grown into a methodological tool for the study of polarization, magnetism, strongly-correlated electrons, transport, and large-scale electronic systems. This workshop has provided a forum where these novel ideas were discussed and compared across very diverse research fields.

### **Description of the scientific content of and discussion at the event**

The workshop focused on the theory and application of maximally localized Wannier functions, which give an alternative description of the electronic structure with respect to the energy eigenfunctions (i.e. the Bloch states, which are eigenstates of the translation operator). At variance with Bloch states, which are spatially delocalized and offer a description which is not very intuitive, MLWFs give a representation of the electronic structure in terms of functions localized in real space. These functions are obtained by unitary transformations of the energy eigenfunctions and therefore provide a fully equivalent description of the ground state. Through their center, extension and shape, MLWFs provide a description of the electronic structure which is physically insightful. The electron orbitals can be visualized and located with respect to the positions of the atoms. Essentially, a MLWF provides information on the local electronic structure in a straightforward and compact form. The workshop focused on various research areas in which MLWFs are experiencing an increasing success as a new tool of electronic-structure theory.

The workshop started with an introductory talk by David Vanderbilt, who kindly accepted to provide an overview of the field at large, its history, the current state-of-the-art, open problems, etc. His talk was followed by a session on *General Theory and Algorithms*. This session highlighted how analyzing the properties of MLWFs is a topic closely connected and of great interest to mathematical physics. In particular, exponential localization of MLWFs has been recently demonstrated, extending to two and three dimensions the original work for one dimension of Walter Kohn, dating back to 1959. Furthermore, the real nature of MLWFs, empirically observed in many applications, could be formally demonstrated. This session also illustrated how a simple algorithm based on Jacobi rotations can lead to the approximate simultaneous diagonalization of the position operator matrices, thereby providing a simple path towards efficient construction of MLWFs, especially suited for parallel computations.

The first conference day also comprised a session on *Polarization*. Since polarization and the centers of the MLWFs are intimately related, the property of MLWFs of providing a decomposition of the electronic structure in local components can be easily exploited to analyze the polarization locally. It has been shown how this can lead to the definition of a local dielectric constant, the method of choice to investigate the dielectric response in insulator-insulator or insulator-metal interfaces. In particular, this methodology has allowed one to make progress in

the understanding of the “dead layer” in capacitors. Furthermore, the concept of Wannier functions was generalized by the introduction of Wannier-Bloch functions which optimally localize the spread in both space and energy. This concept found successful applications both in the treatment of electronic and vibrational states, as illustrated for a disordered material.

The morning of the second day was devoted to a session on *Interpolation*. In this session, two notions were highlighted. First, it was shown that the information inherent to the Bloch functions on coarse meshes in the Brillouin zone could be used to obtain a much finer sampling of the Brillouin zone through “Wannier interpolation”. Successful applications include the study of large-scale nanostructures (carbon nanotubes, DNA), the anomalous Hall effect of ferromagnets, and the electron-phonon coupling in superconductivity. Second, attention was drawn on the possibility of defining Hamiltonians on reduced basis sets through the use of disentanglement procedures (disentanglement is designed to separate the contribution of the bands that one wishes to describe from other ones).

The definition of Hamiltonians on reduced basis sets was immediately illustrated in the session on *Transport*, which took place in the afternoon of the second day. It was shown how the use of MLWFs has led to important advances in the development of efficient techniques to compute quantum conductance from first principles. Applications include molecular devices, carbon nanotubes systems, and ferroelectric tunnel junctions.

The morning session on the third day was mostly devoted to *Magnetic Systems*. It was discussed how the notion of MLWFs has allowed one to find the proper definition of the orbital magnetization. The relation between Chern number and the localization has been discussed. The use of the Haldane model has been instrumental to understand these basic relations. It was shown in particular that it is not possible to construct MLWFs in Chern insulators.

The workshop closed with a session on *Strongly Correlated Electrons*. In this research area, the possibility of describing localized orbitals is particularly important. The construction and use of localized functions was illustrated. Such localized functions are essential in the framework set up within the dynamical mean field theory. Also, the use of localized functions is particularly useful in setting up model Hamiltonians with parameters based on first-principles calculations.

The workshop also comprised a session on *Applications*, which was distributed over the three days. It was shown how the use of ultralocalized wave functions can speed up calculations of quasi-particle spectra at the GW level. The ultralocalized wave functions are even more localized than MLWFs because the condition of orthonormality is relaxed. In an application to *ab initio* molecular dynamics, it was shown how an integrator should be developed in order to preserve the localization properties during the course of the evolution. MLWFs turn out to be particularly useful also for interpreting photoemission shifts at semiconductor surfaces and interfaces, since they allow one to separate contributions arising from local strain and from the electronegativity of second-nearest neighbors.

Finally, it should be mentioned that a Tutorial for the use of MLWFs had been organized during the day preceding the workshop. The goal of the Tutorial was to provide a guide for new users of the codes PWSCF and Wannier. Both codes carry opensource licences and are

openly available to the electronic-structure community. The Tutorial was very successful insofar it attracted more than 10 researchers doctoral students and post-docs, which then remained in Lyon to follow the workshop.

### **Assessment of the results and impact of the event on the future direction of the field**

The invited participants (26) that attended the workshop came either from the United States (14) or from Europe (12). The European countries represented were Italy (4), Switzerland (3), Germany (2), Denmark (1), France (1), and United Kingdom (1). The high attendance from overseas was made possible by the funding from different sources: CECAM and ESF. In addition, three of the US-based invited speakers managed to obtain an individual travelling grant from NSF, courtesy of the Materials Computation Center (UIUC). The workshop attracted a lot of interest in the electronic-structure community as could be measured by the number of additional non-invited participants (19). The total number of participants reached 45, close to the limit of CECAM's auditorium in Lyon. The other participants mainly came from European countries: Germany (8), France (3), Italy (3), United States (2), Belgium (1), Netherlands (1), and United Kingdom (1). The workshop also drew attention across disciplines. Physics, chemistry, materials science, and mathematics were all represented.

This gathering of researchers resulted in a lively and challenging environment in which the ample discussion time was always fully used. The main benefit of the workshop is most likely the cross-fertilizing effects that it will have across different disciplines but also across different research communities. Furthermore, the interaction between development and application will be beneficial to both parties leading to more focused developments on the one side, and to richer applications on the other. Eventually this will lead to the optimal exploitation of the concept of MLWFs in various contexts.

For a photo-gallery of the meeting, visit:

<http://irrmawww.epfl.ch/~pasquarello/cecam2007/wannier.html>

# Program of Tutorial

Tuesday 26 June 2007

- 9:30–12:30 **PWSCF Tutorial**  
*Plane wave selfconsistent calculations, non-selfconsistent diagonalizations, band structures*
- 12:30–15:00 Lunch break
- 15:00–18:00 **Wannier90 Tutorial**  
*Wannier functions of occupied manifolds, disentanglement, and metals*

# Program of Workshop

Wednesday 27 June 2007

- Introductory Session, Chairman **A. Pasquarello**
- 8:45–8:50 Opening remarks
- 8:50–9:30 **D. Vanderbilt**  
*Wannier Functions: Past, Present, and Future*
- 9:30–9:45 Discussion
- General Theory and Algorithms, Chairman **N. Marzari**
- 9.45–10:15 **Ch. Brouder**  
*Exponential Localization of Wannier Functions in Insulators*
- 10:15–10:30 Discussion
- 10:30–11:00 Coffee break
- 11:00–11:30 **E. Prodan**  
*The Complex Analytic Structure of the Bands in Linear Molecular Chains*
- 11:30–11:45 Discussion
- 11:45–12:15 **F. Gygi**  
*Large-Scale Computations of Maximally Localized Wannier Functions and Compact Representations of Kohn-Sham Invariant Subspaces*
- 12:15–12:30 Discussion
- 12.30-14:30 Lunch break
- Polarization, Chairman **R. Resta**
- 14:00–14:30 **A. Pasquarello**

- Wannier Functions for Locally Probing Dielectric and Spectral Properties*
- 14:30–14:45 Discussion
- 14:45–15:15 **M. Stengel**  
*First-Principles Modeling of Field Effects at Metal-Oxide Heterojunctions*
- 15:15–15:30 Discussion
- 15:30–16:00 Coffee break
- 16:00–16:30 **O. Dieguez**  
*Wannier-Based Definition of Layer Polarizations in Perovskite Superlattices*
- 16:30–16:45 Discussion
- 16:45–17:15 **M. Posternak**  
*Structural and Electronic Properties of TiO<sub>2</sub> Polymorphs: a Wannier Functions Approach*
- 17:15–17:30 Discussion
- Applications I, Chairman **A. Pasquarello**
- 17:30–18:00 **P. Umari**  
*Faster GW Calculations in Larger Model Structures Using Ultralocalized Nonorthogonal Wannier Functions*
- 18:00–18:15 Discussion

**Thursday 28 June 2007**

- Applications II, Chairman **F. Gygi**
- 8:45–9:15 **R. Car**  
*Dipolar Correlations and Dielectric Permittivity of Water*
- 9:15–9:30 Discussion
- 9:30–10:00 **M. E. Tuckerman**  
*Computational Spectroscopy and Theory of Molecular Pseudopotentials: Two Applications of Wannier Functions*
- 10:00–10:15 Discussion
- 10:15–10:45 Coffee break
- Interpolation, Chairman **D. Vanderbilt**
- 10:45–11:15 **N. Marzari**  
*Making Mountains out of Molehills, and Other Tails of Disentanglement*
- 11:15–11:30 Discussion
- 11:30–12:00 **J. R. Yates**  
*Spectral and Fermi Surface Properties from Wannier Interpolation*

- 12:00–12:15 Discussion
- 12:15–12:45 **F. Giustino**  
*Electron-Phonon Interaction with Wannier Functions*
- 12:45–13:00 Discussion
- 13:00–14:30 Lunch break
- Transport, Chairman **R. Car**
- 14:30–15:00 **M. Buongiorno Nardelli**  
*Wannier Functions and Quantum Transport in Nanostructures*
- 15:00–15:15 Discussion
- 15:15–15:45 **Y.-S. Lee**  
*Predicting the Electronic Transport Properties of Chemically Functionalized Carbon Nanotubes: A Maximally Localized Wannier Function Approach*
- 15:45–16:00 Discussion
- 16:00–16:30 Coffee break
- 16:30–17:00 **K. S. Thygesen**  
*Partially Occupied Wannier Functions and Quantum Transport in Nano-Scale Contacts*
- 17:00–17:15 Discussion
- 17:15–17:45 **A. Ferretti**  
*Maximally Localized Wannier Functions: Ultrasoft Pseudopotentials and Related Applications*
- 17:45–18:00 Discussion

### Friday 29 June 2007

#### Applications III, Chairman **A. Pasquarello**

- 8:45–9:15 **O. V. Yazyev**  
*Wannier Function Analysis as a Tool for Interpreting Core-Level Photoelectron Spectra*
- 9:15–9:30 Discussion
- Magnetic Systems, Chairman **O. K. Andersen**
- 9:30–10:00 **R. Resta**  
*Hermaphrodite Orbitals with and without Time-Reversal Symmetry*
- 10:00–10:15 Discussion
- 10:15–10:45 Coffee break
- 10:45–11:15 **I. Souza**  
*Dichroic  $f$ -Sum Rule and the Orbital Magnetization of Many-*

	<i>Electron Systems</i>
11:15–11:30	Discussion
11:30–12:00	<b>T. Thonhauser</b> <i>On the Impossibility of Constructing Maximally Localized Wannier Functions in Chern Insulators</i>
12:00–12:15	Discussion
	<u>Strongly Correlated Electrons, Chairman <b>I. Souza</b></u>
12:15–12:45	<b>O. K. Andersen</b> <i>Direct Generation of Wannier Functions by Downfolding, Polynomial Approximation, and Symmetrical Orthonormalization</i>
12:45–13:00	Discussion
13:00–14:30	Lunch break
14:30–15:00	<b>W. Ku</b> <i>Symmetry-Respecting Wannier Functions and Their Applications in Strongly Correlated Materials: New Development of First-Principles Many-Body Down-Folding Approach</i>
15:00–15:15	Discussion
15:15–15:45	<b>F. Lechermann</b> <i>Wannier Functions for Strongly Correlated Systems: the Intriguing Physics of <math>\text{BaVS}_3</math> as a Test Case</i>
15:45–16:00	Discussion
	<u>Closing Session</u>
16.00–16:05	Concluding remarks
16.05	End of Workshop

## Wannier Functions: Past, Present, and Future

David Vanderbilt

*Department of Physics and Astronomy, Rutgers University  
Piscataway, NJ 08854-8019, USA*

In this talk I will give an introduction to the theory of Wannier functions (WFs) and discuss some of the reasons why interest in WFs has expanded rapidly in recent years.

I will briefly introduce WFs, starting with the simplest case of orthonormal WFs for a single isolated band in a periodic crystal and discussing the non-uniqueness associated with the choice of phases. I will then discuss some of the ways in which the definition of WFs can be generalized, including: (i) multiband WFs and their associated gauge freedom; (ii) non-orthonormal WFs; (iii) Wannier-like functions (“localized molecular orbitals”) for the occupied states of finite systems (molecules and clusters) and of disordered infinite systems; (iv) “disentangled” or “downfolded” orbitals that can be used as a basis to describe the occupied states and/or the states near  $\varepsilon_F$  in a metal; and (v) hybrid or “hermaphrodite” WFs that are Bloch-like in one or more Cartesian directions while being Wannier-like in the orthogonal direction(s). Unfortunately the terminology in the field is not well established, and there is little consensus about whether or not such generalized objects still deserve to be called WFs. I will discuss my views on this question and make some modest suggestions about it.

I will then briefly discuss two approaches for resolving the phase or gauge freedom: the use of projection methods, and the generation of maximally localized WFs. I will make several comments about the projection methods, especially concerning how well-localized non-orthonormal WFs are best constructed using a projection method.

I will present only a very brief outline of the types of applications of WF methods that are currently of interest, as these will be well illustrated by other talks in the workshop.

I will devote the last part of the talk to discussing several problems connected with the theory of WFs that have only recently been solved or that remain unsolved. In the former category, a proof of the exponential localization of WFs in the three-dimensional multiband case has recently been given. Among the latter, I will focus mainly on issues relating to the definition of WFs for systems with broken time-reversal symmetry. Most of the work done in the last decade on the theory of electric polarization, finite electric fields, localization, and the nature of the insulating state have been limited, implicitly or explicitly, to the case in which time-reversal symmetry is preserved. However, much remains to be done to bring our understanding of systems with broken time-reversal symmetry up to the same level. For example, is there an appropriate generalization of the concept of WFs for a Chern insulator (that is, an insulator with a non-zero Chern invariant)? Can the recently given derivation for the orbital magnetization of

an ordinary insulator be extended to the case of a metal or a Chern insulator using a derivation based on the Wannier representation? If time permits, some tentative and partial steps in these directions may be discussed.

**Wednesday 27 June, 9:45–10:15**

### **Exponential Localization of Wannier Functions in Insulators**

Ch. Brouder<sup>(1)</sup>, G. Panati<sup>(2)</sup>, M. Calandra<sup>(1)</sup>, Ch. Mourougane<sup>(3)</sup> and N. Marzari<sup>(4)</sup>

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<sup>(2)</sup> *Zentrum Mathematik and Physik Department, Technische Universität München, 80290 München, Germany.*

<sup>(3)</sup> *Institut de Mathématiques de Jussieu, 175 rue du Chevaleret, 75013 Paris, France.*

<sup>(4)</sup> *Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge MA 02139-4307, USA.*

The question of the exponential localization of generalized Wannier functions has long been one of the last open problems of one-body solid-state physics. The exponential localization of Wannier functions in two and three dimensions is important from a theoretical point of view, because it implies the existence of multipoles of all orders, and from a computational point of view, because it ensures the exponential convergence of some numerical algorithms.

We proved recently [1] that 2D and 3D generalized Wannier functions decay exponentially in insulators if and only if the single Chern number in 2D and the three Chern numbers in 3D are zero.

After a brief history of the problem, we sketch the steps of the proof, that boils down to a recent theorem on the topology of the Brillouin zone [2]. The role played by the Berry connection and the Chern numbers in the proof of the theorem is explained. Some of the practical consequences of exponential decay are presented.

[1] Ch. Brouder, G. Panati, M. Calandra, Ch. Mourougane, N. Marzari, *Phys. Rev. Lett.* **98**, 046402 (2007).

[2] G. Panati, *Ann. Henri Poincaré* **8**, (2007).

**Wednesday 27 June, 11:00–11:30**

### **The Complex Analytic Structure of the Bands in Linear Molecular Chains**

Emil Prodan

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In a classic paper [1], Walter Kohn found that the band energies of periodic Schroedinger operators in 1 dimension have a beautiful structure when one lets the  $k$ -wavevector be complex. He discovered that the energies of different bands are nothing but the same function evaluated on different sheets of a certain Riemann surface. This Riemann surface is generic in 1 dimension, in the sense that its shape does not depend on the particular form of the periodic potential. The asymptotic behavior of almost all correlation functions can be computed from the Riemann surface. In particular, properly defined Wannier functions decay exponentially with a decay rate dictated by the branch points of the Riemann surface.

In this talk I will review recent results [2] that generalize all the above to linear molecular chains in 3D. They are based on a new approach, which is quite different from the original one. The approach relies on topological arguments (plus elementary functional analysis) rather than the theory of second order differential equations. Based on this, I will discuss the generic structure of the Riemann surface for periodic molecular chains and present several explicitly computed examples.

I will conclude with a discussion of the exponential localization of the Wannier and Green's functions and of the density matrix. If time allows, I will also cover some recent applications to electronic nearsightedness [3] and transport [4].

[1] W. Kohn, Phys. Rev. **115**, 809 (1959).

[2] E. Prodan, Phys. Rev. B **73**, 035128 (2006).

[3] E. Prodan and W. Kohn, PNAS **102**, 11635 (2005).

[4] E. Prodan and R. Car, cond-mat/0702192 (2007).

**Wednesday 27 June, 11:45–12:15**

## **Large-Scale Computations of Maximally Localized Wannier Functions and Compact Representations of Kohn-Sham Invariant Subspaces**

François Gygi

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Maximally Localized Wannier Functions (MLWFs) can be computed using iterative algorithms to minimize the wavefunction spread, but also by approximate simultaneous diagonalization of non-commuting matrices [1]. In large-scale electronic structure calculations, the cost of a

simultaneous diagonalization scales as  $O(n^3)$  for  $n$  electrons. This unfavorable scaling makes it necessary to develop efficient scalable algorithms for massively parallel computers. We present a new parallel algorithm for simultaneous diagonalization and demonstrate its scalability on up to 1024 processors for applications to the calculations of MLWFs.

Simultaneous diagonalization can also be used to compute reduced numerical representations of the solutions of the Kohn-Sham equations. We present a data compression method that allows for *a priori* control of the error caused by the reduction process. When applied to Kohn-Sham wavefunctions expanded on a plane-wave basis, this approach leads to a substantial reduction of the size of the datasets used to restart first-principles simulations, with controlled loss of accuracy. Examples of applications to liquid water and carbon nanotubes will be presented.

[1] F. Gygi, J.-L. Fattebert, and E. Schwegler, *Comput. Phys. Comm.* **155**, 1 (2003).

**Wednesday 27 June, 14:00–14:30**

## **Wannier Functions for Locally Probing Dielectric and Spectral Properties**

Alfredo Pasquarello\*

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Two developments originating from the concept of maximally localized Wannier functions are discussed. In the first one, maximally localized Wannier functions are used within a theoretical scheme for determining local permittivities [1,2]. The local permittivity is obtained from the microscopic charge density induced by an applied electric field. By analyzing the permittivity in terms of maximally localized Wannier functions, we can relate variations of the microscopic dielectric response to specific features of the local bonding arrangement. The potential of our scheme is illustrated through an application to the permittivity of Si slabs of finite thickness [1]. Our approach indicates that the local permittivity in the slab interior approaches the corresponding value for bulk Si within a few atomic layers from the surface. Therefore, the decrease of the average slab permittivity with thickness originates from the lower permittivity of the outer planes and the increasing surface-to-volume ratio. In the second development, following up with a suggestion of Gygi *et al.* [3], we go beyond maximally localized Wannier functions to construct a partitioning of the electronic structure in terms of functions which simultaneously provide an approximate diagonalization of the Hamiltonian and the position operator [4]. These functions, that we call mixed Wannier-Bloch functions, carry both spatial localization and limited spectral broadening, and are therefore particularly convenient to associate specific spectral features to the underlying atomic-scale mechanisms. By introducing a lattice position operator

analogous to the electronic Berry-phase position operator, Wannier-Bloch functions can trivially be extended to the analysis of vibrational modes [4]. Application to vitreous SiO<sub>2</sub> demonstrates that mixed Wannier-Bloch functions constitute a powerful tool for tracking fingerprints of short- and medium-range structural order in electronic and vibrational spectra [4].

\* Work done in collaboration with Feliciano Giustino.

- [1] F. Giustino and A. Pasquarello, Phys. Rev. B **71**, 144104 (2005).
- [2] F. Giustino, P. Umari, and A. Pasquarello, Phys. Rev. Lett. **91**, 267601 (2003).
- [3] F. Gygi, J.-L. Fattebert, and E. Schwegler, Comput. Phys. Comm. **155**, 1 (2003).
- [4] F. Giustino and A. Pasquarello, Phys. Rev. Lett. **96**, 216403 (2006).

**Wednesday 27 June, 14:45–15:15**

## **First-Principles Modeling of Field Effects at Metal-Oxide Heterojunctions**

Massimiliano Stengel and Nicola A. Spaldin

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When the thickness of an oxide film is reduced to few unit cells, its dielectric properties (which are relevant, e.g., for nonvolatile ferroelectric memories and as gate oxides in MOSFET transistors) start to deviate from those predicted by macroscopic models, and crucially depend on the atomic and electronic structure of the interfaces. One particularly important issue is the “dielectric dead layer”, which plagues the performance of thin-film perovskite capacitors by substantially reducing the effective permittivity ( $\kappa$ ) of the active high- $\kappa$  material. The microscopic origins of this reduced permittivity, and in particular whether it stems from defects or from the fundamental properties of an ideal metal/insulator junction, are not well understood.

To address this problem from first principles, we will first show how the macroscopic polarization (and the coupling to an external field) can be rigorously defined for a periodic metal-insulator heterostructure [1], by using techniques and ideas borrowed from Wannier-function theory [2]. We will then demonstrate our new method by calculating the dielectric properties of realistic SrRuO<sub>3</sub>/SrTiO<sub>3</sub>/SrRuO<sub>3</sub> nanocapacitors [3]. Building on these ideas, we will finally present two recent applications of our finite-field method: i) critical thickness for monodomain ferroelectricity, and ii) carrier-mediated magnetoelectric effects at the interface between a dielectric and a metallic ferromagnet.

- [1] M. Stengel and N. A. Spaldin, accepted in Phys. Rev. B, cond-mat/0511042.

[2] M. Stengel and N. A. Spaldin, Phys. Rev. B **73**, 075121 (2006).

[3] M. Stengel and N. A. Spaldin, Nature (London) **443**, 679 (2006).

**Wednesday 27 June, 16:00–16:30**

### **Wannier-Based Definition of Layer Polarizations in Perovskite Superlattices**

Xifan Wu,<sup>(1)</sup> Oswaldo Dieguez,<sup>(2)</sup> Karin M. Rabe,<sup>(3)</sup> and David Vanderbilt<sup>(3)</sup>

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In insulators, the method of Marzari and Vanderbilt [1] can be used to generate maximally localized Wannier functions whose centers are related to the electronic polarization. In the case of layered insulators, this approach can be adapted to provide a natural definition of the local polarization associated with each layer, based on the locations of the nuclear charges and one-dimensional Wannier centers comprising each layer. Here, we use this approach to compute and analyze layer polarizations of ferroelectric perovskite superlattices, including changes in layer polarizations induced by sublattice displacements (i.e., layer-decomposed Born effective charges) and local symmetry breaking at the interfaces. The method provides a powerful tool for analyzing the polarization-related properties of complex layered oxide systems.

[1] N. Marzari and D. Vanderbilt, Phys. Rev. B **56**, 12 847 (1997).

**Wednesday 27 June, 16:45–17:15**

### **Structural and Electronic Properties of TiO<sub>2</sub> Polymorphs: a Wannier Functions Approach**

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The one-particle description of the electronic structure of periodic crystalline solids is usually based on extended Bloch functions (BF's). An alternative description can be derived in terms of localized Wannier functions (WF's), which are defined in real space via a unitary transformation performed on the BF's. By imposing the further condition of maximal localization, the problem of the nonuniqueness of WF's has been mostly resolved by Marzari and Vanderbilt [1], and their method has now become a standard tool for practical applications. In contrast to BF's, WF's are useful in visualizing chemical bonds, and provide furthermore complementary informations regarding dielectric properties. As an illustration of this aspect of the WF's description, we analyze here the microscopic origin of differences in structural and electronic properties of the four natural TiO<sub>2</sub> polymorphs, *i.e.*, rutile, anatase, brookite, and the monoclinic TiO<sub>2</sub> (B) form. Indeed, because of the similarity of the local crystal environment in these phases, the use of a delocalized-basis approach (BF's) precludes a conclusive explanation of the subtle differences observed in their physical properties. In the case of rutile and anatase, physical properties have been commonly analyzed in the literature assuming that the basic building units are TiO<sub>6</sub> octahedra, which are distorted and assembled differently [2]. In contrast, our WF's analysis for these two phases has shown that the OTi<sub>3</sub> triangular complex is in fact the relevant building unit for understanding their electronic properties [3]. WF's differences between the two phases are directly related to the opposite distortion from equilateral shape that the isosceles Ti<sub>3</sub> coordination triangle has in these structures. In particular, this explains quantitatively the opposite anisotropy of the calculated dynamical Born charge tensors. We have extended these results to the case of brookite [4], where the corresponding (non-planar) OTi<sub>3</sub> structural units break up into an equal number of rutilelike and anatase-like units. The WF's of the two non-equivalent O sites display an anisotropy which is in line with the structural data, and this trend applies also to the case of the Born dynamical charge tensor. Physical properties of brookite are expected to be intermediate between those of rutile and anatase. A further phase, TiO<sub>2</sub> (B), which coexists with, and derives from natural anatase has been recently identified [5]. It is monoclinic with  $C_{2h}^3$  space group, and its conventional cell contains 8 TiO<sub>2</sub> formula units. At variance with the three cases discussed above, the 16 O atoms in TiO<sub>2</sub> (B) are *not* all threefold coordinated: indeed, 12 O atoms belong to anatase-like OTi<sub>3</sub> structural units, and the remaining 4 O atoms are twofold coordinated. The outcome of structural differences on electronic properties of these various TiO<sub>2</sub> phases is analyzed.

[1] N. Marzari and D. Vanderbilt, Phys. Rev. B **56**, 12847 (1997).

[2] A. F. Wells, *Structural Inorganic Chemistry* (Clarendon Press, Oxford, 1975), p. 200.

[3] G. Cangiani, A. Baldereschi, M. Posternak, and H. Krakauer, Phys. Rev. B **69**, 121101(R) (2004).

[4] M. Posternak, A. Baldereschi, E.J. Walter, and H. Krakauer, Phys. Rev. B **74**, 125113 (2006).

[5] J.F. Banfield, D.R. Veblen, and D.J. Smith, Am. Mineral. **76**, 343 (1991).

Wednesday 27 June, 17:30–18:00

## Faster GW Calculations in Larger Model Structures Using Ultralocalized Nonorthogonal Wannier Functions

Paolo Umari

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We introduce a novel approach for performing first-principles GW calculations of large model structures. A description of the valence and conduction manifolds in terms of ultra-localized non-orthogonal generalized Wannier functions permits to minimize the dimension of the basis set required for describing the space of single electron transitions. This dimension scales linearly with the size of the system. Then a real-space imaginary-time approach is used to calculate the self-energy operator in the space of Kohn-Sham eigenstates. Ultrasoft pseudopotentials are straightforwardly implemented within this scheme. We validate our approach by calculating the vertical ionization energies of small molecules and find excellent agreement with the experiment. Then we show its potentiality by addressing a model structure of vitreous silica. An overall speedup factor of up to two orders of magnitude is observed.

Thursday 28 June, 8:45–9:15

## Dipolar Correlations and Dielectric Permittivity of Water

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The static dielectric properties of liquid and solid water are investigated within linear response theory in the context of ab-initio molecular dynamics. Using maximally localized Wannier functions to treat the macroscopic polarization we formulate a first-principle, parameter-free, generalization of the phenomenological theory due to Kirkwood and Onsager. Our calculated static permittivity is in good agreement with experiment [1]. The same approach based on Wannier functions is also useful to identify the effect of intramolecular and intermolecular dynamic dipolar correlations on the infrared spectrum of water [2].

[1] M. Sharma, R. Resta, and R. Car, Phys. Rev. Lett., in press (2007).

[2] M. Sharma, R. Resta, and R. Car, Phys. Rev. Lett. **95**, 187401 (2005).

Thursday 28 June, 9:30–10:00

## Computational Spectroscopy and Theory of Molecular Pseudopotentials: Two Applications of Wannier Functions

Mark E. Tuckerman

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The methodology of *ab initio* molecular dynamics, wherein finite-temperature dynamical trajectories are generated using forces computed “on the fly” from electronic structure calculations, allows chemical bond breaking and forming events to be treated explicitly within a dynamical simulation. Direct access to the electronic structure also allows spectroscopic observables, such as the IR spectrum, to be determined in a relatively straightforward manner. *Ab initio* molecular dynamics has benefited substantially from its combination with maximally localized Wannier functions. The latter exploit the unitary invariance of the total energy to generate spatially localized electronic orbitals. Recently, we showed how ideas from quantum field theory can be used to reformulate the Car-Parrinello equations of motion such that these orbitals are preserved during an *ab initio* molecular dynamics calculation [1,2]. In this talk, these methods will be briefly reviewed. It will then be shown how Wannier functions can be used to compute both IR spectra and IR difference spectra with considerable efficiency. Next, the problem of QM/MM simulations will be considered, and it will be shown how Wannier functions can be used as the basis of a new theory of molecular pseudopotentials for use in such simulations. Finally, a new localized basis set approach [3,4,5,6] will be described, which, when combined with Wannier functions, could lead to a new linear-scaling approach.

- [1] J. W. Thomas, R. Iftimie and M. E. Tuckerman, Phys. Rev. B **69**, 125105 (2004).
- [2] R. Iftimie, J. W. Thomas and M. E. Tuckerman, J. Chem. Phys. **120**, 2169 (2004).
- [3] Y. Liu, D. A. Yarne and M. E. Tuckerman, Phys. Rev. B **68**, 125110 (2003).
- [4] H. S. Lee and M. E. Tuckerman, J. Phys. Chem. A **110**, 5549 (2006).
- [5] H. S. Lee and M. E. Tuckerman, J. Chem. Phys. **125**, 154507 (2006).
- [6] H. S. Lee and M. E. Tuckerman, J. Chem. Phys. **126**, 164501 (2007).

Thursday 28 June, 10:45–11:15

## Making Mountains out of Molehills, and Other Tails of Disentanglement

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Maximally-localized Wannier functions (MLWFs) can be used as building blocks for the electronic-structure of complex and realistic nanostructures [1,2]. Two broad alternatives are envisioned: 1) MLWFs can act as a minimal basis set, alternative to LCAO, onto which the Hamiltonian is diagonalized with or without a self-consistent update of the charge density, or 2) the Hamiltonian in the MLWFs representation can be directly constructed from the short-ranged Hamiltonians of smaller constituent units, taken either as molecular or periodically-repeated fragments.

In all cases, a robust strategy for constructing MLWFs spanning both the occupied and unoccupied orbitals is required; we'll discuss here examples and applications drawn from the study of pristine and functionalized carbon nanotubes, silicon and silicon-germanium nanowires, and DNA helices [3].

[1] Y.-S. Lee, M. B. Nardelli, and N. Marzari, *Phys. Rev. Lett.* **95**, 076804 (2005).

[2] Y.-S. Lee and N. Marzari, *Phys. Rev. Lett.* **97**, 116801 (2006).

[3] A. Mostofi and N. Marzari, in preparation (2007).

**Thursday 28 June, 11:30–12:00**

## **Spectral and Fermi Surface Properties from Wannier Interpolation**

Jonathan R. Yates<sup>(1)</sup>, Xinjie Wang<sup>(2)</sup>, David Vanderbilt<sup>(2)</sup>, and Ivo Souza<sup>(3)</sup>

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08854-8019, USA*

<sup>(3)</sup> *Department of Physics, University of California, Berkeley, CA 94720, USA*

We describe a widely-applicable Wannier function (WF) based scheme for interpolating both the energy bands and any given one-electron operator. This provides an efficient first-principles approach for calculating Fermi surface averages and spectral properties of solids [1]. The first step is to perform a conventional first-principles calculation and store the low-lying Bloch functions evaluated on a uniform grid of  $k$ -points in the Brillouin zone. We then map those states onto a set of maximally-localized Wannier functions, and evaluate the matrix elements of the Hamiltonian and the other needed operators between the Wannier orbitals, thus setting up an “exact tight-binding model.” In this compact representation the  $k$ -space quantities are evaluated

inexpensively using a generalized Slater-Koster interpolation. Because of the strong localisation of the Wannier orbitals in real space, the smoothness and accuracy of the  $k$ -space interpolation increases rapidly with the number of grid points originally used to construct the Wannier functions. This allows  $k$ -space integrals to be performed with *ab-initio* accuracy at low cost. In the Wannier representation, band gradients, effective masses, and other  $k$ -derivatives needed for transport and optical coefficients can be evaluated analytically, producing numerically stable results even at band crossings and near weak avoided crossings. We present its application to the calculation of the spontaneous anomalous Hall conductivity [2] and magnetic circular dichroism [1] of ferromagnets. The possibility of similar field-induced effects in paramagnets, including an anomalous contribution to the low-field Hall effect, is discussed.

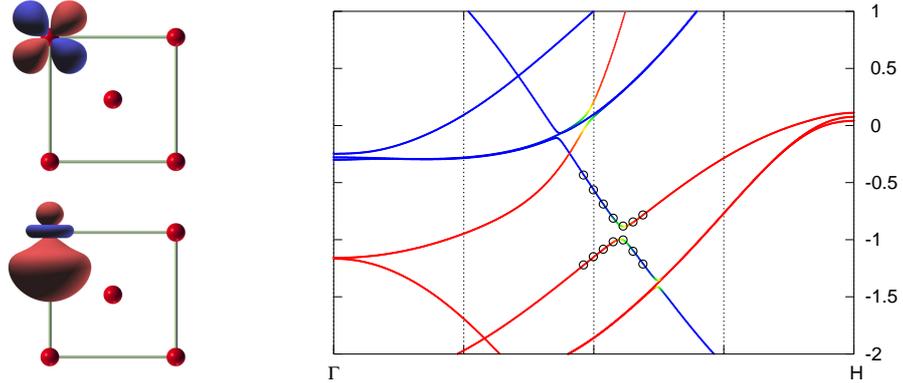


Figure 1: Left: WFs for bcc Fe. Right: Wannier-interpolated bands of bcc Fe along  $\Gamma$ -H. The bands are color-coded according to the value of  $\langle S_z \rangle$ : red for spin up and blue for spin down. The energies are given in eV and the Fermi level is at 0 eV. The vertical dashed lines indicate  $k$ -points on the *ab-initio* mesh used for constructing the WFs. For comparison, points from a full *ab-initio* calculation are shown as open circles.

[1] J. R. Yates, X. Wang, D. Vanderbilt, and I. Souza, cond-mat/0702554.

[2] X. Wang, J. R. Yates, I. Souza, and D. Vanderbilt, Phys. Rev. B **74**, 195118 (2006).

**Thursday 28 June, 12:15–12:45**

## Electron-Phonon Interaction with Wannier Functions

Feliciano Giustino<sup>†</sup>

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94720, USA*

The electron-phonon interaction plays a central role in a variety of phenomena, including for example electrical resistivity, superconductivity, Peirls instability, and polaronic transport in conducting polymers. Despite the continued interest in the electron-phonon problem, modern first-principles calculations are still limited to simple bulk systems with a few atoms per unit cell,

and only sporadic attempts have been made to address complex materials such as nanostructures or doped superconductors. The current situation is at least partly due to the significant computational burden in the study of phenomena involving electron-phonon coupling, where a detailed account of the electron and phonon scattering processes in proximity of the Fermi surface is required. In this talk I will present a methodology based on electronic and lattice Wannier functions which reduces by several orders of magnitude the computational cost of such studies [1]. The underlying idea is to exploit the spatial localization of electrons and phonons in the Wannier representation in order to compute from first-principles only a limited set of electronic and vibrational states and electron-phonon matrix elements. The results thus obtained are then used to calculate the corresponding quantities at arbitrary electron and phonon momenta in the Bloch representation through a Wannier-Fourier interpolation. In most practical cases the final results carry the same accuracy of a direct first-principles calculation, while the computational cost is comparable to that of a standard phonon dispersion calculation. In the first part of the talk I will describe how we calculate the electron-phonon vertex in the joint electron/phonon Wannier representation. The localization properties of the vertex will be analyzed by making connection with the electronic Hamiltonian in the Wannier basis and with the matrix of the Interatomic Force Constants [2]. By considering a simple virtual crystal model of boron-doped diamond, I will demonstrate the accuracy of the Wannier-Fourier interpolation in Bloch space, and discuss the convergence of the electron and phonon self-energies with the sampling of the Brillouin zone. In the second part of the talk I will review a few recent applications to systems of technological relevance. I will discuss the mechanism of superconductivity in boron-doped diamond [1], show how the electron-phonon interaction affects the carrier lifetimes and the velocity of Dirac fermions in graphene [2], and clarify the relation between the superconducting properties of super-hard transition metal carbides and the Fermi surface topology in these materials [3].

† Work done in collaboration with J. R. Yates, I. Souza, C.-H. Park, J. Noffsinger, M. L. Cohen, and S. G. Louie

[1] F. Giustino, J. R. Yates, I. Souza, M. L. Cohen, and S. G. Louie, *Phys. Rev. Lett.* **98**, 047005 (2007).

[2] F. Giustino, M. L. Cohen, and S. G. Louie, *unpublished*.

[3] C.-H. Park, F. Giustino, M. L. Cohen, and S. G. Louie, *unpublished*.

[4] J. Noffsinger, F. Giustino, S. G. Louie, and M. L. Cohen, *unpublished*.

**Thursday 28 June, 14:30–15:00**

## **Wannier Functions and Quantum Transport in Nanostructures**

Marco Buongiorno Nardelli

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Determining the quantum ballistic conductance of a nanosystem has become of primary interest in recent years for the promise of novel technological applications for nanoscale quantum electronic devices. In particular, on the theoretical side, a fully first principle theory of electronic transport is highly desirable. In this talk, I will discuss how the use of Maximally-Localized Wannier functions has led to important advances in the development of efficient techniques to compute quantum conductance from first principles [1] and show examples of prototypical applications, ranging from molecular devices and carbon nanotubes systems to ferroelectric tunnel junctions.

[1] WanT project, <http://www.wannier-transport.org>

**Thursday 28 June, 15:15–15:45**

## **Predicting the Electronic Transport Properties of Chemically Functionalized Carbon Nanotubes: A Maximally Localized Wannier Function Approach**

Young-Su Lee and Nicola Marzari

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Chemical functionalizations are one of the most promising routes to engineer the electronic properties of carbon nanotubes. While understanding the effect of various chemical groups is of fundamental interest, a full first-principles description on these complex nanostructures having thousands of atoms and randomly-distributed functional groups is still prohibitively expensive.

We calculate the quantum conductance of functionalized carbon nanotubes mapping first-principles calculations to tight-binding Hamiltonians built upon maximally localized Wannier function (MLWF) basis [1]. We apply this method to study two prototypical cases: monovalent and divalent functional groups, categorized according to the number of the covalent bonds that bind them to the nanotube backbone. One additional bond introduced by a monovalent group converts an  $sp^2$  carbon to an  $sp^3$  carbon on the sidewall. These  $sp^3$  carbons strongly perturb the conduction  $\pi$ -manifold; a rapid decrease in the conductance is predicted as the number of the functional groups increases [1]. Divalent groups exhibit more interesting characteristic. The sidewall bond between the two neighboring carbon atoms associated with a functional group can either be broken or remain closed, which is determined by the curvature of the nanotubes and the chemical nature of the functional groups. Bond breaking transforms the two carbon atoms back to the  $sp^2$  hybridized state; the conductance then approaches that of pristine nanotubes in

contrast with the  $sp^3$  hybridized case [2]. This theoretical prediction presents a novel concept of controlling the electronic transport of carbon nanotubes through an orbital rehybridization.

[1] Y.-S. Lee, M. Buongiorno Nardelli, and N. Marzari, *Phys. Rev. Lett.* **95**, 076804 (2005).

[2] Y.-S. Lee and N. Marzari, *Phys. Rev. Lett.* **97**, 116801 (2006).

**Thursday 28 June, 16:30–17:00**

## Partially Occupied Wannier Functions and Quantum Transport in Nano-Scale Contacts

K. S. Thygesen

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I will present a method for constructing maximally localized Wannier functions (WFs) for general systems including non-periodic metallic systems such as molecules adsorbed on a metal surface or a molecule attached between metallic electrodes. The resulting partially occupied WF's [1] have improved symmetry and localization properties as compared to the WF's constructed from the occupied subspace. In the second part I discuss how the partially occupied WF's can be used to calculate the Landauer-Büttiker conductance of nano-scale contacts with plane-wave accuracy within a DFT framework [2]. As an application of the WF-transport scheme it is demonstrated how the presence of impurity gas atoms can affect the electrical properties of Ag and Au monatomic chains. Finally, it is shown how the minimal WF basis can be combined with the GW approximation to address correlation effects in quantum transport through realistic nano-scale contacts [3].

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[3] K. S. Thygesen and A. Rubio, *J. Chem. Phys.* **126**, 091101 (2007).

**Thursday 28 June, 17:15–17:45**

## Maximally Localized Wannier Functions: Ultrasoft Pseudopotentials and Related Applications

Andrea Ferretti

<sup>(1)</sup> *Dipartimento di Fisica, Università di Modena e Reggio Emilia, I-41100 Modena, Italy*

<sup>(2)</sup> *National Research Center S3 of INFN-CNR, I-41100 Modena, Italy*

The use of maximally localized Wannier functions (MLWFs) recently became very popular in the electronic structure community, as a supplementary analysis tool. On one hand, MLWFs are attractive because they constitute a localized basis set which is complete and orthonormal, while on the other hand, they also carry physical information. Is it therefore a direct interest of the community to improve and generalize the current methods and algorithms to compute MLWFs.

In the framework of the WANT [1] project, we developed and implemented [2] a theoretical scheme that enables the calculation of maximally localized Wannier functions in the formalism of projector-augmented-waves [3] and ultrasoft-pseudopotentials [4]. I will describe this formalism as well as some technical issues related to the computation of MLWFs. I will also discuss some application of the above method to the calculation of spontaneous polarization and surface dipole for SiC polytypes, and to the evaluation of transport properties in organic-silicon interfaces.

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**Friday 29 June, 8:45–9:15**

## **Wannier Function Analysis as a Tool for Interpreting Core-Level Photoelectron Spectra**

Oleg V. Yazyev\*

<sup>(1)</sup> *Institut de Théorie des Phénomènes Physiques (ITP), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland*

<sup>(2)</sup> *Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), CH-1015 Lausanne, Switzerland*

<sup>(3)</sup> *Institute of Chemical Sciences and Engineering (ISIC), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland*

X-ray photoemission spectroscopy (XPS) involving excitations of core electrons is a versatile experimental technique for the characterization of surfaces and interfaces. However, even in the cases of the Si(100)2×1 surface and technologically relevant Si(100)-SiO<sub>2</sub> interface, which have

been the objects of numerous highly resolved XPS investigations, the origin of subsurface XPS signals is not fully understood. While the shifts pertaining to the first-layer dimer atoms of the Si(100)2×1 surface have been identified, the other lines appearing in highly resolved Si 2*p* spectra still lack a consensual assignment [1]. For the Si(100)-SiO<sub>2</sub> interface, highly resolved spectra show fine structure in the nonoxidized Si line, with extra components at lower (Si<sup>α</sup>) and higher binding energy (Si<sup>β</sup>) with respect to the Si bulk line [2]. First principles calculations are able to predict accurately the Si 2*p* core-level binding energies at silicon surfaces and interfaces [3]. Binding energy shifts of the subsurface Si atoms with identically composed first-neighbor shells are caused by electron density displacements due to either the local strain fields or electronegativity effects. In order to distinguish between these two effects, we propose a simple analysis in terms of maximally localized Wannier functions (MLWFs) [4]. Our approach is based on the correlation between the core electron binding energies and the positions of MLWF centers and covalent bond centers [5]. For the Si(100)-c(4×2) surface, we find that, apart from the shifts associated with the dimer atoms, the other shifts mainly result from the local strain induced by the surface reconstruction. For the interface, the Si atoms with second-neighbor O atoms contribute to the Si<sup>α</sup> line, while the Si<sup>β</sup> line originates from bond elongations of Si atoms without second-neighbor O atoms. From the experimental shift of about 0.3 eV, we infer the occurrence of Si atoms with an average bond length elongation of  $\sim 0.05$  Å. A key result of our work is that XPS spectra in combination with electronic structure calculations and Wannier function analysis provide an atomic-scale probe of the strain in the structure. This confers to photoelectron spectroscopy a new functionality.

\* Work done in collaboration with A. Pasquarello.

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**Friday 29 June, 9:30–10:00**

## **Hermaphrodite Orbitals with and without Time-Reversal Symmetry**

Raffaele Resta

*Dipartimento di Fisica Teorica, Università di Trieste, Italy*

The localization tensor, alias second cumulant moment  $\langle r_\alpha r_\beta \rangle_c$  of the electron distribution, is an intensive quantity characterizing the ground-state wavefunction, and is finite in any insulator [1]. In absence of time-reversal (TR) symmetry, this same tensor acquires an off-diagonal imaginary part [2], proportional to the Chern number  $C_1$  (in 2d). I specialize here to the case of noninteracting electrons (either HF or KS). Within either periodic or “open” (cluster-like) boundary conditions we have

$$\text{Re} \langle r_\alpha r_\beta \rangle_c = \frac{1}{2N} \int d\mathbf{r} d\mathbf{r}' (\mathbf{r} - \mathbf{r}')_\alpha (\mathbf{r} - \mathbf{r}')_\beta |\rho(\mathbf{r}, \mathbf{r}')|^2, \quad (1)$$

where  $\rho$  is the one-body density matrix, and single orbital occupancy is assumed. When performing a localization transformation upon the occupied orbitals, the real part of  $\langle r_\alpha r_\beta \rangle_c$  sets a minimum for the quadratic spread in any given direction, averaged over all the orbitals; this statement holds, again, within both kinds of boundary conditions [3]. From now on, I further specialize to the crystalline case. Then the trace of  $\langle r_\alpha r_\beta \rangle_c$  equals the Marzari-Vanderbilt  $\Omega_I$  (divided by the number of occupied bands) while the orbitals which actually minimize the quadratic spread in a given direction have been called “hermaphrodite orbitals” (Wannier-like in one direction, Bloch-like in the orthogonal ones); they decay faster than any polynomial [4]. As for the cases where TR symmetry is broken, we have some experience only in 2d, for either the quantum-Hall (noninteracting) fluid, or the Haldane model Hamiltonian [5]. In a quantum-Hall fluid the dc longitudinal conductance vanishes, hence the system is effectively an insulator. Then  $\text{Re} \langle r_\alpha r_\beta \rangle_c$  is finite, while  $\text{Im} \langle r_\alpha r_\beta \rangle_c$  is proportional to  $C_1$  (hence to the Hall conductivity). Despite the finiteness of  $\text{Re} \langle r_\alpha r_\beta \rangle_c$ , two-dimensional localization of the orbitals *cannot* be achieved. Instead, the hermaphrodite orbitals do exist. All can be worked out analytically in the case of a flat substrate potential, where the density matrix appearing in Eq. (1) has a Gaussian decay and the trace of  $\langle r_\alpha r_\beta \rangle_c$  equals precisely the squared magnetic length (at filling one). The hermaphrodite orbitals happen to coincide with the Landau-gauge orbitals [2]; notice that  $\rho$  is *not* gauge-invariant by a change of the magnetic gauge (although its modulus is such). Depending on its parameters, the Haldane model may represent either a normal insulator ( $C_1 = 0$ ) or a Chern insulator ( $C_1 = \pm 1$ ). While the normal case is such by all counts, the Chern case is like the quantum-Hall case:  $\text{Re} \langle r_\alpha r_\beta \rangle_c$  is finite,  $\text{Im} \langle r_\alpha r_\beta \rangle_c$  is proportional to  $C_1$ , and two-dimensional localization of the orbitals *cannot* be achieved [6]. I conjecture that hermaphrodite orbitals still exist. Other issues, related to macroscopic orbital magnetization, will be possibly discussed.

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**Friday 29 June, 10:45–11:15**

# Dichroic $f$ -Sum Rule and the Orbital Magnetization of Many-Electron Systems

Ivo Souza<sup>(1)</sup> and David Vanderbilt<sup>(2)</sup>

<sup>(1)</sup> *Department of Physics, University of California, Berkeley, USA*

<sup>(2)</sup> *Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey, USA*

Magnetic circular dichroism (MCD), the difference in absorption of left- and right-circularly-polarized light by magnetic systems, is described by  $\sigma''_{A,\alpha\beta}(\omega)$ , the imaginary, antisymmetric part of the optical conductivity. We obtain a sum rule for the MCD spectrum of many-electron systems which is the dichroic counterpart of the  $f$ -sum rule for linearly polarized light:

$$\int_0^\infty \sigma''_A(\omega) d\omega = \frac{\pi e c}{\hbar} \mathbf{M}_{\text{CD}},$$

where  $\sigma''_{A,\gamma} = (1/2)\epsilon_{\alpha\beta\gamma}\sigma''_{A,\alpha\beta}$ . The conventional wisdom is that the total ground state orbital magnetization  $\mathbf{M}_{\text{orb}}$  should appear on the right-hand-side [1]. Instead, we find that the sum rule yields a subtly different quantity  $\mathbf{M}_{\text{CD}}$ , which turns out to be one of the two contributions to  $\mathbf{M}_{\text{orb}}$  recently identified in the theory of bulk magnetism [2–4]:

$$\mathbf{M}_{\text{orb}} = \mathbf{M}_{\text{CD}} + \Delta\mathbf{M}.$$

$\Delta\mathbf{M}$  is generally nonzero for systems with more than one electron, and  $\mathbf{M}_{\text{CD}}$  is basically the wavepacket self-rotation term of Ref. [2]. By independently measuring their sum via gyromagnetic experiments,  $\mathbf{M}_{\text{CD}}$  and  $\Delta\mathbf{M}$  can in principle be separated out in macroscopic samples with a net magnetization. The dichroic  $f$ -sum rule is discussed alongside three other sum rules for optical absorption, including one which relates the dichroic spectrum to the interband (Karplus-Luttinger) Hall conductivity in solids. The sum rules for bounded and extended systems are first considered separately. We then show that for conventional insulators the bulk sum rules can be recovered from the bounded-system ones by taking the thermodynamic limit using a Wannier-function representation.

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- [2] D. Xiao, J. Shi, and Q. Niu, *Phys. Rev. Lett.* **95**, 137204 (2005).
- [3] T. Thonhauser, Davide Ceresoli, D. Vanderbilt, and R. Resta, *Phys. Rev. Lett.* **95**, 137205 (2005).
- [4] Davide Ceresoli, T. Thonhauser, D. Vanderbilt, and R. Resta, *Phys. Rev. B* **74**, 024408 (2006).

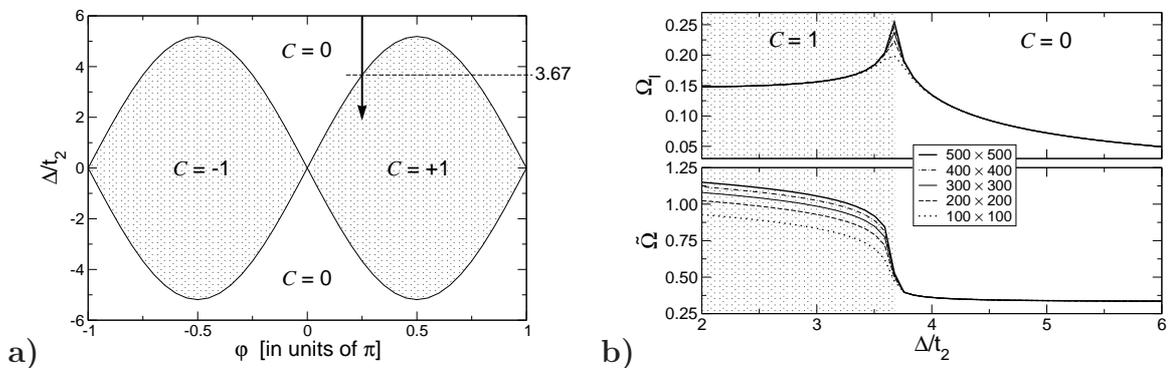
**Friday 29 June, 11:30–12:00**

## On the Impossibility of Constructing Maximally Localized Wannier Functions in Chern Insulators

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<sup>(2)</sup> *Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.*

The Haldane model [1] is a simple tight-binding model that exhibits a regular insulating phase ( $C = 0$ ) as well as a Chern-insulator phase ( $C = \pm 1$ ), depending on the model parameters  $\varphi$  and  $\Delta/t_2$  (see Fig. a). This provides us with a simple means to study the behavior of several physical properties as the system turns into a Chern insulator. In particular, we can use this approach to clarify how the usual algorithms for constructing Wannier functions break down as one crosses into the Chern-insulator region of the phase diagram. Using numerical calculations on finite and periodic samples, we find that the total spread  $\Omega$  of the maximally-localized Wannier functions [2] diverges for Chern insulators. However, its gauge-invariant part  $\Omega_I$ , related to the localization length of Resta and Sorella [3], is finite in both insulating phases and diverges as the phase boundary is approached, as depicted in Fig. b. Furthermore, we find that the usual Wannier-function construction is bound to fail in Chern insulators because of singularities that appear in overlap matrices in both the real-space finite-sample and  $\mathbf{k}$ -space extended-sample approaches. In addition, we find that the density matrix has exponential decay in both insulating phases, while having a power-law decay, more characteristic of a metallic system, precisely at the phase boundary [4].



**a)** Phase diagram of the Haldane model as a function of the model parameters  $\varphi$  and  $\Delta/t_2$ . For our study we have chosen to cross into the Chern insulator phase along the vertical line at  $\varphi = 1/4$ . **b)** Gauge-independent part  $\Omega_I$  and gauge-dependent part  $\tilde{\Omega}$  of the spread  $\Omega = \Omega_I + \tilde{\Omega}$  for different dense  $\mathbf{k}$ -point meshes. The divergence is clearly visible at  $\Delta/t_2 \approx 3.67$ .

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## Direct Generation of Wannier Functions by Downfolding, Polynomial Approximation, and Symmetrical Orthonormalization

O. K. Andersen

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Localized, minimal basis sets are useful for numerous purposes in electronic-structure calculations. Such a basis may pick a single band or a complex of bands, say the occupied bands, and may uncover the bonding, enable real-space order- $N$  calculations, provide understanding, or be used to construct low-energy Hubbard Hamiltonians for correlated systems. We shall explain how to generate such basis sets directly by Löwdin downfolding (partitioning) from a large, complete, basis set of energy-independent, highly localized orbitals such as AOs or LMTOs, and subsequent removal of the energy dependence of the downfolded orbitals by the  $N$ -ization technique [1,2]. When applied to energy-dependent partial waves, rather than AOs or LMTOs, this gives rise to the NMTO method [3-6]. An orbital of the minimal basis set is simply the original orbital, dressed by a cloud of those orbitals which have been removed from the original set by downfolding. If the minimal basis set is chosen to span particular bands, symmetrical orthonormalization yields a set of localized Wannier functions. Wannier functions which are maximally localized in some other sense may be obtained by a subsequent unitary transformation for a local cluster [1,2]. For most correlated  $d$ - and  $f$ -electron systems, no further localization is achieved by the last step [1,2,7]. Examples from NMTO calculations will be presented [8-12].

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**Friday 29 June, 14:30–15:00**

**Symmetry-Respecting Wannier Functions and Their Applications in Strongly Correlated Materials: New Development of First-Principles Many-Body Down-Folding Approach**

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Based on a flexible first-principles construction of symmetry-respecting Wannier functions, a novel many-body down-folding approach is recently developed to derive the low-energy effective Hamiltonian that governs the physics of strongly correlated materials. In this talk, representative applications of these Wannier functions will be surveyed, including studies of ferromagnetism in half-filled cuprates [1], gapless charge density wave in dichalcogenides [2], charge/orbital order in manganites [3,4], and charge excitations in the oxides [5,6]. As an illustration of the new many-body down-folding method, detail discussions will focus on the recent discovery of the super-repulsion effect in the high-Tc cuprates and its significant implications [7].

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**Friday 29 June, 15:15–15:45**

# Wannier Functions for Strongly Correlated Systems: the Intriguing Physics of BaVS<sub>3</sub> as a Test Case

Frank Lechermann

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An understanding of the physics of strongly correlated multi-orbital electron systems is one of the key ingredients in order to describe a wide range of novel solid state compounds. The complex interplay of the crystal structure with the competition between the localized and the itinerant character of electrons in a manifestly multi-orbital case is giving rise to highly interesting physical phenomena.

By combining the Dynamical Mean Field Theory (DMFT) with the Local Density Approximation (LDA) to Density Functional Theory, a powerful many-body approach is provided to tackle the given problem on a realistic level. This unified approach is naturally formulated by introducing Wannier(-like) functions as the basis representation for the electronic structure problem [1,2,3]. The choice of Wannier functions is not unique in various senses and has to be tailored to the physical problem of interest as well as to the utilized theoretical framework.

We will discuss recent developments in this important area of interfacing realistic band-structure methods with DMFT by presenting results for the complex BaVS<sub>3</sub> compound. In the latter system, electronic correlations are relevant in driving orbital charge transfers and Fermi-surface deformations in the metallic regime [3,4,5]. The paramagnetic insulating charge-density wave state shows moreover a complex orbital structure with important differences between the V ions [5].

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## **2.4.2 Report on Workshop "THEORY MEETS INDUSTRY"**

### **WORKSHOP**

#### **"THEORY MEETS INDUSTRY"**

#### **THE IMPACT OF DENSITY-FUNCTIONAL CALCULATIONS ON MATERIALS SCIENCE**

JUNE 12-14, 2007

ERWIN-SCHRÖDINGER-INSTITUTE FOR MATHEMATICAL PHYSICS  
Boltzmannngasse, A-1090 WIEN, AUSTRIA

sponsored by

**Center for Computational Materials Science, Wien**  
**Erwin Schrödinger Institute for Mathematical Physics, Wien**  
**Universität Wien**  
**ESF Research Programme "Towards Computational Materials Design"**

#### **Scientific Scope**

In 1998 a workshop called "Theory Meets Industry" was held at the Technical University in Wien to celebrate the start of the Research Programme "Electronic Structure Calculations for Elucidating the Complex Atomistic Behavior of Solids and Surfaces" sponsored by the European Research Foundation (ESF) - better known as the "psik-network". The aim of the workshop was to confront the potential of the ab-initio simulation codes developed in academia with the necessities arising from industrial research.

The Research Programme has been renewed under the title "Towards Atomistic Materials Design" and is now approaching the end of the second funding period. Everybody will agree that much progress has been realized since the 1998 workshop and that density-functional theory develops an increasingly important impact on materials research, not only in academia, but also in industry. Therefore it was timely to organize a second workshop "Theory Meets Industry". The workshop took place on June 12-14 in the Erwin-Schrödinger Institute in Wien. The scientific program was planned by a Scientific Advisory Board (SAB) consisting of Risto Nieminen (TU Helsinki), Chris Wolverton (Ford Motors and NWU Evanston), Herve Toulhoat (Institut Francais du Petrole), Ryoji Asahi (Toyota), Erich Wimmer (Materials Design) and Jürgen Hafner (U Wien).

As for the previous meeting the aim was to highlight the most recent progress in the development of ab-initio density-functional, post-DFT methods and in front-line applications in academia and

to present recent achievements in industrial research. About 40 talks and posters, coming in an equal percentage from researchers in academia and industry, have been presented. the full program of the meeting and abstracts of all contributions are appended. Proceedings of the workshop will be published in a special issue of the Journal of Physics: Condensed Matter.

For details on the workshop programme and abstracts of presented papers see

[http://psi-k.dl.ac.uk/index.html?workshops\\_2007](http://psi-k.dl.ac.uk/index.html?workshops_2007) .

### 3 News from UK's CCP9 Programme

#### UK's Collaborative Computational Project 9 (CCP9) on "Computational Studies of the Electronic Structure of Solids"

##### 3.1 CCP9 Workshop Announcements

###### 3.1.1 Workshop on solving the Bogliubov-de Gennes and Gross-Pitaevskii equations for superconductors, superfluids and BEC

Britannia Hotel, Manchester, UK

28-30 September 2007

James F. Annett, Walter Temmerman and Balazs L. Gyorffy

##### Motivation

Pairing and condensation in degenerate Fermi and Bose systems remain at the centre of theoretical and experimental research in condensed matter physics. The equations referred to by the names of Bogoliubov, de Gennes and Gross-Pitaevskii provide a powerful, unifying conceptual framework for the study of quantum many-body phenomena associated with broken gauge symmetry, corresponding to the wide range of physical systems, such as superconductors, Bose-Einstein condensates of atoms and rotating nuclei. These are scientific communities which do not meet as often as would be desirable from the point of view of rapid dissemination of new results and conceptual developments. The aim of the proposed workshop is to overcome such natural fragmentation and stimulate cross-fertilization of new ideas in these fields.

##### Programme

###### Friday 28 September

*Arrival*

###### Saturday 29 September

###### Ab initio theory of superconductivity

E.K.U. Gross (Berlin)	9.00-9.45
O.K. Andersen (Stuttgart) (TBC)	9.45-10.30
K.I. Wysokinski (Lublin)	10.45-11.30
T. Maier (ORNL)	11.30-12.15
F. Mauri (Paris)	12.15-1.00

**BEC in Cold Atoms**

M. Szymanska (Oxford)	2.00-2.45
F. Marchetta (Oxford)	2.45-3.30
J. Ruostekoski (Southampton)	4.00-4.45
Robin Scott (Nottingham)	4.45-5.30

*Banquet - Yang Sing* 7pm

**Sunday 30 September****Nanoscale superconductivity**

I. Sosnin (RHUL)	9.00-9.45
C. Lambert (Lancaster) (TBC)	9.45-10.30
I. Grigorieva (Manchester)	10.45-11.30
F. Kusmartsev (Loughborough) (TBC)	11.30-12.15

Attendance: space at the workshop is limited. Please contact James Annett or Walter Temmerman to register to attend.

## 4 General Workshop/Conference Announcements

### 4.1 ThUL ACTINET School 2007

#### **”Theoretical methods and experimental techniques for the investigation of solid actinide compounds”**

**Centre d’Etudes de Cadarache, France, November 12 - 17, 2007**

The school will be held from November 12 to 17, 2007 at the Centre d’Etudes de Cadarache (40 km from Aix-en-Provence, south of France).

Scope:

The main objective of the Theoretical User Lab (ThUL) within ACTINET is to promote the interaction between theory and experiment and mutual understanding of experimentalists and theoreticians. The ThUL organises schools open to a limited number of experimentalists and theoreticians working in the field of actinide physics and chemistry. The 2007 school will focus on solid state physics, and will provide a general introduction to computational methods at the atomic scale, as well as present specific approximations relevant for the study of the properties of solid actinide compounds, such as relativistic effects, strong electronic correlations, and magnetism. The basics of various experimental methods (X-ray spectroscopy, measurement of thermodynamical data) will also be covered. The School will mainly consist of lectures on theoretical methods and experimental techniques. In addition, practical computer sessions and discussions of case studies directed by the lecturers should help the participants to improve their understanding of modelling approaches.

Program of the school

- DFT, pseudopotentials, beyond LDA (SIC, LDA+U)
- Classical molecular dynamics and empirical potentials
- Magnetism in actinides compounds
- X-ray spectroscopies (absorption, photoemission)
- Thermodynamics

Target audience

This school is a training course designed for experimentalists and theoreticians who are interested both in the modelling of actinide compounds and their physical properties, and in their experimental characterisation. The number of participants will be limited to 24 to enable interaction between lecturers and participants and between participants, as well as facilitate practical

sessions. This school is first addressed to graduate students and young researchers, but more senior researchers interested in actinide physics are also welcome.

The school is organized by the CEA Cadarache and CEA Bruyères-le-Châtel together with the ThUL task group.

Dr. Marjorie Bertolus (CEA, Cadarache)

Dr. Bernard Amadon (CEA, Bruyères le Châtel), Dr. François Jollet (CEA, Bruyères le Châtel)

Dr. Bernd Schimmelpfennig (INE-FZK Karlsruhe, Germany)

A web site is in preparation.

Pre-registration can be sent to [marjorie.bertolus@cea.fr](mailto:marjorie.bertolus@cea.fr) or [bernard.amadon@cea.fr](mailto:bernard.amadon@cea.fr) with a short C.V.

Dr Nikolas Kaltsoyannis

Department of Chemistry

University College London

Christopher Ingold Laboratories

20 Gordon Street

London WC1H 0AJ

UK

e-mail: [n.kaltsoyannis@ucl.ac.uk](mailto:n.kaltsoyannis@ucl.ac.uk)

tel: +44 (0)20 7679 4670

fax: +44 (0)20 7679 7463

## 4.2 Workshop on "Polymers in Nanotechnology"

27-28 September, 2007

Salerno, Italy

We would like to inform you that we are organizing in Salerno a workshop entitled "Polymers in Nanotechnology" that will be held at the end of September (27-28 September 2007).

The invited speakers belong to an excellence network (workshop is one of the actions of the excellence network) named: "New Polymeric Materials, Synthesis, Characterization and Simulations" financed by our government and coordinated by us (Italy) and composed by Max-Planck Institut of Mainz (Germany), Technical University of Darmstadt (Germany), Charles Sadron (France) and Institute and Technical University of Aachen (Germany).

The workshop got the auspices of European Polymer Federation (EPF) and our national polymer science and technology association (AIM Associazione Italiana Macromolecole).

Last but not least, in order to facilitate the participation of students and young researchers, we choose to have the workshop WITHOUT FEE.

Salerno September 27-28, 2007 "Polymers in Nanotechnology" website:

<http://www.chem.unisa.it/polnan/>

You are kindly asked to spread information about the workshop.

Dr. Andrea Correa  
University of Salerno  
Department of Chemistry  
via Ponte don Melillo -I-84084 - Fisciano (SA)  
Tel: +39 089 96 9391  
Fax: +39 089 96 9603  
E-mail: [acorrea@unisa.it](mailto:acorrea@unisa.it)  
webpage: [www.chem.unisa.it/groups/molnac](http://www.chem.unisa.it/groups/molnac)

### **4.3 Symposium on "Atomistic calculations in condensed matter physics, surface physics, and nanophysics"**

**International Conference in Computational Methods in Science and Engineering 2007- ICCMSE 2007**

<http://www.iccmse.org/>

**Hotel Marbella, Corfu, Greece, 25-30 September 2007**

The symposium "Atomistic calculations in condensed matter physics, surface physics, and nanophysics" (symposium 2) in conjunction with the International Conference in Computational Methods in Science and Engineering 2007- ICCMSE 2007 (<http://www.iccmse.org/>) will take place in Hotel Marbella, Corfu, Greece, 25-30 September 2007.

Organizer:

Aristides D. Zdetsis

Department of Physics, University of Patras, Greece

E-mail address: [zdetsis@upatras.gr](mailto:zdetsis@upatras.gr)

All papers on related subjects are welcome: from basic theory to computational studies. Please send queries and contributions to the Organizer. The contributed papers (3-4 pages) will be published as a collection in the Proceedings Volume (to be published by the American Institute of Physics) and must be prepared according to the specific instructions given at

<http://www.iccmse.org/abstract.htm>

## 5 General Job Announcements

### Postdoctoral Position

Institut des Nanosciences de Paris, Paris, France

#### Simulation of oxide nano-objects

##### Job description

We have an immediate opening for postdoctoral position in the area of materials modeling and simulation. The project focuses on (1) simulation and theory of the effect of environment on equilibrium and growth properties of oxide nano-objects and (2) development and application of a new, quantum-based approach for modeling large-scale ionic-covalent systems.

The project offers the opportunity to collaborate with experimental and simulation groups at the Institut des Nanosciences de Paris, the Centre de Recherche en Matière Condensée et Nanosciences (Marseille), and the Centre de Chimie de la Surface (Strasbourg). The candidate will have access to computational facilities, which include a local cluster and the supercomputers of the French national facility (IDRIS/CNRS).

##### Qualifications

Applicants must hold a recent Ph.D. or equivalent in physics, chemistry or materials science. Expertise in materials modeling and simulation would be desired, strong background in programming (Fortran) would be highly regarded, and a previous experience with semi-empirical approaches would be advantageous. Aptitude to communicate effectively with coworkers and a demonstrated ability to conduct original research, are expected. The position is full-time for one year, with a possible extension.

To apply, send an application addressing the selection criteria, including a CV with a list of publications, and names, addresses, e-mails, and phone numbers of two or more confidential Referees.

##### Further information

Jacek Goniakowski (Jacek.Goniakowski@insp.jussieu.fr), tel: +33 (0)1 44 27 46 17

Fabio Finocchi (Fabio.Finocchi@insp.jussieu.fr), tel: +33 (0)1 44 27 51 16

Claudine Noguera (Claudine.Noguera@insp.jussieu.fr), tel: +33 (0)1 44 27 46 65

Institut des Nanosciences de Paris

Campus de Boucicaut

140 Rue de Lourmel

75015 PARIS, France

<http://www.insp.upmc.fr>

# PhD Position in Electronic Structure Theory - AlCu Systems

Centre Interuniversitaire de Recherche et d'Ingénierie des  
MATériaux

118 route de Narbonne

31077 Toulouse Cedex 4 - France

<http://cirimat.ensiacet.fr/>

A PhD position is available starting in September 2007.

The scientific activity of the 'CIRIMAT' involves all aspects of condensed matter sciences, from the conception to the properties of materials. Studies of the reactivity of surfaces of metallic alloys are developed and include experiments and ab initio calculations.

Copper-containing aluminum alloys are of particular industrial interest, especially in the aeronautic field. They have good mechanical properties and develop a protective coating by oxidation.

The research project is on the electronic structure of AlCu systems (solid solutions, stable and metastable crystalline phases) and their surface. It aims at understanding the microscopic mechanisms underlying the reactivity of the surface of AlCu alloys (especially with oxygen), using ab-initio calculations.

Candidates should have a degree in physics, chemistry, applied mathematics, or engineering and possess a good background in solid state physics. Basic knowledge in quantum chemistry is required.

The position is fully funded, including salary and social benefits, by the French ministry of high education and research (three-year contract).

Applications including a Curriculum Vitae and recommendation letters should be sent to:

Dr Corinne Dufaire

Maître de Conférences

CIRIMAT - ENSIACET

118 route de Narbonne

31077 Toulouse Cedex 4 - France

l: Tel.: + 33 (5) 62 88 57 05

Corinne.Dufaire@ensiacet.fr

**Position of the Director  
of the Institute for Theoretical Solid State Physics  
at the IFW Dresden, Germany**

The Leibniz-Institute for Solid State and Materials Research Dresden (IFW) is a publicly funded research institution with approximately 400 employees. It consists of five Institutes, which deal with modern materials science ranging from basic research in physics, chemistry and materials science to the development of new materials, technologies and products ([www.ifw-dresden.de](http://www.ifw-dresden.de)).

We invite applications for the position of the

Director

of the Institute for Theoretical Solid State Physics

at the IFW Dresden

combined with a

Full Professorship (W3) 'Solid State Theory'

at the Mathematics and Natural Sciences Faculty of the Technische Universitaet Dresden. The appointment will be effective 01 April 2008.

Applicants should be internationally recognised experts in the field of theoretical solid state physics carrying out independent research in the area of solid state theory and should be prepared to cooperate actively with groups carrying out experimental work at the IFW Dresden.

As a member of the Mathematics and Natural Sciences Faculty, the appointee will be engaged in teaching Solid State Theory at the Technische Universitaet Dresden. Interest for collaborations with the institutes at the Technische Universitaet Dresden, with other research institutions and universities and also with industry is implied. The applicants have to fulfill the employment conditions of 40 Schsisches Hochschulgesetz in its current version.

Applicatins from women are particularly welcome. The same applies to the disabled.

The application documents containing the curriculum vitae, certificates, list of publications, and a short statement of present research activities will be made available to the responsible committees of the Technische Universitaet Dresden and the IFW.

Applications should be submitted by 31 August 2007 to

Prof. Dr. L. Schultz  
IFW Dresden  
PF 27 01 16  
01171 Dresden  
Germany

## Postdoctoral Position at the CEA, France

A postdoc position is available at the CEA on the following topic: "Ab initio approach of the polymer ageing mechanisms: interaction of various polymers with oxides surfaces".

This project lies in the framework of the COPOLA (Composite and POLymer Ageing) research program. Depending on their industrial uses, polymers age more or less rapidly. A best understanding of the polymers ageing mechanisms will allow to select and optimise certain functionalities of materials. The aim of this thesis is to study with ab initio molecular modelling (DFT and Hartree-Fock based methods) various processes of ageing, namely: charges/polymers interactions, formation of radicals, chemical reactivity with water or oxygen.

The work will be co-directed by the CEA, EDF and ENSCP (Paris).

The project requires a good knowledge in the field of materials science and a good knowledge of molecular modelling (density functional theory and Hartree-Fock approximations).

The study is granted by the CEA.

The age limit is 28 years old.

The candidates must send us the most rapidly, a curriculum vitae, a cover letter, letters of reference. These documents must be sent obligatorily at the CEA contacts (see addresses below) by conventional and electronic mails; each document must be signed by the candidat.

Contacts :

For CEA :

Mireille Defranceschi

CEA Saclay

Bt. 391, DPC/SEC

91191 Gif-sur-Yvette Cedex, Franc

Phone : (00) 33 1 69 08 91 3

Email : mireille.defranceschi@cea.fr

Christophe Moulin

CEA Saclay

Bt. 391, DPC/SEC

91191 Gif-sur-Yvette Cedex, Franc

Phone : (00) 33 1 69 08 77 5

Email : christophe.moulin@cea.f

For EDF :

Philippe Baranek

Laboratoire de Simulations des Matériaux

EDF R&D

Département MMC (Moret sur Loing, near Fontainebleau-Paris)

Phone : (00) 33 1 60 73 76 08

Email : philippe.baranek@edf.fr

For ENSCP :

Professor Carlo Adamo

team Modélisation des Systèmes Complexes (LECA, ENSCP, Paris)

Phone : (00) 33 1 44 27 67 28

Email : carlo-adamo@enscp.fr

**Ph. D. Position in Electronic Structure Theory**  
**Laboratoire de Chimie Théorique CNRS - Université Pierre et**  
**Marie Curie[2mm]**  
**Paris, France**

A PhD position is available starting in September 2007.

The scientific activity of the 'Laboratoire de Chimie Théorique' involves modeling of complex systems (concerning molecular chemistry, biochemistry, astrophysics and surface reactivity), as well as methodological advances (in Density Functional Theory and Quantum Monte Carlo approaches).

The prospective candidate should mainly work on properties obtained from accurate wave functions (in particular obtained from Quantum Monte Carlo), focusing on using them for the description of the chemical bond in molecules and solids. Development of algorithms and programming are envisaged.

Candidates should have a degree in physics, chemistry, applied mathematics, or engineering. Basic knowledge in quantum chemistry is required. Programming skills in Fortran or C are an advantage.

The position is fully funded, including salary and social benefits, by the French ministry of high education and research (three-year contract).

Interested candidates should contact one of us.

Andreas SAVIN - [savin@lct.jussieu.fr](mailto:savin@lct.jussieu.fr)  
<http://www.lct.jussieu.fr/pagesperso/savin/>

Roland ASSARAF - [assaraf@lct.jussieu.fr](mailto:assaraf@lct.jussieu.fr)

Benoît BRAÏDA - [braida@lct.jussieu.fr](mailto:braida@lct.jussieu.fr)

## Research Fellow Positions

### Materials Modeling, Theory and Simulation Laboratory, Institute of High Performance Computing, Singapore

The Materials Theory, Modeling and Simulation Laboratory (MMSL), a basic research organization sponsored by the Institutes of High Performance Computing (IHPC) and Materials Research and Engineering (IMRE), Singapore, invites applications from outstanding candidates for up to four research fellow positions. The MMSL, under the directorship of Prof. David J. Srolovitz, has existing expertise in a wide range of areas including ab initio theory, dislocation dynamics, phase-field models, solid mechanics, and molecular dynamics. The successful candidates will have latitude in defining and pursuing research into theory, modeling, and simulation of materials. MMSL, located within IHPC, provides access to several supercomputers for large-scale materials simulations. Qualified candidates will possess a PhD degree in materials science, physics, chemistry, solid mechanics or a closely related discipline. Initial appointments are for two-year terms. The remuneration, relocation, and travel budgets are competitive. International candidates are encouraged to apply.

The evaluation of applications will begin immediately, and will continue until all positions are filled. Applicants should submit a resume, their research interests, and three references to (with Job Reference: MMSL) [recruitment@ihpc.a-star.edu.sg](mailto:recruitment@ihpc.a-star.edu.sg), or by mail to Prof. David J. Srolovitz, Institute of High Performance Computing, 1 Science Park Road, #01-01 The Capricorn, Singapore 117528, Republic of Singapore.

## Ph. D Positions

### Physical and Theoretical Chemistry, University of Saarland, Saarbrücken, Germany

Applications are invited for two PhD studentships (starting at the earliest possible time) at the Institute for Physical and Theoretical Chemistry, University of Saarland, Saarbrücken, Germany.

The positions are funded via the German Research Council (Deutsche Forschungsgemeinschaft, DFG) and the projects are devoted to the development and application of theoretical methods and accompanying computer codes for the determination of structural, energetic, electronic, and thermodynamic properties of clusters with up to 100-200 atoms. The funding is available for 2–3 years with extensions possible up to 4 years. The **net** salary is approximately 1100–1200 euros (after deduction of tax, social security, health insurance, etc.).

The candidates should have a Diploma/MSc in Physics, Chemistry, or Materials Science and have a solid background in theoretical chemistry, quantum mechanics, and/or computational physics. Good skills in mathematics and programming are important. It is expected that the candidates will also participate in the teaching activities of the group, most notably in supervising undergraduate students in a lab course in physical chemistry. Therefore knowledge of the German language at least at the intermediate level is required.

Interested applicants should submit a letter of application, including curriculum vitae, and should arrange for one or two letters of reference to be sent to the address below (preferably via electronic mail):

*Prof. Dr. Michael Springborg (e-mail: [m.springborg@mx.uni-saarland.de](mailto:m.springborg@mx.uni-saarland.de))*

or

*Dr. Valeri G. Grigoryan (vg.grigoryan@mx.uni-saarland.de)*

Physical and Theoretical Chemistry

University of Saarland

Bld. B2.2

66123 Saarbrücken

Germany

For further details and for applications, please contact via e-mail (see above).

**Ph. D. Position**  
**Physics Department, Lund University, Sweden**

Physics Department, Lund University announces a PhD studentship for four years.

For further details please see

<http://www.teorfys.lu.se/phd07.html>

Carl-Olof Almbladh

Physics Department, Mathematical Physics Lund university P.O Box 118 SE-22100 Lund, SWEDEN

## Marie Curie ToK-DEV Fellowships (MTKD-CT-2006-042459)

### in "Hybrid Nanocrystals" (theory)

#### Ab-initio and semi-empirical calculations

#### Heraklion, Crete

One (1) EC funded postdoctoral position (theory) is available at the Institute of Electronic Structure and Laser at FORTH as part of the Marie Curie Host Fellowship for Transfer of Knowledge (ToK) program NANOTAIL, "Hybrid nanocrystals exhibiting advanced and tailored properties".

Context:

The overall objective of the project is to design and develop new multi-functional nanocrystals, to understand their formation, their assembly and their properties (optical, magnetic, electrical). Research topics focus on the optimization of hybrid nanocrystal materials (involving transition metal oxides, II-VI semiconductors etc.) for modern technologies, ranging from magneto-optical data recording to biological sensing/labeling. The successful applicant is going to have strong interaction with the NANOTAIL's theory group at FORTH, led by Dr. Antonis Andriotis [1], as well as collaborate with the teams of the Partner Institutes at:

- National Nanotechnology Laboratory, CNR, Lecce (ITALY);  
contact person: Dr. Liberato Manna (liberato.manna@unile.it)
- Centre d'Elaboration de Materiaux et d'Etudes Structurales, CNRS, Toulouse (FRANCE);  
contact person: Dr. Etienne Snoeck (snoeck@cemes.fr)

The project will fortify your skills via cooperation and exchange of ideas involving a variety of expertise i.e. ab-initio and semi-empirical theoretical modeling of geometric/electronic structure, materials' growth mechanisms, surface functionalization. The NANOTAIL's experimental team will provide support by 'testing' the fundamental physico-chemical processes through key studies proposed by the theory.

Qualifications and Application Procedure:

You should have a PhD degree in Chemistry or Physics and be keen to integrate within an interdisciplinary and multinational team. Possible good skills in mathematical modeling will be an advantage. To apply (Deadline: 1 September 2007) please send a short statement of research interests and experience, CV, publication list and arrange for the submission of three (3) letters of recommendation, to: Dr. Alexandros Lappas; Functional Nanocrystals Laboratory [2], Institute of Electronic Structure & Laser, Foundation for Research & Technology - Hellas (FORTH), Vassilika Vouton, 71110 Heraklion, Greece.

Informal discussions are welcome. E-mail: lappas@iesl.forth.gr, Phone: +30 2810 391300.

Salary, Terms, Eligibility:

The salary will be approximately 41,000 EURO per annum + mobility allowances. The position is available from 15 September 2007 or as soon as possible thereafter, with duration 1-2 years. Applications are open to citizens from within EU member or associated states. Women and minority groups are particularly encouraged to apply. For eligibility criteria see the Marie Curie for ToK Handbook [3].

[1] <http://www.iesl.forth.gr/research/tccc/condensed/magnetic/index.asp> \\  
[2] <http://www.iesl.forth.gr/research/material/magnetic/index.asp> \\  
<http://fun.iesl.forth.gr>

[3] [ftp://ftp.cordis.europa.eu/pub/fp6/docs/calls/mariecurie-action/handbook\\_tok\\_200502\\_e](ftp://ftp.cordis.europa.eu/pub/fp6/docs/calls/mariecurie-action/handbook_tok_200502_e)

Dr. Alexandros Lappas

Institute of Electronic Structure & Laser (IESL) Foundation for Research & Technology - Hellas (FORTH) P.O. Box 1385, Vassilika Vouton 711 10 Heraklion, Crete GREECE

Tel: +30 2810 391344, Fax: +30 2810 391305 <http://www.iesl.forth.gr/users/fun>

## Postdoctoral Position at Max-Planck-Institut for Iron Research Düsseldorf, Germany

The department 'Computational Materials Design' offers a postdoctoral position.

The research will focus on first-principles calculations for binary and ternary III/V semiconductors used in LED devices (GaN, InGaN, GaInP). The aim of the project is the development of state-of-the-art simulation tools in close collaboration with our industrial partners to study electric, thermodynamical, and transport properties of point defects that are responsible for the long-term degradation of LEDs. For this, high-quality density-functional theory (DFT) calculations will have to be combined with concepts from statistical mechanics, thermodynamics, and kinetics.

Applicants should have a PhD in physics, chemistry, or materials science, and have experience with atomic-scale simulations and electronic-structure theory. As we use an in-house DFT library ([www.sxlib.de](http://www.sxlib.de)) that is constantly being developed, programming experience is welcome, but not required. The candidate should enjoy working in an open and dynamic environment, and actively interact with the other groups in the department as well as with the experimental co-workers.

The research is part of a joint project with several partners from industry, university, and research institutes, which is funded by the German ministry of education and research. The salary will be according to the rules of the MPIE (E13/TVöD). The position is limited to two years, with the possibility of extension.

The Max Planck Society is an equal opportunities employer. Women are encouraged to apply.

Interested candidates should send an application letter, CV, and list of publications, preferably by email or fax, to:

Prof. Jörg Neugebauer ([neugebauer@mpie.de](mailto:neugebauer@mpie.de))

or

Christoph Freysoldt ([freysoldt@mpie.de](mailto:freysoldt@mpie.de))

Postal address:

Max-Planck-Institut für Eisenforschung GmbH

Postfach 140444

40074 Düsseldorf

Fax: +49 211 6792 465

Lecturer in Theoretical Materials Chemistry or Physics

The University of Kent, U. K.

Reference number: 353

Department: School of Physical Sciences

Location: Canterbury Campus

Closing date: 12 Noon Wednesday 22 August 2007

Salary: Grade 7: £27,465 - £31,840 pa or Grade 8: £32,795 - £39,160 pa

Contract: Full-time and Ongoing

Brief description:

We are seeking to appoint a lecturer with an outstanding research record in theoretical and/or computational studies of materials or with exceptional research promise.

You will have a PhD degree and high quality published research; you will be expected to establish an effective individual research programme in the School, including seeking external funding support for research.

You will also be responsible for the development of innovative teaching materials and have the opportunity to make a significant contribution to the development of our Forensic Science degree programmes.

Informal enquiries may be made to the Head of School, Professor Paul Strange, P.Strange@kent.ac.uk

Interviews will be held on Friday 14 September 2007.

Further details may be found at <http://www.kent.ac.uk/jobs/academic/353.html>.

## **Postdoctoral Position**

### **Ab initio phase diagrams modelling in the Mo-Si-Ru and Mo-Si-Pt systems**

**Laboratoire d'accueil à l'ONERA**

**Branch : Matériaux**

**Department : LEM, Unité mixte CNRS-ONERA, UMR 104**

**Location : Châtillon, France Contact : Gilles Hug**

**Tél. : 01 46 73 45 42 email : Gilles.Hug@onera.fr**

The design of new refractory materials for high temperature applications is now required to increase the performances and the efficiency of turbine engines, in particular in view of a reduction of CO<sub>2</sub> emissions. In order to allow for a substantial increase of service temperatures, the intermetallic compounds based on molybdenum silicides are presently developed. However, these studies rely on a preliminary fundamental knowledge of the equilibrium phase diagrams as well as diffusion properties since most of the databases for the systems of interest are presently only scarcely documented.

Thus a multidisciplinary team for basic research has been set up between the Laboratoire de Chimie du Solide Minéral in Nancy, the Laboratoire d'Etude des Microstructures (ONERACNRS) in Châtillon and the Laboratoire de Chimie Métallurgique des Terres Rares in Thiais and is granted by the French National Research Agency (ANR) under the MITECT project (Modelling Intermetallics using Theory, Experiments and Computational Thermodynamics). Its scope consists in a multiscale study of multicomponent refractory systems based on Mo, Si, B elements with Pt or Ru precious metal additions.

The experimental work which is performed by the Nancy and Thiais partners consists in the determination as a function of temperature at a macroscopic scale of the equilibrium phases, their crystallography, their thermodynamic properties as well as the kinetics of the reactions.

The theoretical work will consist in the determination of the critical parameters needed to assess the thermodynamical properties based on Density Functional Theory (DFT) calculations and is the scope of the present proposed post-doc position. It includes the determination of the fundamental state of the phases of interest, calculation of defects and/or Cp. These different factors will be introduced gradually in order of increasing complexity.

Both experimental and theoretical studies are meant at feeding appropriate databases in order to perform CALPHAD type modeling of phase diagrams. Thus part of the theoretical work will be focused on parameters that cannot be experimentally determined. A strong interaction between experimental and theoretical work will be sought for in this project.

The successful candidate is expected to hold a PhD with a background in solid state physics, physical chemistry or materials science. An skillful knowledge in numerical calculation using the DFT will be required. A previous expertise in thermodynamic modeling will be appreciated too. She/He will be in charge of conducting the ab initio calculations in the project and should have a strong interest for interaction and communication with the other teams in the consortium. She/He must be fluent in English. French language is advisable although not mandatory.

The position is presently open for a one year period with a possible starting point from September 2007 or later.

## Postdoc Position in Computational Physics/Materials Science Trinity College Dublin, Ireland

A postdoctoral position is available within the School of Physics at Trinity College Dublin. The successful applicant will work together with Dr. Claude Ederer on one (or both) of the following projects:

- 1.) Implementation and application of the combination of density functional theory with dynamical mean-field theory (LDA+DMFT)
- 2.) Computational study and modeling of multiferroic materials and oxide hetero-structures.

The initial appointment will be for one year, with possible extension for up to three years. The anticipated starting date is November 1st 2007, but a later starting date is also possible. Candidates must have a PhD in Physics, Materials Science, or a related area and experience with electronic structure calculations using density functional theory and/or many-body simulations using dynamical mean-field theory. A strong overall motivation, experience in code development, and a keen interest in materials science are other desirable qualifications.

Applications containing a CV, a brief description of research interests and past experience, and contact information of two references should be send to (email and PDF-format preferred):

Dr. Claude Ederer  
Department of Physics  
Columbia University  
538 West 120th Street  
New York, NY 10027  
USA  
email: [ederer@phys.columbia.edu](mailto:ederer@phys.columbia.edu)

The School of Physics at TCD provides an innovative interdisciplinary research environment in the area of Magnetic, Electronic and Photonic Materials, Nanoscience and Computational Physics, and is strongly linked to the new Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN). Further information about Trinity College Dublin, the School of Physics, and CRANN can be found at [www.tcd.ie](http://www.tcd.ie), [www.tcd.ie/Physics](http://www.tcd.ie/Physics), and [www.crann.tcd.ie](http://www.crann.tcd.ie). More detailed information about this position can be obtained directly from Dr. Ederer (see also <http://phys.columbia.edu/ederer>).

**Postdoctoral, Ph.D., and MSc Positions**  
**at the Computational Nanoscience Center, Laboratory of**  
**Physics,**  
**Helsinki University of Technology, Finland**  
**(<http://www.fyslab.hut.fi/comp>)**

From the fall of 2007 various positions from the postdoctoral, to the PhD and finally the MSc level are available in the Computational Nanoscience Center (COMP), Helsinki, Finland. The group is led by Academy Professor Risto Nieminen, and has been selected as a national Centre of Excellence for 2006-2011. Here, we advertise in particular possibilities arising from the recently started close collaboration with the Nokia Ltd Nano Systems Group, operating jointly at the HUT campus and at the nearby Nokia Research Center. Projects are available in several of COMP's subgroups, with topics ranging from mesoscopic models of Carbon Nano-Tube networks to atomistic simulations of materials for the electronics of the future.

Those interested in the possibilities should consult the web page

<http://www.fyslab.hut.fi/jobs>,

where more information is found about the particulars along with descriptions of various projects, and email addresses for further inquiries. The web site also includes a form for potential applicants, for contacting COMP.

**FACULTY POSITION**  
**THEORETICAL CONDENSED MATTER PHYSICS**  
**DEPARTMENT OF APPLIED PHYSICS**  
**UNIVERSITY OF TOKYO, JAPAN**

Department of Applied Physics, University of Tokyo invites applications for a full-time tenure-track faculty position at the Associate Professor level in the area of Theoretical Condensed Matter Physics, beginning as early as April of 2008. A Ph.D., or equivalent, is required along with the ability to teach effectively at both graduate and under-graduate levels. We seek an individual of high international caliber who conducts vigorous and significant research programs.

For full consideration for the coming academic year, completed applications should be received before August 31, 2007. Review of the applications will continue until the position is filled. Salary will be commensurate with qualifications and with regulations for employee of University of Tokyo. Medical insurance and other benefits are equivalent to those of employees of Japanese government.

Applicants should submit via postal mail a curriculum vitae, a publication list, a summary of research plan and accomplishments, a health certificate, a list of invited talks in international conferences and workshops, a description on experience on public outreach if any, a description on educational experience if any, an awards list, and two recommendation letters or addresses of two references to:

Professor Seigo Tarucha  
Chair, Department of Applied Physic  
University of Tokyo  
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

For inquiry, please contact Seigo Tarucha at [tarucha@ap.t.u-tokyo.ac.jp](mailto:tarucha@ap.t.u-tokyo.ac.jp)

## Postdoctoral Position

### Imperial College London, United Kingdom

A postdoctoral position in the departments of Materials and Physics, and associated with the Thomas Young Centre for Materials Theory and Simulation ([www.thomasyoungcentre.org](http://www.thomasyoungcentre.org)), is available to work with Dr Peter Haynes on the development and application of the ONETEP code for linear-scaling first-principles quantum-mechanical calculations.

Further details about the post and application procedure may be found at

<http://www.jobs.ac.uk/jobfiles/UB145.html>

or

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## RESEARCH FELLOW POSITIONS

### Materials Theory, Modeling and Simulation Laboratory, Singapore

The Materials Theory, Modeling and Simulation Laboratory (MMSL), a basic research organization sponsored by the Institutes of High Performance Computing (IHPC) and Materials Research and Engineering (IMRE), Singapore, invites applications from outstanding candidates for up to four research fellow positions. The MMSL, under the directorship of Prof. David J. Srolovitz, has existing expertise in a wide range of areas including ab initio theory, dislocation dynamics, phase-field models, solid mechanics, and molecular dynamics. The successful candidates will have latitude in defining and pursuing research into theory, modeling, and simulation of materials. MMSL, located within IHPC, provides access to several supercomputers for large-scale materials simulations. Qualified candidates will possess a PhD degree in materials science, physics, chemistry, solid mechanics or a closely related discipline. Initial appointments are for two-year terms. The remuneration, relocation, and travel budgets are competitive. International candidates are encouraged to apply.

The evaluation of applications will begin immediately, and will continue until all positions are filled. Applicants should submit a resume, their research interests, and three references to (with Job Reference: MMSL) [recruitment@ihpc.a-star.edu.sg](mailto:recruitment@ihpc.a-star.edu.sg), or by mail to Prof. David J. Srolovitz, Institute of High Performance Computing, 1 Science Park Road, #01-01 The Capricorn, Singapore 117528, Republic of Singapore.

**SFB/Transregio 49 Frankfurt - Kaiserslautern - Mainz**

**Project title: Correlated electron systems and ab initio modelling**

**Job type: Postdoctoral Researcher**

**Salary: BAT IIa**

**Duration: The position is available from Oct. 1st, 2007 and renewable on a yearly basis for a maximum of three years.**

Job description:

This position is part of a DFG funded project in the TRR 49 "Systems with variable many-body interactions" on the topic of "Correlations in doped antiferromagnets".

Applications are invited for PostDoc research positions in solid state physics at the Institute for Theoretical Physics of the J.W. Goethe University. The candidates should have a PhD in physics with an excellent academic background and good computational skills. Experience in the fields of correlated electron systems and/or first principle calculations (Density Functional Theory) are expected. The research activities of the groups are in the field of numerical and analytical approaches to strongly correlated electron systems.

Interested applicants should submit a curriculum vitae and arrange for three letters of reference to be sent to the address below.

For more information see <http://www.itp.uni-frankfurt.de/~valenti>

<http://www.itp.uni-frankfurt.de/~gros>

<http://www.itp.uni-frankfurt.de/~jeschke>

Applicants with children are welcome. We explicitly encourage qualified female candidates to apply. Disabled persons with equivalent qualifications will be considered first.

Apply to: Institute for Theoretical Physics Secretariate

E-mail: [secretariate@itp.uni-frankfurt.de](mailto:secretariate@itp.uni-frankfurt.de)

Post:

Institute for Theoretical Physics

Secr. Prof. Valenti/Prof. Gros

Max von Laue-Str. 1

60438 Frankfurt a. M.

Germany

Application deadline: August. 31st, 2007

Further questions to: Alexander Struck, + 49 0631-2052863 or via e-mail (see above).

**SFB/Transregio 49 Frankfurt - Kaiserslautern - Mainz**

**Project title: Correlated electron systems and ab initio modelling**

**Job type: Ph. D. Position**

**Salary: BAT IIa/2**

**Duration: The position is available from Oct. 1st, 2007 and renewable on a yearly basis for a maximum of three years.**

Job description:

These positions are part of a DFG funded project in the TRR 49 "Systems with variable many-body interactions" on the topic of "Correlations in doped antiferromagnets".

Applications are invited for PhD positions in solid state physics at the Institute for Theoretical Physics of the J.W. Goethe University, in the groups of Prof. R. Valent, Prof. C. Gros and Dr. H. Jeschke.

The candidates should have a Diploma/MSc in physics with an excellent academic background and good computational skills. Experience in the fields of correlated electron systems and/or first principle calculations (Density Functional Theory) are expected. The research activities of the groups are in the field of numerical and analytical approaches to strongly correlated electron systems.

Applicants need to have scientific research experience on the level of a German physics Diplom/Master. Interested applicants should submit a curriculum vitae and arrange for three letters of reference to be sent to the address below.

For more information see

<http://www.itp.uni-frankfurt.de/~valenti>

<http://www.itp.uni-frankfurt.de/~gros>

<http://www.itp.uni-frankfurt.de/~jeschke>

Applicants with children are welcome. We explicitly encourage qualified female candidates to apply. Disabled persons with equivalent qualifications will be considered first.

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E-mail: [secretariate@itp.uni-frankfurt.de](mailto:secretariate@itp.uni-frankfurt.de)

Post:

Institute for Theoretical Physics

Secr. Prof. Valenti/Prof. Gros

Max von Laue-Str. 1, 60438 Frankfurt a. M., Germany

Application deadline: August. 31st, 2007

Further questions to: Alexander Struck, + 49 0631-2052863 or via e-mail (see above).

## 6 Abstracts

### Collinear versus non-collinear magnetic order in Pd atomic clusters: Ab-initio calculations

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<sup>1</sup>*Departamento de Física Teórica, Atómica y Óptica, Universidad de Valladolid, E-47011 Valladolid, Spain*

<sup>2</sup>*Departamento de Física. Universidad de Oviedo, Spain*

#### Abstract

We present a thorough theoretical assessment of the stability of non-collinear spin arrangements in small palladium clusters. We generally find that ferromagnetic order is always preferred, but that antiferromagnetic and non-collinear configurations of different sorts exist and compete for the first excited isomers. We also show that the ground state is insensitive to the choice of atomic configuration for the pseudopotential used and to the approximation taken for the exchange and correlation potential. Moreover, the existence and relative stability of the different excited configurations also depends weakly on the approximations employed. These results provide strong evidence on the transferability of pseudopotential and exchange and correlation functionals for palladium clusters as opposed to the situation found for the bulk phases of palladium.

(Physical Review B 74, 174416 (2006) )

Contact person: faustino@dec1.ifisica.uaslp.mx

### Magnetic anisotropies of late transition metal atomic clusters

Lucas Fernández Seivane, Jaime Ferrer Rodríguez

*Departamento de Física, Universidad de Oviedo, 33007 Oviedo, Spain*

#### Abstract

We analyze the impact of the magnetic anisotropy on the geometric structure and magnetic ordering of small atomic clusters of palladium, iridium, platinum and gold, using Density Functional Theory. Our results highlight the absolute need to include self-consistently the spin orbit interaction in any simulation of the magnetic properties of small atomic clusters, and a complete lack of universality in the magnetic anisotropy of small-sized atomic clusters.

(Submitted to PRL)

Latex-file available from: <http://arxiv.org/abs/cond-mat/0610879>

# Predictions for the formation of new atomic chains in Mechanically Controllable Break Junction experiments

Lucas Fernández Seivane, Jaime Ferrer Rodríguez

*Departamento de Física, Universidad de Oviedo, 33007 Oviedo, Spain*

Víctor Manuel García Suárez

*Department of Physics, Lancaster University, Lancaster, LA1 4YB, U. K.*

## Abstract

We analyze the stability and magnetic properties of infinite zigzag atomic chains of a large number of late third, fourth and fifth-row transition metal atoms, as well as of the Group IV elements Si, Ge, Sn and Pb. We find that zigzag chains of third- and fourth-row elements are not stable, while those made of Si, Ge, Sn, Pb, W, Os, Ir, Pt and Au are. These results correlate well with known data in Mechanically Controllable Break Junction experiments (MCBJE). We therefore conjecture that the stability of an infinite chain is at least a necessary condition for the formation of a finite sized one in MCBJE. We therefore predict that Sn and Os, and possibly W and Pb chains may be found in those experiments. We also find that the bonds in Hg chains are extremely soft. We finally show that the magnetic moments and anisotropies of Ir and Pt chains show a non-trivial behavior.

(Submitted to PRB)

Latex-file available from: <http://arxiv.org/abs/cond-mat/0611624>

# Spin configuration in a frustrated ferromagnetic/antiferromagnetic thin film system

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A L Vázquez de Parga,<sup>6</sup> T Mizoguchi,<sup>1</sup> and H van Kempen<sup>7</sup>

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## Abstract

We have studied the magnetic configuration in ultrathin antiferromagnetic Mn films grown around monoatomic steps on an Fe(001) surface by spin-polarized scanning tunneling microscopy/spectroscopy and *ab-initio*-parametrized self-consistent real-space tight binding calculations in which the spin quantization axis is independent for each site thus allowing noncollinear magnetism. Mn grown on Fe(001) presents a layered antiferromagnetic structure. In the regions where the Mn films overgrows Fe steps the magnetization of the surface layer is reversed across the steps. Around these defects a frustration of the antiferromagnetic order occurs. Due to the weakened magnetic coupling at the central Mn layers, the amount of frustration is smaller than in Cr and the width of the wall induced by the step does not change with the thickness, at least for coverages up to seven monolayers.

(Nanotechnology **18** No 23, 235702 (2007))

Contact person: Eduardo Martínez (edmartin@uos.de)

# Structural, elastic and electronic properties of SiC, BN and BeO nanotubes

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*Institut für Festkörperteorie, Universität Münster,  
48149 Münster, Germany*

## Abstract

We present the results of a comparative *ab initio* study of single-walled SiC, BN and BeO nanotubes (NTs) in zigzag and armchair configurations. Within density functional theory, we employ self-interaction-corrected pseudopotentials that were shown previously to yield reliable results for both structural and electronic properties of related bulk crystals. Using these pseudopotentials, we investigate the dependence of the atomic relaxation, strain energy, Young's modulus and electronic structure on nanotube diameter and compound ionicity. Qualitatively, the NTs of all three wide-band-gap compounds show similar radially buckled geometries upon atomic relaxation, similar strain energy progressions with NT diameter and a saturation of Young's modulus as well as the band gap energy for large NT diameters. The band gap progression with NT diameter, which is of crucial importance for device applications, is presented and analysed in detail. For SiC and BN, the calculated band gap energies of zigzag NTs vary much stronger for small and medium diameters than those of their armchair counterparts showing a significant narrowing of the band gaps. In contrast, the band gap progression in zigzag and armchair BeONTs shows a very peculiar behavior for small diameters. No band gap breakdown occurs and the gap goes through a minimum for zigzag BeONTs. The qualitative difference in the nature of the lower conduction band states in SiC and BN NTs, as compared to BeONTs, and the increasing ionicity of these compounds are shown to be responsible for the observed effects.

(Physical Review B, accepted)

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# The hydrogenated SiC(001)-(3×2) surface: Semiconducting and metallic structures

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## Abstract

We report *ab initio* investigations of adsorption processes of atomic hydrogen on the SiC(001)-(3×2) surface. In addition to the previously reported hydrogen-induced metallic surface structures we find semiconducting H adsorption configurations, as well. Most strikingly, the latter turn out to be significantly lower in total energy than the metallic structures. To find out which final adsorption states can actually be reached in experiment, we scrutinize a number of conceivable reaction pathways of additional H atoms from vacuum to different final adsorption sites at the monohydride surface. It turns out that only one of several metallic configurations is most likely while it appears that semiconducting configurations can not be realized although they are lower in total energy. Most interestingly, it seems that H does not easily adsorb on the third layer of the monohydride substrate, as suggested previously by experiment and theory, because it is captured by a Si atom on the second layer when approaching the third layer from vacuum. On the contrary, H adsorption in angular Si-H-Si bonds on the second layer is easily possible and can explain the experimentally observed hydrogen-induced metallization of the SiC(001)-(3×2) surface.

(Phys. Rev. B, submitted)

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# Tunneling magnetoresistance on the sub-nanometer scale

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06099 Halle/Saale, Germany*

## Abstract

The influence of the finite thickness and structure, amorphous or crystalline, of Fe electrodes on the tunneling magnetoresistance (TMR) ratio is investigated by *ab initio* calculations in Fe/MgO/Fe tunnel junctions. It is found that an amorphous Fe layer in direct contact with the MgO barrier causes a low TMR ratio of only 44%. By inserting crystalline Fe monolayers between the barrier and the amorphous Fe the TMR ratio increases rapidly and reaches the same level as for semi-infinite Fe electrodes. Even one crystalline Fe monolayer is sufficient to achieve a giant TMR ratio exceeding 500%. Omitting the amorphous Fe has nearly no influence on the results if there are more than two monolayers of crystalline Fe next to the barrier. The results demonstrate that the reservoirs can be even non-magnetic. The TMR emerges from the interplay of symmetry selection in the barrier and spin filtering at the electrode/barrier interface.

(Accepted for Phys. Rev. Lett., Aug 1st 2007 )

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# The Augmented Spherical Wave Method

## A Comprehensive Treatment

Volker Eyert

*Institut für Physik, Universität Augsburg*

### Abstract

From the cover:

The Augmented Spherical Wave (ASW) method is one of the powerful approaches to handle the requirement of finite basis sets in DFT calculations. While it is particularly suited for the calculation of electronic, magnetic, and optical properties of solid-state materials, recent developments allow to access, in addition, the elastic properties and phonon spectra. The book addresses all those who want to learn about methods for electronic structure calculations and the ASW method in particular.

From the introduction:

The widespread and even commercial use of the ASW method is contrasted by an apparent lack of a comprehensive description. This is where the present book tries to close a gap.

The organization of the book is as follows: Chap. 2 is devoted to the original standard ASW method, which is based on the atomic sphere approximation (ASA) and, hence, while being very efficient does not include any full-potential terms. Chap. 3 deals with the envelope functions as well as the structure constants, which build the analytical anchor of the method. Although this chapter covers exclusively mathematical aspects of the ASW method it does, nevertheless, form the basis for the standard method as well as all further developments. We will benefit from these results especially while introducing in Chap. 4 the full-potential ASW method, which is much more involved than the standard method.

The appendix covers a variety of details regarding the methods dealt with in the main text as well as a chapter on Brillouin-zone integration schemes.

Lect. Notes Phys. 719 (Springer, Berlin Heidelberg 2007)

DOI: 10.1007/978-3-540-71007-3

weblink: <http://dx.doi.org/10.1007/978-3-540-71007-3>

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# Charge Order and the Origin of Giant Magnetocapacitance in $\text{LuFe}_2\text{O}_4$

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## Abstract

The nature of the charge order in the charge frustrated compound  $\text{LuFe}_2\text{O}_4$  and its effect on magnetocapacitance were examined on the basis of first-principles electronic structure calculations and Monte Carlo simulations of electrostatic energy. Our work shows that two different types of charge order of almost equal stability (i.e.,  $\sqrt{3} \times \sqrt{3}$  and chain types) occur in the  $\text{Fe}_2\text{O}_4$  layers of  $\text{LuFe}_2\text{O}_4$ , and that the ground state of  $\text{LuFe}_2\text{O}_4$  has a ferrielectric arrangement of the  $\text{Fe}_2\text{O}_4$  layers with  $\sqrt{3} \times \sqrt{3}$  charge order. The giant magnetocapacitance effect of  $\text{LuFe}_2\text{O}_4$  at room temperature is accounted for in terms of charge fluctuations arising from the interconversion between the two types of charge order, that becomes hindered by an applied magnetic field.

(Phys. Rev. Lett. **98**, 246403 (2007))

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# Ionic radii calculation by combination of the classical model and *ab initio* method for the simple ionic crystals

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<sup>(2)</sup> *Natural Science Center, Kim Il Sung University, Ryongnam-Dong, Taesong-District, Pyongyang, DPR Korea*

## Abstract

Hard sphere models of ionic crystals are combined with *ab initio* calculations of the electronic charge densities, lattice constants and inter ionic distances in the simple  $A_nB_m$ -type ionic crystals, in order to obtain the theoretical ionic radii. Our results are in good agreement with the experiment-derived ionic radii and we suggest that they are able to be adopted in the structure prediction of more complicated crystals.

submitted : Acta Crystallographica A

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## References

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- [2] Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751.
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# On how good DFT exchange-correlation functionals are for H bonds in small water clusters: Benchmarks approaching the complete basis set limit

Biswajit Santra<sup>1</sup>, Angelos Michaelides<sup>1,2</sup>, and Matthias Scheffler<sup>1</sup>

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<sup>2</sup>*Virtual Materials Laboratory, London Center for Nanotechnology and  
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## Abstract

The ability of several density-functional theory (DFT) exchange-correlation functionals to describe hydrogen bonds in small water clusters (dimer to pentamer) in their global minimum energy structures is evaluated with reference to second order Møller Plesset perturbation theory (MP2). Errors from basis set incompleteness have been minimized in both the MP2 reference data and the DFT calculations, thus enabling a consistent systematic evaluation of the true performance of the tested functionals. Among all the functionals considered, the hybrid X3LYP and PBE0 functionals offer the best performance and among the non-hybrid GGA functionals mPWLYP and PBE1W perform the best. The popular BLYP and B3LYP functionals consistently underbind and PBE and PW91 display rather variable performance with cluster size.

(Submitted to Journal of Chemical Physics)

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# Effect of post-growth annealing on the optical properties of InAs/GaAs quantum dots: A tight-binding study

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## Abstract

We present an atomistic study of the strain field, the one-particle electronic spectrum and the oscillator strength of the fundamental optical transition in chemically disordered  $\text{In}_x\text{Ga}_{1-x}\text{As}$  pyramidal quantum dots (QDs). Interdiffusion across the interfaces of an originally pure InAs dot buried in a GaAs matrix is simulated through a simple model, leading to atomic configurations where the abrupt heterointerfaces are replaced by a spatially inhomogeneous composition profile  $x$ . Structural relaxation and the strain field calculations are performed through the Keating valence force field model, while the electronic and optical properties are determined within the empirical tight-binding approach. We analyze the relative impact of two different aspects of the chemical disorder, namely: (i) the effect of the strain relief inside the QD, and (ii) the purely chemical effect due to the group-III atomic species interdiffusion. We find that these effects may be quantitatively comparable, significantly affecting the electronic and optical properties of the dot. Our results are discussed in comparison with recent luminescence studies of intermixed QDs.

(submitted to: J. Appl. Phys.)

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# Density functional theory study of flat and stepped NaCl(001)

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<sup>2</sup>*London Center for Nanotechnology and Department of Chemistry,  
University College London, London WC1E 6BT, UK*

## Abstract

The properties of bulk NaCl, NaCl(001), and stepped NaCl(001) surfaces have been examined with density functional theory within the plane-wave pseudopotential approach. Aiming to remedy the lack of quantitative energetic and structural knowledge of such surfaces, we employ the local-density approximation and generalized gradient approximation Perdew-Burke-Ernzerhof of (PBE) exchange-correlation functionals as well as the PBE Wu-Cohen functional [Phys. Rev. B. **73**, 235116 (2006)] to determine the surface energy and surface structure of NaCl(001). A range of 9–15 meV/Å<sup>2</sup> is obtained for the surface energy of NaCl(001), and the surface is predicted to undergo only small relaxation of the top layer atoms, consistent with low-energy electron diffraction *I-V* analyses. The isolated step formation energy of monoatomic (100)-like steps on NaCl(001) is estimated to be about 40–60 meV/Å<sup>2</sup> and the interaction energy between adjacent steps is weak. Thermodynamics has been employed to determine the relative stabilities of stoichiometric (100)-like and non-stoichiometric (111)-like steps on NaCl(001), revealing that (100)-like steps are significantly more stable than (111)-like steps at all accessible values of the chlorine chemical potential.

(submitted to: Phys. Rev. B)

Contact person: Angelos Michaelides (michaeli@fhi-berlin.mpg.de)

# Simulating ice nucleation, one molecule at a time, with the 'DFT microscope'

Angelos Michaelides

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*Virtual Materials Laboratory, London Center for Nanotechnology and  
Department of Chemistry, University College London, London WC1E 6BT, UK*

## Abstract

Few physical processes are as ubiquitous as the nucleation of water into ice. However, ice nucleation and, in particular, heterogeneously catalyzed nucleation remains poorly understood at the atomic level. Here, we report an initial series of density functional theory (DFT) calculations aimed at putting our understanding of ice nucleation and water clustering at metallic surfaces on a firmer footing. Taking a prototype hydrophobic metal surface, Cu(111), for which scanning tunneling microscopy measurements of water clustering have recently been performed, possible structures of adsorbed clusters comprised of 26 H<sub>2</sub>O molecules have been computed. How the water clusters in this size regime differ from those in the gas phase is discussed, as is the nature of their interaction with the substrate.

(Faraday Discussions, in press)

Contact person: angelos.michaelides@ucl.ac.uk

# Ice nanoclusters at hydrophobic metal surfaces

Angelos Michaelides<sup>1,2</sup> and Karina Morgenstern<sup>3</sup>

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## Abstract

Studies of the structure of supported water clusters provide a means for obtaining a rigorous molecular-scale description of the initial stages of heterogeneous ice nucleation; a processes of importance to fields as diverse as atmospheric chemistry, astrophysics, and biology. Here we report the observation and characterization of metal-supported water hexamers and a family of hydrated nanoclusters - heptamers, octamers, and nonamers through a combination of low temperature scanning tunnelling microscopy experiments and first principles electronic structure calculations. Aside from achieving unprecedented resolution of the cyclic water hexamer the so-called smallest piece of ice we identify and explain a hitherto unknown competition between the ability of water molecules to simultaneously bond to a substrate and to accept H bonds. This competition also rationalizes previous structure predictions for water clusters on other substrates.

(Nature. Mater., in press)

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# Ambipolar doping of SnO<sub>2</sub>

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## Abstract

SnO<sub>2</sub> is widely used as a transparent conductor and sensor material. Better understanding and control of its conductivity would enhance its performance in existing applications and enable new ones, such as in light emitters. Using density functional theory we show that the conventional attribution of *n*-type conductivity to intrinsic point defects is incorrect. Unintentional incorporation of hydrogen provides a consistent explanation of experimental observations. Most importantly, we find that SnO<sub>2</sub> offers excellent prospects for *p*-type doping by incorporation of acceptors on the Sn site. Specific strategies for optimizing acceptor incorporation are presented.

(submitted to: Phys. Rev. Lett.)

Contact person: Matthias Scheffler (scheffler@fhi-berlin.mpg.de)

# Density-functional study of Mn-mono-silicide on Si(001) and Si(111) surfaces: film formation *versus* island nucleation

M. Hortamani<sup>1</sup>, P. Kratzer,<sup>1,2</sup> and M. Scheffler<sup>1</sup>

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## Abstract

The stability of thin films and of small crystallites of Mn-mono-silicide (MnSi) on the low-index Si(001) and Si(111) surfaces is investigated by density-functional theory calculations. The calculated total energies enable us to identify the conditions for the formation of three-dimensional (3D) MnSi islands, either in the B20 crystal structure or as pseudomorphic islands in the B2 structure. On Si(001), 3D islands, even if they are just a few lattice constants wide, are found to be already more stable than a homogeneous MnSi film. A bipyramidal ‘iceberg’ island consisting of MnSi in the B20 structure on the Si(001) substrate is found to be most stable among the structures investigated. For MnSi on Si(111), the critical nucleus for 3D islands is found to be somewhat larger. Therefore flat 2D islands form at low Mn coverage. On Si(111), the lowest-energy structure for such islands is found to be similar to the B20 structure of bulk MnSi, whereas on Si(001) this structure is incompatible with the substrate lattice. Our results are in agreement with the experimental observations, formation of an almost closed film with  $(\sqrt{3} \times \sqrt{3})$  structure on Si(111), and nucleation of 3D islands on Si(001). Similar to previous predictions for MnSi films on Si(001), our calculations indicate that MnSi films on Si(111) have large magnetic moments at the Mn atoms near the surfaces and interfaces, and a high degree of spin polarization at the Fermi level.

(submitted to: Phys. Rev. B)

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## 7 Presenting Other Initiatives: President of Ireland Young Researcher Award (PIYRA) 2008

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Estimated Number of Awards: up to 10 awards.

## 8 SCIENTIFIC HIGHLIGHT OF THE MONTH: "Relativistic Effects and Disordered Local Moments in Magnets"

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### Relativistic Effects and Disordered Local Moments in Magnets

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#### Abstract

A brief review of the 'disordered local moment' (DLM) theory of magnetism at finite temperatures is given. This has recently been enhanced so that it includes relativistic (R) effects such as spin-orbit coupling. The relevance of the R-DLM theory for providing an ab-initio account of the temperature dependence of magnetic properties including magnetotransport is stressed. Magnetic anisotropy is discussed in particular. In this context a new magnetic torque based method is described and demonstrated with an application to iron nanoclusters on a platinum substrate. The R-DLM theory is illustrated by a study of the temperature dependence of the magnetic anisotropy of the technologically important *FePt* alloy in both its magnetically hard  $L1_0$ -ordered and soft cubic compositionally disordered phases.

*Acknowledgements:* It is a pleasure to acknowledge the collaboration of many colleagues on the various aspects occurring in this selective review: in particular *S.Bornemann, J.Minar and H.Ebert* on the magnetic torque calculations on deposited clusters (see [1]) and *B.Gyorffy, S.Ostapin, S.S.A.Razee, L.Szunyogh, A.Buruzs, L.Udvardi and P.Weinberger* on the development of the R-DLM theory (see [2-4]).

## 1 Introduction

In principle, relativistic density functional theory [5] (R-DFT) can describe a magnetic material completely, providing a free energy,  $F$ , ab initio.  $F$  is a functional of the magnetisation,  $\mathbf{M}(\mathbf{r})$ . For a ferromagnetic material the magnetisation is often characterised in terms of  $M_s$ , the saturation magnetisation and a direction  $\mathbf{n} = (n_x, n_y, n_z)$  which is assumed to vary over length scales long compared with atomic ones, i.e.  $\mathbf{M}(\mathbf{r}) = M_s \mathbf{n}(\mathbf{r})$ .  $F$  can now be approximated by the familiar micromagnetic sum of an exchange term with exchange constant  $A$ , an anisotropy term involving  $K$ , a magnetocrystalline anisotropy constant, a term describing the interaction with an applied magnetic field and finally a magnetostatic 'shape anisotropy' term [6]. Materials are typically characterised by a set of  $M_s$ ,  $A$  and  $K$  constants combined into two important length quantities, an 'exchange length',  $l_{ex} = \sqrt{A/M_s^2}$  and a domain wall thickness  $l_w = \sqrt{A/2K}$ .

In nanostructured systems however, such as nanoparticles and thin films, the free energy can no longer be parameterised by three such constants.  $A$ ,  $M_s$  and  $K$  all vary profoundly with composition, dimensionality and shape. The relativistic effect, spin-orbit coupling, is particularly influential.

For low temperatures, calculations of the characteristics of the free energy (ground state energy) of a magnetic material are all based on an electronic band structure which has a fixed spin-polarisation e.g. a uniform spin-polarisation for a ferromagnet and fixed sublattice spin polarisations for an antiferromagnet. With increasing temperature, spin fluctuations are induced which eventually destroy the long-range magnetic order and hence the overall spin polarization of the system's electronic structure. These collective electron modes interact as the temperature is raised and are dependent upon and affect the underlying electronic structure. For many materials the magnetic excitations can be modelled by associating local spin-polarisation axes with all lattice sites and the orientations vary very slowly on the time-scale of the electronic motions. [7] These 'local moment' degrees of freedom produce local magnetic fields on the lattice sites which affect the electronic motions and are self-consistently maintained by them. By taking appropriate ensemble averages over the orientational configurations the system's magnetic properties can be determined. In this article we review our recent work on incorporating relativistic effects into the 'disordered local moment' (DLM) DFT-based theory which is used in this context to describe the onset and type of magnetic order in many magnetic systems [8,9]. In particular inclusion of relativistic effects into DLM theory produces an ab-initio description of the temperature dependence of magnetic anisotropy of metallic ferromagnets which agrees well with experimental results and deviates qualitatively from simple, widely used models [2,3].

It is well-known that a description of magnetic anisotropy,  $K$ , can be provided once relativistic effects such as the spin-orbit coupling on the electronic structure of materials are considered. Over recent years 'first-principles' R-DFT work has been quite successful in describing trends in  $K$  for a range of magnetic materials in bulk, film and nanostructured form [5,10,11] at  $T = 0\text{K}$ , e.g. [12–17]. As well as pinning down the  $K$  constants of micromagnetic models which describe phenomena such as magnetisation reversal processes in magnetic recording materials [18], a careful treatment of spin-orbit coupling also has implications for electronic transport effects such as anisotropic magnetoresistance (AMR) [19]. Until only very recently [2,3], however, little attention was paid to how these relativistic consequences might be influenced by the thermally excited 'local moment' fluctuations. Instead the temperature dependence of  $K$  and associated quantities are related without justification to single ion anisotropy models developed by Callen and Callen and others over 40 years ago [20]. In this article we review our ab-initio theory for the temperature dependence of magnetic anisotropy which challenges this simple outlook.

This consideration is rather topical. In the search for magnetic data storage media with densities well in excess of TBytes/ $\text{in}^2$ , assemblies of increasingly smaller magnetic nanoparticles are being fabricated. [21,22] Thermally driven demagnetisation and loss of data over a reasonable storage period threatens, however, if a particle size limit is breached. A way of fending off this limit is to use materials with high magnetocrystalline anisotropy,  $K$ , since the superparamagnetic diameter of a magnetic particle is proportional to  $(k_B T/K)^{\frac{1}{3}}$ , where  $k_B T$  is the thermal energy. [6] Writing to media of very high  $K$  material can be achieved by temporary heating. [23,24]  $K$  is reduced significantly during the magnetic write process and the information is locked in as the material

cools. Modelling this process and improving the design of high density magnetic recording media therefore requires an understanding of how  $K$  varies with temperature. This consideration also affects estimates of the related blocking temperatures of nanoparticles [25].

In the next section we describe and illustrate briefly our magnetic torque-based method for carrying out ab-initio studies of the magnetic anisotropy of nanoparticles, films, multilayers and bulk materials restricted to 0K. This is rather precise and versatile. We then review the well-tried and tested fluctuating local moment picture of magnetism at finite temperatures and go on to show how relativistic effects can be incorporated into it. The next section has results of an application of this theory to the important magnetic material *FePt* where we demonstrate the profound effect of geometrical structure upon magnetic anisotropy. The final section mentions some ongoing and future developments.

## 2 Ab-initio theory of magnetic anisotropy via the magnetic torque

Magnetocrystalline anisotropy (MAE) is caused largely by spin-orbit coupling and receives an ab-initio description from the relativistic generalisation of spin density functional (R-DFT) theory. [5] Spin-orbit coupling effects are either treated perturbatively or with a fully relativistic theory [12,26]. Typically the total energy, or the single-electron contribution to it (if the force theorem is used), is calculated for two or more magnetisation directions,  $\hat{n}_1$  and  $\hat{n}_2$  separately, and then the MAE is obtained from the difference,  $\Delta F$ .  $\Delta F$  is typically small ranging from meV to  $\mu\text{eV}$  and high precision in calculating the energies is required. For example, we used this rationale with a fully relativistic theory to study the MAE of magnetically soft, compositionally disordered binary and ternary component alloys [26,27] and the effect upon it of short-range [12] and long range chemical order [28] in harder magnets such as *CoPt* and *FePt*.

Experimentally, measurements of magnetocrystalline anisotropy constants of magnets can be obtained from torque magnetometry [6]. From similar considerations of magnetic torque, ab-initio calculations of MAE can be also made. There are obvious advantages in that a single calculation only is needed and reliance is not placed on the accurate extraction of a small difference between two energies. In particular the torque method has been used to good effect by Freeman and co-workers [29] in conjunction with their state-tracking method to study the MAE of a range of uniaxial magnets including layered systems. Recently we described how to calculate the torque directly and obtain the MAE using spin-polarised, relativistic multiple scattering theory [3]. This scattering theoretical basis makes the approach very versatile and precise, relevant to the study of nanoclusters and thin films [1,4,30] as well as bulk systems [3]. We describe the method briefly here and illustrate it with a calculation of Fe clusters on Pt substrates before proceeding to the finite temperature extension. Full details can be found in ref. [3].

If the free energy of a material magnetised along a direction specified by

$$\hat{n} = (\sin \vartheta \cos \varphi, \sin \vartheta \sin \varphi, \cos \vartheta) \quad (2)$$

is  $F^{(\hat{n})}$ , then the torque is

$$\vec{T}^{(\hat{n})} = -\frac{\partial F^{(\hat{n})}}{\partial \hat{n}}. \quad (3)$$

The contribution to the torque from the anisotropic part of  $F^{(\hat{n})}$  leads to a direct link between the gap in the spin wave spectrum and the MAE by the solution of the equation [31]

$$\frac{d\hat{n}}{dt} = \gamma(\hat{n} \wedge \vec{T}^{(\hat{n})}). \quad (4)$$

where  $\gamma$  is the gyromagnetic ratio. Closely related to  $\vec{T}^{(\hat{n})}$  is the variation of  $F^{(\hat{n})}$  with respect to  $\vartheta$  and  $\varphi$ , i.e.  $T_\vartheta(\vartheta, \varphi) = -\frac{\partial F^{(\hat{n})}}{\partial \vartheta}$  and  $T_\varphi(\vartheta, \varphi) = -\frac{\partial F^{(\hat{n})}}{\partial \varphi}$ . As shown by Wang et al. [29], for most uniaxial magnets, which are well approximated by a free energy of the form

$$F^{(\hat{n})} = F_{iso} + K_2 \sin^2 \vartheta + K_4 \sin^4 \vartheta, \quad (5)$$

(where  $K_2$  and  $K_4$  and magnetocrystalline anisotropy constants and  $F_{iso}$  is the isotropic part of the free energy),  $T_\vartheta(\vartheta = \pi/4, \varphi = 0) = -(K_2 + K_4)$ . This is equal to the MAE,  $\Delta F = F^{(1,0,0)} - F^{(0,0,1)}$ . For a magnet with cubic symmetry so that

$$F^{(\hat{n})} \approx F_{iso} + K_1(\sin^4 \vartheta \sin^2 2\varphi + \sin^2 2\vartheta), \quad (6)$$

a calculation of  $T_\varphi(\vartheta = \pi/2, \varphi = \pi/8)$  gives  $-K_1/2$ , the leading MAE constant.

The derivation of our formalism for  $\vec{T}$  starts from the single electron energy sum part of the free energy from R-DFT. In terms of the integrated electronic density of states,  $N^{(\hat{n})}(\varepsilon)$ , for a system magnetised along a direction  $(\hat{n})$ , this is

$$F^{(\hat{n})} = - \int^{\varepsilon_F^{(\hat{n})}} d\varepsilon N^{(\hat{n})}(\varepsilon). \quad (7)$$

In multiple scattering theory the integrated density of states is written particularly succinctly using the Lloyd formula [32]

$$N^{(\hat{n})}(\varepsilon) = N_0(\varepsilon) - \frac{1}{\pi} \text{Im} \ln \det \left( \underline{\underline{t}}(\hat{n}; \varepsilon)^{-1} - \underline{\underline{G}}_0(\varepsilon) \right), \quad (8)$$

where  $\underline{\underline{t}}(\hat{n}; \varepsilon)$  describes an array of single site scattering t-matrices (combined into a super matrix in site and angular momentum space) and  $\underline{\underline{G}}_0(\varepsilon)$  specifies the structure constants which contain all the information as to where the scatterers are spatially located. At this point we restrict the discussion to all scatterers being determined by spin-only magnetic fields aligned with a single direction  $\hat{n}$ .

At a site  $i$  the t-matrix describing the scattering from a scalar potential and vector magnetic field, located in the unit cell surrounding the site, is obtained from the solution of the Dirac equation. Following a Gordon decomposition of the 4-current and neglect of diamagnetic effects, the magnetic field  $B(\mathbf{r})\hat{n}$  couples only to the spin-only current. This means that fields  $V(\mathbf{r})\tilde{\mathbf{I}}$  and  $\tilde{\beta}\tilde{\sigma}_z B(\mathbf{r})$  are included in the Dirac equation [33] where the z-axis of the local coordinate frame is aligned with  $\hat{n}$ . ( $\tilde{\mathbf{I}}$ ,  $\tilde{\beta}$  and  $\tilde{\sigma}$  are the usual  $4 \times 4$  matrices). A simple transformation produces a t-matrix for the general coordinate frame,

$$t_i(\hat{n}; \varepsilon) = \underline{\underline{R}}(\hat{n}) t_i(\hat{z}; \varepsilon) \underline{\underline{R}}(\hat{n})^+ \quad (9)$$

where  $\underline{\underline{R}}(\hat{n}) = \exp i\alpha_{\hat{m}}(\hat{m} \cdot \underline{\underline{J}})$  where  $\alpha_{\hat{m}}$  is the angle of rotation about an axis  $\hat{m} = (\hat{z} \wedge \hat{n})/|\hat{z} \wedge \hat{n}|$  and  $\underline{\underline{J}}$  is the total angular momentum. The torque quantity  $T_{\alpha_{\hat{a}}}^{(\hat{n})} = -\frac{\partial F^{(\hat{n})}}{\partial \alpha_{\hat{a}}}$ , describing the

variation of the total energy with respect to a rotation of the magnetisation about a general axis  $\hat{u}$ , is

$$T_{\alpha_{\hat{u}}}^{(\hat{n})} = -\frac{1}{\pi} \int^{\varepsilon_F^{(\hat{n})}} d\varepsilon \operatorname{Im} \frac{\partial}{\partial \alpha_{\hat{u}}} \left[ \ln \det \left( \underline{t}(\hat{n}; \varepsilon)^{-1} - \underline{G}_0(\varepsilon) \right) \right] \quad (10)$$

which can be written

$$T_{\alpha_{\hat{u}}}^{(\hat{n})} = -\frac{1}{\pi} \int^{\varepsilon_F^{(\hat{n})}} d\varepsilon \operatorname{Im} \sum_i \operatorname{tr} \left( \underline{\tau}_{ii}^{(\hat{n})}(\varepsilon) \frac{\partial}{\partial \alpha_{\hat{u}}} \left( \underline{R}(\hat{n}) \underline{t}(\hat{n}; \varepsilon)^{-1} \underline{R}(\hat{n})^+ \right) \right) \quad (11)$$

where the KKR scattering path operator [34] is

$$\underline{\tau}^{(\hat{n})} = \left( \left( \underline{t}^{(\hat{n})} \right)^{-1} - \underline{G}_0 \right)^{-1}. \quad (12)$$

Since  $\frac{\partial \underline{R}(\hat{n})}{\partial \alpha_{\hat{u}}} = i(\underline{J} \cdot \hat{u}) \underline{R}(\hat{n})$  and  $\frac{\partial \underline{R}(\hat{n})^+}{\partial \alpha_{\hat{u}}} = -i(\underline{J} \cdot \hat{u}) \underline{R}(\hat{n})^+$ , we obtain the key expression

$$T_{\alpha_{\hat{u}}}^{(\hat{n})} = \frac{1}{\pi} \int^{\varepsilon_F^{(\hat{n})}} d\varepsilon \operatorname{Im} i \sum_i \operatorname{tr} \left( \underline{\tau}_{ii}^{(\hat{n})}(\varepsilon) \left[ (\underline{J} \cdot \hat{u}) \underline{t}(\hat{n}; \varepsilon)^{-1} - \underline{t}(\hat{n}; \varepsilon)^{-1} (\underline{J} \cdot \hat{u}) \right] \right). \quad (13)$$

For  $T_{\vartheta(\varphi)}^{(\hat{n})}$ ,  $(\underline{J} \cdot \hat{u})$  is just  $\underline{J}_{y(z)}$ .

As an illustration of this approach we show in Figure 1 results of an investigation of the magnetic anisotropy of iron dimers and trimers on an Pt surface [1]. It is evident that the torque  $T_{\vartheta}$  and hence the MAE drop significantly when going from the dimer to the trimer. Adding the Pt decoration to the three atom cluster, however, restores a high MAE. With the inner  $Fe_3$  part of the  $Fe_3Pt_3$  cluster surrounded the variation of the MAE with  $\varphi$  is strongly reduced.

The magnetic anisotropy of a system diminishes rapidly as the temperature is raised from 0K and the rapidity of this decrease is, like magnetic anisotropy itself, strongly affected by the system's geometrical structure - typically the higher the symmetry the faster the collapse. In the next section we show how this effect emerges from a simple 'spin' model and then, later on, from a fully ab-initio interacting electron description of a magnetic material. We will see, however, how the latter is sometimes qualitatively different from the former.

### 3 Magnetic anisotropy of a single ion model

For a crystal of a magnet the symmetry connection can be made explicit by writing its magnetic anisotropy as  $K = \sum_{\gamma} K_{\gamma} g_{\gamma}(\hat{n})$  where the  $K_{\gamma}$ 's are coefficients,  $\hat{n}$  is the magnetisation direction and  $g_{\gamma}$ 's are polynomials (spherical harmonics) of the angles  $\vartheta$ ,  $\varphi$ . The  $g_{\gamma}$ 's belong to the fully symmetric representation of the crystal point group - particular examples for uniaxial and cubic magnets have already been used in the last section. As the temperature rises,  $K$  decreases rapidly. The key features of the results of the theoretical work carried out over 40 years ago on this effect [20] come from simple classical spin models of magnetic insulators. Here magnetic moments are associated with the lattice sites of the material. The anisotropic behaviour of such a set of localised 'spins' is given by a term in the hamiltonian  $H_{an} = \sum_i \sum_{\gamma} k_{\gamma} g_{\gamma}(\hat{e}_i)$  with  $\hat{e}_i$  a unit vector denoting the spin direction on the site  $i$ . As the temperature is raised, the 'spins' sample the energy surface over a small angular range about the magnetisation direction  $\hat{n}$  and

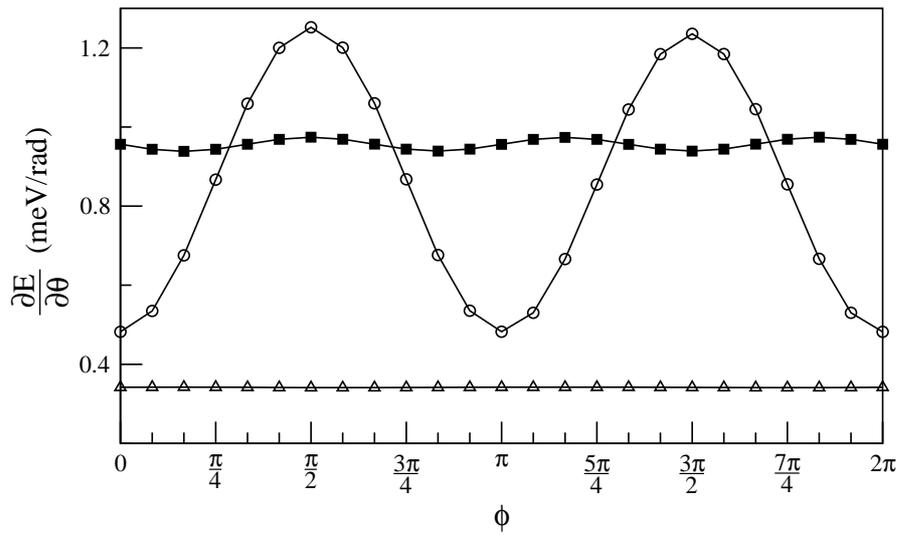
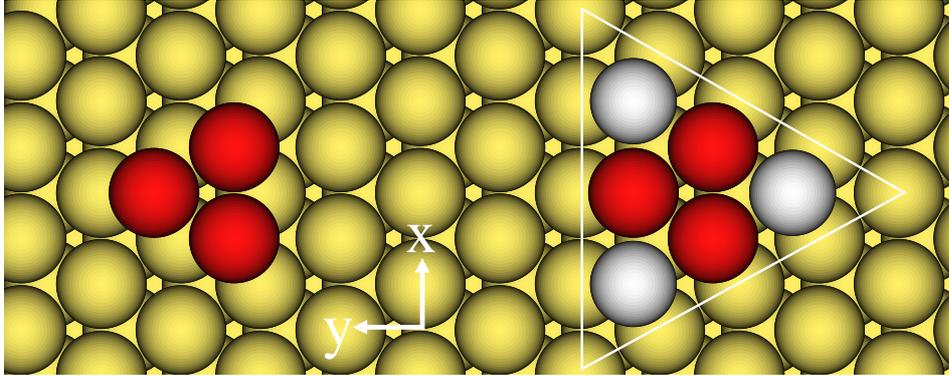


Figure 1: From ref. [1]. Top panel: Structure of a Fe trimer on Pt(111) without (left) and with (right) decoration by three Pt atoms. Bottom panel: torque component  $T_\theta(\theta, \phi)$  for Fe<sub>2</sub> (circles), Fe<sub>3</sub> (triangles) and Pt<sub>3</sub>Fe<sub>3</sub> (squares) for  $\theta = \frac{\pi}{4}$  as a function of the azimuth angle  $\phi$ .

the anisotropy energy is given from the difference between averages taken for the magnetisation along the easy and hard directions. If the coefficients  $k_\gamma$  are assumed to be rather insensitive to temperature, the dominant thermal variation of  $K$  for a ferromagnet is given by  $K(T)/K(0) = \langle g_l(\hat{e}) \rangle_T / \langle g_l(\hat{e}) \rangle_0$ . The averages  $\langle \dots \rangle_T$  are taken such that  $\langle \hat{e} \rangle_T = m(T)$ , the magnetisation of the system at temperature  $T$ , and  $l$  is the order of the spherical harmonic describing the angular dependence of the local anisotropy i.e.  $l = 2$  for a uniaxial system and 4 for a cubic one. At low temperatures  $K(T)/K(0) \approx (m(T)/m(0))^{l(l+1)/2}$  and near the Curie temperature  $T_c$ ,  $K(T)/K(0) \approx (m(T)/m(0))^l$ .

It is helpful for later discussion of the ab-initio theory to show where these results come from in a little more detail. Consider a classical spin hamiltonian for, say, a uniaxial ferromagnet.

$$H = -\frac{1}{2} \sum_{i,j} J_{ij} \hat{e}_i \cdot \hat{e}_j - k \sum_i (\hat{n}_0 \cdot \hat{e}_i)^2 \quad (14)$$

where  $\hat{e}_i$  describes the orientation of a classical spin at site  $i$  and  $J_{ij}$  and  $k$  are exchange and anisotropy parameters.  $\hat{n}_0$  is a unit vector along the magnetic easy axis. A mean field description of the system is given by reference to a hamiltonian  $\sum_i \vec{h} \cdot \hat{e}_i$  where the orientation of Weiss field  $\vec{h}$ , i.e.  $\vec{h} = h\hat{n}$ , determines the direction of the magnetisation of the system and has direction cosines  $(\sin \vartheta \cos \varphi, \sin \vartheta \sin \varphi, \cos \vartheta)$ . Within this mean field approximation the magnetisation  $m$  is  $\vec{m}(T) = \int \hat{e} P(\hat{e}) d\hat{e}$  where the probability of a spin being orientated along  $\hat{e}$  is  $P(\hat{e}) = e^{-\beta h \hat{n} \cdot \hat{e}} / Z_0$  with  $Z_0 = \int e^{-\beta h \hat{n} \cdot \hat{e}} d\hat{e}$ . The free energy difference per site between the system magnetised along two directions  $\hat{n}_1$  and  $\hat{n}_2$  is

$$K(T) = -\frac{k}{Z_0} \int ((\hat{n}_0 \cdot \hat{e})^2 e^{-\beta h \hat{n}_1 \cdot \hat{e}} - (\hat{n}_0 \cdot \hat{e})^2 e^{-\beta h \hat{n}_2 \cdot \hat{e}}) d\hat{e} \quad (15)$$

If  $\hat{n}_1$  and  $\hat{n}_2$  are parallel and perpendicular to the magnetic easy axis  $\hat{n}_0$  respectively then

$$K(T) = -\frac{k}{Z_0} \int g_2(\hat{n}_0 \cdot \hat{e}) e^{-\beta h \hat{n}_0 \cdot \hat{e}} d\hat{e} \quad (16)$$

where  $g_2$  is the Legendre polynomial  $(3(\hat{n}_0 \cdot \hat{e})^2 - 1)/2$ . As a function of the magnetisation  $m(T)/m(0)$ ,  $K(T)/K(0)$  varies as specified above, i.e. quadratically near the Curie temperature  $T_c$  and cubically at low  $T$ . The same dependence can be shown for this simple spin model for the rate of variation of magnetic anisotropy with angle  $\vartheta$  that the magnetisation makes with the system's easy axis, namely the magnetic torque [6]  $T_\vartheta = -\partial K / \partial \vartheta$ .

Of course in a real magnetic system with itinerant electrons it is not correct to apportion electrons among the sites at which the material's nuclei are positioned. Instead it is necessary to return to the fundamentals of R-DFT and to see how a tractable finite temperature generalisation can be worked out.

## 4 Magnetism at finite temperatures - 'Disordered Local Moments'

In principle the extension of electronic density functional theory to finite temperatures was carried out by Mermin [35] soon after the pioneering papers of Hohenberg, Kohn and Sham [36].

The single particle entropy is included and the effective one-electron fields involve  $\Omega_{xc}$ , the exchange-correlation part of the Gibbs Free Energy functional of particle and magnetisation densities. Formally this can be expressed in terms of spin-dependent pair correlation functions  $g_\lambda(\sigma, \sigma'; \mathbf{r}, \mathbf{r}')$ , i.e.

$$\Omega_{xc}[n, \mathbf{m}] = \frac{e^2}{2} \int_0^1 d\lambda \int d\mathbf{r} \int d\mathbf{r}' \sum_{\sigma, \sigma'} \frac{n_\sigma(\mathbf{r})n_{\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} g_\lambda(\sigma, \sigma'; \mathbf{r}, \mathbf{r}') \quad (17)$$

where  $n_\sigma(\mathbf{r})$  is the spin resolved density.

It would seem logical then simply to make the finite temperature extension of the LDA (or GGA) that is successfully exploited in applications on the ground state of magnetic materials. So, for example,  $\Omega_{xc}[n, \mathbf{m}]$  is replaced by  $\int d\mathbf{r} n(\mathbf{r}) \Omega_{xc}^0(n(\mathbf{r}))$  where  $\Omega_{xc}^0$  is the exchange-correlation part of the Gibbs Free Energy of a homogeneous electron gas. This assumption allows the thermally averaged magnetisation,  $\bar{M}$ , along with the spin splitting of the electronic structure to decrease only by the excitation of particle-hole, ‘Stoner’ excitations across the Fermi surface. However, it severely underestimates the effects of the thermally induced spin-wave excitations. The calculated Curie temperatures are often up to an order of magnitude too high, there is no obvious mechanism for moments in the paramagnetic state and the uniform static paramagnetic susceptibility does not follow a Curie-Weiss behaviour as found for many metallic systems.

Evidently, part of the pair correlation function  $g_\lambda(\sigma, \sigma'; \mathbf{r}, \mathbf{r}')$  should be related by the fluctuation dissipation theorem to the magnetic susceptibilities harbouring information about spin waves. These spin fluctuations interact as temperature is increased and so  $\Omega_{xc}[n, \mathbf{m}]$  should deviate significantly from the local approximation with a consequent impact upon the form of the effective single electron states. Indeed accounts of modern electronic structure theory for magnetic systems [10, 11] have large sections devoted to work which is concerned with the of modelling spin fluctuation effects whilst maintaining the spin-polarised single electron basis.

Most of this work is based on a rather simple, pervasive picture of fluctuating ‘local moments’ which stems from the belief of a time scale separation of the electronic degrees of freedom. An electron travels from site to site on a much faster timescale than that of the spin waves. So the dominant thermal fluctuation of the magnetisation which the straightforward finite temperature extension of spin-polarised band theory misses can be pictured quite simply as orientational fluctuations of ‘local moments’. These entities are the magnetisations within each unit cell of the underlying crystal lattice which are set up by the collective behaviour of all the electrons. Their orientations persist on timescales long compared to electronic ‘hopping’ times. At low temperatures, their long wavelength, slow spin wave dynamics can be directly extracted from the transverse part of the magnetic susceptibility. At higher temperatures the more complex behaviour can be described with a classical treatment. The energy is considered of the many interacting electron system constrained so that its local magnetisations are oriented along prescribed directions, i.e. a ‘local moment’ configuration. Averages over such orientational configurations are subsequently taken to determine the equilibrium properties of the system.  $\bar{M}$  can now vanish as the disorder of the ‘local moments’ grows. There remains, however, the issue as to which fluctuations are the most important.

Formally R-DFT [5, 8] specifies the ‘generalised’ grand potential,  $\Omega^{(\hat{n})}(\{\hat{e}\})$ , of an itinerant electron system which is constrained in such a way that the site by site spin polarisation axes

are configured according to  $\{\hat{e}\} = \{\hat{e}_1, \hat{e}_2, \dots, \hat{e}_N\}$  where  $N$  is the number of sites (moments) in the system. The  $\{\hat{e}\}$ , classical unit vectors, are thus the degrees of freedom describing the local moment orientations and  $\Omega^{(\hat{n})}(\{\hat{e}\})$  is the ‘local moment’ hamiltonian. With relativistic effects such as spin-orbit coupling included, magnetic anisotropy can be described. This means that orientations of the local moments with respect to a specified direction  $\hat{n}$  within the material are relevant.

One way forward from this point is to carry out calculations of  $\Omega^{(\hat{n})}(\{\hat{e}\})$  for a selection of configurations (‘spin’ spirals, 2 impurities in a ferromagnet, magnetically ordered supercells etc.) by making some assumptions about the most dominant fluctuations. One then fits the set of  $\Omega^{(\hat{n})}(\{\hat{e}\})$ ’s to a simple functional form. For the non-relativistic limit typically a classical Heisenberg model,  $\Omega^{(\hat{n})}(\{\hat{e}\}) = -\frac{1}{2} \sum_{ij} J_{ij} \hat{e}_i \cdot \hat{e}_j$  is set up and various statistical mechanics methods (e.g. Monte Carlo) are used to produce the desired thermodynamic averages. Many useful studies have been carried out in this way but there is a risk that a bias is produced so that some of the physics is missed. The spin polarised electronic structures of the restricted set of constrained systems are not guaranteed to generate magnetic correlations that are consistent with the chosen sampling of the orientational configurations. In other words the electronic and magnetic structures are not necessarily mutually consistent. When spin-orbit coupling effects are included these worries grow - there is the question about what form the anisotropy of the effective spin model should take. Should it, perhaps, be a classical isotropic Heisenberg model with a single site anisotropy term that was illustrated in the last section or will this be inconsistent with the underlying electronic behaviour? In the following we summarise the main points of our ‘disordered local moment’ (DLM) theory which avoids these problems. Full details can be found in references [8,9] and in references [2,3] for the relativistic extension. In particular its description of the temperature dependent magnetic anisotropy can be qualitatively different from that of simple spin models as we will show later.

The ‘disordered local moment’ (DLM) picture is implemented within a multiple-scattering (Korringa-Kohn-Rostoker, KKR) [37–39] formalism. Some applications include the description of the experimentally observed local exchange splitting and magnetic short-range order in both ultra-thin Fe films [40] and bulk Fe [8], the damped RKKY-like magnetic interactions in the compositionally disordered CuMn ‘spin-glass’ alloys [41] and the onset of magnetic order in a range of alloys [42,43]. By combining it with the local self-interaction correction (L-SIC) [44] for strong electron correlation effects, we have also recently used it to account quantitatively for the magnetic ordering in the heavy rare earths [45].

## 5 Relativistic Disordered Local Moment (R-DLM) Theory

We consider a collinear magnetic system magnetised with reference to a single direction  $\hat{n}$  at a temperature  $T$ . (A non-collinear generalisation can be made by making the notation more complicated.) The orientational probability distribution is denoted by  $P^{(\hat{n})}(\{\hat{e}\})$ , and its average

$$\langle \hat{e}_i \rangle = \int \dots \int \hat{e}_i P^{(\hat{n})}(\{\hat{e}\}) d\hat{e}_1 \dots d\hat{e}_N = \hat{n}. \quad (18)$$

is aligned with the magnetisation direction  $\hat{n}$ . The canonical partition function and the probability function are defined as

$$Z^{(\hat{n})} = \int \dots \int e^{-\beta \Omega^{(\hat{n})}(\{\hat{e}\})} d\hat{e}_1 \dots d\hat{e}_N, \quad (19)$$

and

$$P^{(\hat{n})}(\{\hat{e}\}) = \frac{e^{-\beta \Omega^{(\hat{n})}(\{\hat{e}\})}}{Z^{(\hat{n})}}, \quad (20)$$

respectively. The thermodynamic free-energy which includes the entropy associated with the orientational fluctuations as well as creation of electron-hole pairs, is given by

$$F^{(\hat{n})} = -\frac{1}{\beta} \ln Z^{(\hat{n})}. \quad (21)$$

By choosing a trial Hamiltonian function,  $\Omega_0^{(\hat{n})}(\{\hat{e}\})$  with  $Z_0^{(\hat{n})} = \int \dots \int e^{-\beta \Omega_0^{(\hat{n})}(\{\hat{e}\})} d\hat{e}_1 \dots d\hat{e}_N$ ,

$$P_0^{(\hat{n})}(\{\hat{e}\}) = \frac{e^{-\beta \Omega_0^{(\hat{n})}(\{\hat{e}\})}}{Z_0^{(\hat{n})}} \quad (22)$$

and  $F_0^{(\hat{n})} = -\frac{1}{\beta} \ln Z_0^{(\hat{n})}$  the *Feynman-Peierls Inequality* [46] implies an upper bound for the free energy, i.e.,

$$F^{(\hat{n})} \leq F_0^{(\hat{n})} + \left\langle \Omega^{(\hat{n})} - \Omega_0^{(\hat{n})} \right\rangle^0, \quad (23)$$

where the average refers to the probability  $P_0^{(\hat{n})}(\{\hat{e}\})$ . By expanding  $\Omega_0^{(\hat{n})}(\{\hat{e}\})$  as

$$\Omega_0^{(\hat{n})}(\{\hat{e}\}) = \sum_i \omega_i^{1(\hat{n})}(\hat{e}_i) + \frac{1}{2} \sum_{i \neq j} \omega_{i,j}^{2(\hat{n})}(\hat{e}_i, \hat{e}_j) + \dots, \quad (24)$$

the ‘best’ trial system is found to satisfy [8, 9]

$$\left\langle \Omega^{(\hat{n})} \right\rangle_{\hat{e}_i}^0 - \left\langle \Omega^{(\hat{n})} \right\rangle^0 = \left\langle \Omega_0^{(\hat{n})} \right\rangle_{\hat{e}_i}^0 - \left\langle \Omega_0^{(\hat{n})} \right\rangle^0, \quad (25)$$

$$\left\langle \Omega^{(\hat{n})} \right\rangle_{\hat{e}_i, \hat{e}_j}^0 - \left\langle \Omega^{(\hat{n})} \right\rangle^0 = \left\langle \Omega_0^{(\hat{n})} \right\rangle_{\hat{e}_i, \hat{e}_j}^0 - \left\langle \Omega_0^{(\hat{n})} \right\rangle^0, \quad (26)$$

and so on, where  $\langle \cdot \rangle_{\hat{e}_i}$  or  $\langle \cdot \rangle_{\hat{e}_i, \hat{e}_j}$  denote restricted statistical averages with  $\hat{e}_i$  or both  $\hat{e}_i$  and  $\hat{e}_j$  kept fixed, respectively. (In the following we shall omit the superscript 0 from the averages.)

If we set  $\Omega_0^{(\hat{n})}(\{\hat{e}\})$  as a sum of mean field Weiss terms

$$\Omega_0^{(\hat{n})}(\{\hat{e}\}) = \sum_i \vec{h}_i^{(\hat{n})} \cdot \hat{e}_i \quad (27)$$

where  $\vec{h}_i^{(\hat{n})} = h_i^{(\hat{n})} \hat{n}$  with

$$h_i^{(\hat{n})} = \int \frac{3}{4\pi} (\hat{e}_i \cdot \hat{n}) \left\langle \Omega^{(\hat{n})} \right\rangle_{\hat{e}_i} d\hat{e}_i. \quad (28)$$

the probability distribution is

$$P_i^{(\hat{n})}(\hat{e}_i) = \frac{\exp\left(-\beta \vec{h}_i^{(\hat{n})} \cdot \hat{e}_i\right)}{Z_i^{(\hat{n})}} = \frac{\beta h_i^{(\hat{n})}}{4\pi \sinh \beta h_i^{(\hat{n})}} \exp\left(-\beta \vec{h}_i^{(\hat{n})} \cdot \hat{e}_i\right). \quad (29)$$

and the average alignment of the local moments, proportional to the magnetisation, is

$$\vec{m}_i^{(\hat{n})} = \int \hat{e}_i P_i^{(\hat{n})}(\hat{e}_i) d\hat{e}_i = m_i^{(\hat{n})} \hat{n} \quad (30)$$

and

$$m_i^{(\hat{n})} = -\frac{d \ln Z_i^{(\hat{n})}}{d(\beta h_i^{(\hat{n})})} = \frac{1}{\beta h_i^{(\hat{n})}} - \coth \beta h_i^{(\hat{n})} = L(-\beta h_i^{(\hat{n})}) \quad (31)$$

follows, where  $L(x)$  is the Langevin function. Moreover the free energy of the system is

$$F^{(\hat{n})} = \langle \Omega^{(\hat{n})} \rangle + \frac{1}{\beta} \sum_i \int P_i^{(\hat{n})}(\hat{e}_i) \ln P_i^{(\hat{n})}(\hat{e}_i) d\hat{e}_i. \quad (32)$$

This is the key expression for the evaluation of the magnetic anisotropy energy.

Another way of writing the Weiss field is [8]

$$h_i^{(\hat{n})} = S_i^{1,(\hat{n})} = \frac{\partial \langle \Omega^{(\hat{n})} \rangle}{\partial m_i^{(\hat{n})}} \quad (33)$$

Using equations (29) and (31), this is shown to be equivalent to solving the equation of state

$$\frac{\partial F^{(\hat{n})}}{\partial m_i^{(\hat{n})}} = 0. \quad (34)$$

Note that an identical Weiss field  $\vec{h}^{(\hat{n})}$  associated with every site corresponds to a description of a ferromagnetic system magnetised along  $\hat{n}$  with no reference to an external field.

The paramagnetic state is given by the Weiss fields being zero so that the probabilities,  $P_i^{(\hat{n})} = \frac{1}{4\pi}$  and on any site a moment has an equal chance of pointing in any direction. This means the magnetisations,  $m_i^{(\hat{n})}$  vanish. The magnetic transition temperature, onset and type of magnetic order can be extracted by studying the effects of a small inhomogeneous magnetic field on this high  $T$  paramagnetic state [8, 9]. From the equation of state when the effects of the external magnetic field are included the paramagnetic susceptibility can be obtained [8]

$$\chi_{ij} = \frac{\beta}{3} \sum_k S_{ik}^{2,(\hat{n})} \chi_{kj} + \frac{\beta}{3} \delta_{ij} \quad (35)$$

where

$$S_{ik}^{2,(\hat{n})} = \frac{\delta^2 \langle \Omega^{(\hat{n})} \rangle}{\delta m_i^{(\hat{n})} \delta m_k^{(\hat{n})}} = \frac{9}{16\pi^2} \int \int (\hat{e}_i \cdot \hat{n}) \langle \Omega^{(\hat{n})} \rangle_{\hat{e}_i, \hat{e}'_k} (\hat{e}'_k \cdot \hat{n}) d\hat{e}_i d\hat{e}'_k \quad (36)$$

## 5.1 The role of the CPA

In our work we carry out the averaging over local moment configurations using Coherent Potential Approximation (CPA) [38, 39, 47] technology. The electronic charge density and also the magnetisation density, which sets the magnitudes,  $\{\mu\}$ , of the local moments, are determined from a self-consistent field (SCF)-KKR-CPA [39] calculation. For a given set of (self-consistent) potentials, electronic charge and local moment magnitudes the orientations of the local moments are accounted for by the similarity transformation of the single-site t-matrices [48],

$$\underline{t}_i(\hat{e}_i) = \underline{R}(\hat{e}_i) \underline{t}_i(\hat{z}) \underline{R}(\hat{e}_i)^+ , \quad (37)$$

where for a given energy (not labelled explicitly)  $\underline{t}_i(\hat{z})$  stands for the  $t$ -matrix with effective field pointing along the local  $z$  axis [33] and  $\underline{R}(\hat{e}_i)$ , as before, is a unitary representation of the  $O(3)$  transformation that rotates the  $z$  axis along  $\hat{e}_i$ .

The CPA determines an effective medium through which the motion of an electron mimics the motion of an electron *on the average*. In a system magnetised along a direction  $\hat{n}$ , the medium is specified by  $t$ -matrices,  $\underline{t}_{i,c}^{(\hat{n})}$ , which satisfy the condition [38],

$$\langle \underline{\mathcal{T}}_{ii}^{(\hat{n})}(\{\hat{e}\}) \rangle = \int \langle \underline{\mathcal{T}}_{ii}^{(\hat{n})} \rangle_{\hat{e}_i} P_i^{(\hat{n})}(\hat{e}_i) d\hat{e}_i = \underline{\mathcal{T}}_{ii,c}^{(\hat{n})}, \quad (38)$$

where the site-diagonal matrices of the multiple scattering path operator [34] are defined as,

$$\langle \underline{\mathcal{T}}_{ii}^{(\hat{n})} \rangle_{\hat{e}_i} = \underline{\mathcal{T}}_{ii,c}^{(\hat{n})} \underline{D}_i^{(\hat{n})}(\hat{e}_i), \quad (39)$$

$$\underline{D}_i^{(\hat{n})}(\hat{e}_i) = \left( \underline{1} + \left[ \underline{t}_i(\hat{e}_i)^{-1} - \left( \underline{t}_{i,c}^{(\hat{n})} \right)^{-1} \right] \underline{\mathcal{T}}_{ii,c}^{(\hat{n})} \right)^{-1}, \quad (40)$$

and

$$\underline{\mathcal{T}}_c^{(\hat{n})} = \left( \left( \underline{t}_c^{(\hat{n})} \right)^{-1} - \underline{G}_0 \right)^{-1}. \quad (41)$$

Eq. (38) can be rewritten in terms of the excess scattering matrices,

$$\underline{X}_i^{(\hat{n})}(\hat{e}_i) = \left( \left[ \left( \underline{t}_{i,c}^{(\hat{n})} \right)^{-1} - \underline{t}_i(\hat{e}_i)^{-1} \right]^{-1} - \underline{\mathcal{T}}_{ii,c}^{(\hat{n})} \right)^{-1}, \quad (42)$$

in the form

$$\int \underline{X}_i^{(\hat{n})}(\hat{e}_i) P_i^{(\hat{n})}(\hat{e}_i) d\hat{e}_i = \underline{0}. \quad (43)$$

Thus, for a given set of Weiss fields,  $h_i^{(\hat{n})}$ , and corresponding probabilities,  $P_i^{(\hat{n})}(\hat{e}_i)$  Eq.(43) can be solved by iterating together with Eqs.(42) and (41) to obtain the matrices,  $\underline{t}_{i,c}^{(\hat{n})}$  [3].

Using the magnetic force theorem again the single-particle energy part of the R-DFT Grand Potential gives

$$\Omega^{(\hat{n})}(\{\hat{e}\}) \simeq - \int d\varepsilon f_{FD}(\varepsilon; \nu^{(\hat{n})}) N^{(\hat{n})}(\varepsilon; \{\hat{e}\}), \quad (44)$$

as an effective ‘local moment’ Hamiltonian. where  $\nu^{(\hat{n})}$  is the chemical potential,  $f_{FD}(\varepsilon; \nu^{(\hat{n})})$  is the Fermi-Dirac distribution, and  $N^{(\hat{n})}(\varepsilon; \{\hat{e}\})$  denotes the integrated density of states for the orientational configuration,  $\{\hat{e}\}$ . From the Lloyd formula [32]  $N^{(\hat{n})}(\varepsilon; \{\hat{e}\})$ ,

$$N^{(\hat{n})}(\varepsilon; \{\hat{e}\}) = N_0(\varepsilon) - \frac{1}{\pi} \text{Im} \ln \det \left( \underline{t}^{(\hat{n})}(\varepsilon; \{\hat{e}\})^{-1} - \underline{G}_0(\varepsilon) \right), \quad (45)$$

( $N_0(\varepsilon)$  being the integrated DOS of the free particles) and properties of the CPA effective medium, the partially averaged electronic Grand Potential is given by

$$\begin{aligned} \langle \Omega^{(\hat{n})} \rangle_{\hat{e}_i} &= - \int d\varepsilon f_{FD}(\varepsilon; \nu^{(\hat{n})}) N_c^{(\hat{n})}(\varepsilon) + \frac{1}{\pi} \int d\varepsilon f_{FD}(\varepsilon; \nu^{(\hat{n})}) \text{Im} \ln \det \underline{M}_i^{(\hat{n})}(\varepsilon; \hat{e}_i), \\ &+ \sum_{j \neq i} \frac{1}{\pi} \int d\varepsilon f_{FD}(\varepsilon; \nu^{(\hat{n})}) \text{Im} \langle \ln \det \underline{M}_j^{(\hat{n})}(\varepsilon; \hat{e}_j) \rangle, \end{aligned} \quad (46)$$

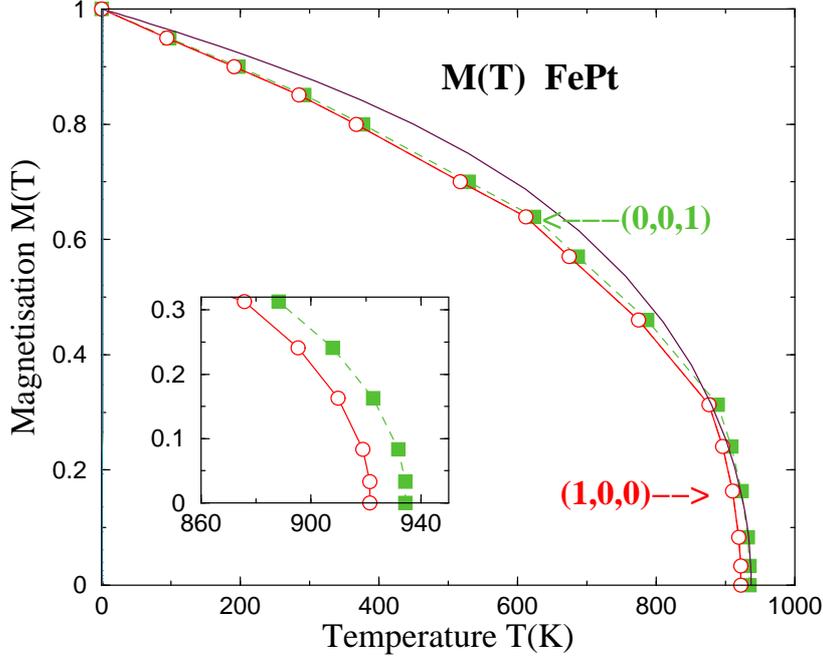


Figure 2: The magnetisation of FePt versus temperature [2]. The filled squares/open circles refer to a magnetisation along  $\hat{n} = (0, 0, 1)/(1, 0, 0)$ . In the inset, near  $T_c$ , the lower intercept shows what  $T_c$  would be with the system constrained to become magnetically ordered along  $(1, 0, 0)$ .

and the Weiss field,  $h_i^{(\hat{n})}$ , can be expressed, using Eq.(28), as

$$h_i^{(\hat{n})} = \frac{3}{4\pi} \int (\hat{e}_i \cdot \hat{n}) \left[ \int d\varepsilon f_{FD}(\varepsilon; \nu^{(\hat{n})}) \frac{1}{\pi} \text{Im} \ln \det \underline{M}_i^{(\hat{n})}(\varepsilon; \hat{e}_i) \right] d\hat{e}_i. \quad (47)$$

where  $\underline{M}_i^{(\hat{n})}(\varepsilon; \hat{e}_i) = \left( \underline{1} + \left[ (\underline{t}_i(\hat{e}_i))^{-1} - (\underline{t}_{i,c}^{(\hat{n})})^{-1} \right] \underline{\mathcal{T}}_{ii,c}^{(\hat{n})} \right)$  and  $N_c^{(\hat{n})}(\varepsilon) = -\frac{1}{\pi} \text{Im} \ln \det \left( \underline{t}_c^{(\hat{n})}(\varepsilon)^{-1} - \underline{G}_0(\varepsilon) \right)$ .

The solution of Eqs.(47) and (31) produces the variation of the magnetisation  $m_i^{(\hat{n})}$  with temperature  $T$  with  $m_i^{(\hat{n})}$  going to zero at  $T = T_c^{(\hat{n})}$ . When relativistic effects are included, the magnetisation direction  $\hat{n}$  for which  $T_c^{(\hat{n})}$  is highest indicates the easy direction for the onset of magnetic order. We can define a temperature range  $\Delta T_{aniso} = T_c^{(\hat{n}_e)} - T_c^{(\hat{n}_h)}$  where  $\hat{n}_e$  and  $\hat{n}_h$  are the system's high temperature easy and hard directions respectively, which is related to the magnetic anisotropy of the system at lower temperatures. In Figure 2 we show the example of the hard magnet  $L1_0$ -ordered-FePt.  $T_c$  is at 935K with the easy axis,  $(0, 0, 1)$ . This mean field approximation is in reasonable agreement with the experimental value of 750K. (An Onsager cavity field technique could be used to improve this estimate, see [9], without affecting the quality of the following results for the MAE.) The full line shows the mean field approximation to a classical Heisenberg model for comparison.

## 6 A torque-based formula for the magnetisation dependence of magnetic anisotropy

We return to Eq.(32) for the expression for the free energy  $F^{(\hat{n})}$  of a system magnetised along a direction  $\hat{n} = (\sin \vartheta \cos \varphi, \sin \vartheta \sin \varphi, \cos \vartheta)$  and consider how it varies with change in magnetisation angles  $\vartheta$  and  $\varphi$ , i.e.  $T_{\vartheta} = -\frac{\partial F^{(\hat{n})}}{\partial \vartheta}$ ,  $T_{\varphi} = -\frac{\partial F^{(\hat{n})}}{\partial \varphi}$ . Since the single site entropy term in Eq.(32) is invariant with respect to the angular variations we can write

$$T_{\vartheta(\varphi)} = -\frac{\partial}{\partial \vartheta(\varphi)} \left[ \sum_i \int P_i^{(\hat{n})}(\hat{e}_i) \langle \Omega^{(\hat{n})} \rangle_{\hat{e}_i} d\hat{e}_i \right]. \quad (48)$$

By using Eq.(46) together with properties of the CPA effective medium [3], we find directly

$$T_{\vartheta(\varphi)} = -\frac{\text{Im}}{\pi} \int d\varepsilon f_{FD}(\varepsilon; \nu^{(\hat{n})}) \left[ \sum_i \int \frac{\partial P_i^{(\hat{n})}(\hat{e}_i)}{\partial \vartheta(\varphi)} \ln \det \underline{M}_i^{(\hat{n})}(\varepsilon; \hat{e}_i) d\hat{e}_i \right] \quad (49)$$

According to the form of  $P_i^{(\hat{n})}(\hat{e}_i)$  given in Eq. (29) the principal expression for the magnetic torque at finite temperature is thus

$$T_{\vartheta(\varphi)} = \frac{\text{Im}}{\pi} \int d\varepsilon f_{FD}(\varepsilon; \nu^{(\hat{n})}) \left[ \sum_i \int \beta h_i P_i^{(\hat{n})}(\hat{e}_i) \left( \frac{\partial \hat{n}}{\partial \vartheta(\varphi)} \cdot \hat{e}_i \right) \ln \det \underline{M}_i^{(\hat{n})}(\varepsilon; \hat{e}_i) d\hat{e}_i \right]. \quad (50)$$

For a uniaxial ferromagnet such as a  $L1_0$  3d-4d/5d transition metal magnet or a magnetic thin film, the performance of a single CPA calculation for appropriate values of the energy  $\varepsilon$  is carried out at fixed values of the  $\beta h_i$  products (and therefore a chosen magnetisation  $m$ ) and for the system magnetised along  $\hat{n} = (\sin \pi/4, 0, \cos \pi/4)$ . Subsequent evaluation of our torque expression, Eq.(50), i.e.  $-T_{\vartheta}(\vartheta = \pi/4, \varphi = 0)$  yields the sum of the first two magnetic anisotropy constants  $K_2$  and  $K_4$ . Similarly  $-T_{\varphi}(\vartheta = \pi/2, \varphi = \pi/8)$  gives an estimate of the leading constant  $K_1/2$  for a cubic system. It can be shown [3] that the expression we found for  $T_{\vartheta(\varphi)}$  for a magnet at  $T = 0\text{K}$ , Eq.(13), is equivalent to Eq.(49) for the limit  $\beta h \rightarrow \infty$ , i.e. when  $T \rightarrow 0\text{K}$ .

## 7 Ferromagnets with tetragonal and cubic crystal symmetry

We compare the MAE of  $FePt$  in both its ordered  $L1_0$  phase with tetragonal symmetry and in its compositionally disordered  $Fe_{50}Pt_{50}$  cubic phase in figures 3 and 4 respectively.

Figure 3 shows the magnetic anisotropy energy,  $\Delta F((0, 0, 1), (1, 0, 0)) = -(K_2 + K_4)$  versus the square of the magnetisation. For all temperatures the magnetic easy axis is perpendicular to the layering in the  $L1_0$  ordered structure in line with experiment [49, 50]. The approximate  $m^2$  variation of  $\Delta F$  is a clear consequence of the itinerant nature of the magnetism in this system. Notably the magnetisation dependence agrees well with experiment [23, 51] and differs significantly from that produced by the single ion model, also shown in the figure. With hindsight, as shown in the figure, we find our the ab-initio results fit quite well to those of classical anisotropic Heisenberg model

$$H = -\frac{1}{2} \sum_{i,j} (J^{\parallel} (e_{x,i} e_{x,j} + e_{y,i} e_{y,j}) + J^{\perp} e_{z,i} e_{z,j}) \quad (51)$$

where  $J^{\parallel} - J^{\perp} = -1.835\text{meV}$ .

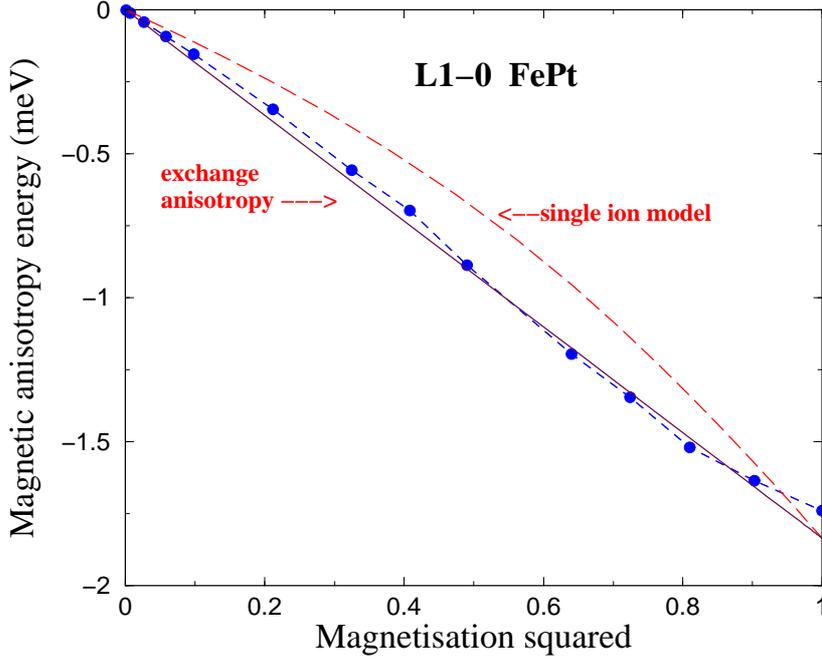


Figure 3: The magnetic anisotropy of  $L1_0$ -FePt as a function of the square of magnetisation. The filled circles show the calculations from the ab-initio theory, the full line the pair-wise anisotropic exchange model  $K_0(m(T)/m(0))^2$  and the dashed line the single-ion model function  $K_0 \langle g_2(\hat{e}) \rangle_T / \langle g_2(\hat{e}) \rangle_0$  with  $K_0 = -1.835\text{meV}$ .

Mryasov et al. [52] have also described the magnetic anisotropy of  $L1_0$ -FePt using a local moment model Hamiltonian with exchange anisotropy, dipolar and single ion anisotropy terms. The parameters were found from with  $T = 0\text{K}$  electronic structure calculations.

Crystal structure has a profound effect upon the magnetic anisotropy. Magnetic anisotropy within a single ion anisotropy model decreases according to  $m^{l(l+1)/2}$  at low  $T$ , ( $m \approx 1$ ) and proportional to  $m^l$  for small  $m$  at higher  $T$ . For materials with tetragonal symmetry,  $l = 2$ , as shown in Fig.3. On this basis a cubic magnet's MAE should possess an  $m$  dependence where  $l = 4$ , i.e.  $m^{10}$  at low  $T$  and  $m^4$  at higher  $T$ . This single ion pattern is not manifested in our ab-initio results of disordered  $Fe_{50}Pt_{50}$  shown in Figure 4 [3]. In this system the lattice sites of the f.c.c. lattice are occupied at random by either  $Fe$  or  $Pt$  atoms. The cubic symmetry causes this alloy to be magnetically very soft. Indeed the overall scale of the MAE is some three orders of magnitude smaller than its  $L1_0$ -ordered counterpart shown in Fig.3. Ordering into a tetragonal  $L1_0$  structure of layers of predominantly  $Fe$  atoms stacked alternately with  $Pt$  layers along the  $(1, 0, 0)$  direction causes a significant increase of  $K$ . Okamoto et al [51] have measured  $K$  of  $FePt$  carefully as a function of compositional order and the trend, for  $T = 0\text{K}$ , has been successfully reproduced in ab-initio calculations [28, 53].

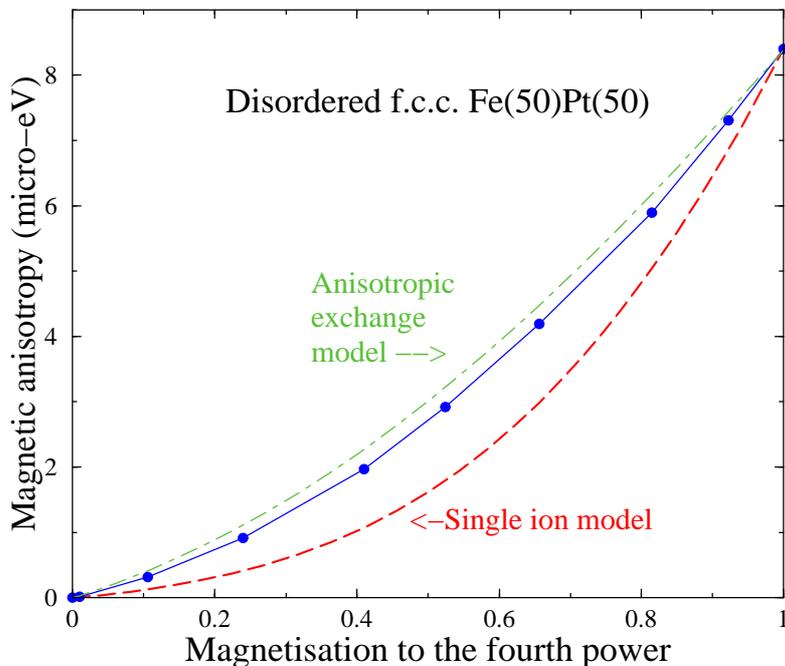


Figure 4: The magnetic anisotropy constant  $K_1$  of the cubic magnet  $\text{Fe}_{50}\text{Pt}_{50}$  as a function of the fourth power of the magnetisation,  $m^4$ . The filled circles show the calculations from the ab-initio theory, the dashed line from the single-ion anisotropy model  $k \sum_i (e_{x,i}^2 e_{y,i}^2 + e_{y,i}^2 e_{z,i}^2 + e_{z,i}^2 e_{x,i}^2)$  and the dot-dashed line from the anisotropic exchange two ion model  $\frac{1}{2} \Delta J \sum_{i,j} (e_{x,i}^2 e_{y,j}^2 + e_{y,i}^2 e_{z,j}^2 + e_{z,i}^2 e_{x,j}^2)$  with  $k = \Delta J = 8.4 \mu\text{eV}$ .

We find a Curie temperature of disordered f.c.c.  $\text{Fe}_{50}\text{Pt}_{50}$  of 1085K, again a mean field value which is in reasonable agreement with the experimental value of 750K [51]. Figure 4 shows our calculations [3] of the magnetisation dependence of the leading magnetic anisotropy constant  $K_1$  (Eq.6). As expected  $K_1$  decreases rapidly with temperature - Fig. 4 depicts  $K_1$  versus the fourth power of the magnetisation. At low  $T$ ,  $K_1$  varies approximately as  $m^7$  whereas this dependence becomes  $m^4$  for smaller  $M$  and higher  $T$ . Fig.4 also shows the behaviour of the single ion model for a cubic system for comparison. As with the uniaxial metallic magnets already investigated, the ab-initio R-DLM results differ significantly. Again with hindsight an interpretation of the ab-initio results can be given by a model which includes both two site anisotropic exchange and single site anisotropy.

It is interesting to note that in some recent work on thin films we have found that thermally induced magnetisation reorientation transitions we calculated for itinerant magnetic thin films can be interpreted as a trade off between single ion and exchange anisotropy aspects [4].

## 8 Conclusions

In this article we have shown how the account of fluctuating local moments provided by the R-DLM describes well the temperature dependence of magnetic anisotropy. There is work in progress to look at the magnetic structures of thin films and multilayers and also the blocking temperatures of magnetic nanoparticles. Strongly correlated electron effects are also currently

being included via the Local Self-Interaction Correction (L-SIC) method [44] so that gamut of magnetic materials can be investigated. At the heart of the R-DLM theory is the fully relativistic electronic structure which is affected by and sustains the fluctuating moments. As the temperature of a material is increased the fluctuations grow and the electronic structure changes in consequence. This means that a quantitative theory for the  $T$ -dependence of spectroscopic measurements is possible. Indeed an early prediction [8] of the DLM theory was the local exchange splitting in b.c.c.  $Fe$  observed above  $T_c$ . Significantly and of relevance to spintronics the temperature dependence of transport properties can be covered- ‘spin’-disorder scattering can be carefully considered. The evolution of the resistivity of materials which are inferred to be half-metallic at  $T = 0K$  are rather pertinent examples. A quantitative theory of anisotropic magnetoresistivity is another promising project.

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