# HCM Newsletter

# $\Psi_k$ Network

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

Number 17 September 1996

# Contents

# 1 Editorial

The **Editorial** is followed by the section **News from the Network**. There Walter Temmerman writes about the near future of the Network, and also two summaries of the *Network Conference* in Schwäbisch Gmünd are given there. One of the summaries is by Volker Heine, the chairman of the Network, and the other by J. Hafner, the spokesperson for the Austrian node of the Network.

In the section **News from the Working Groups** readers will find reports on recent collaborative visits and the Strasbourg Workshop on *Fe/Cr*. Straight after the reports there are announcements of future workshops/conferences and of available positions. After the latter we have book/proceedings announcements.

**Abstracts** follow book announcements.
The last section of the *Newsletter* contains the **Highlight of the Month** article by J.F. Annett (University of Bristol) on *"Electronic Structure using Wavelets"*.

The *Network* has a home page on World Wide Web (WWW). Its *Uniform Resource Locator* (URL) is:
**http://www.dl.ac.uk/TCSC/HCM/PSIK/main.html**

The above contains pointers to several other nodes: *O.K. Andersen (Stuttgart)* which also includes information on the **Network Conference**, *P. Blöchl (IBM, Zürich, M. Gillan (Keele), E.K.U. Gross (Univ. Würzburg), B.L. Györffy (Bristol), V. Heine (Univ. Cambridge), R. Jones (Univ. Exeter), J. Kübler (TH, Darmstadt), R. Nieminen (TU, Helsinki), J. Nørskov (TU, Lyngby)* with information on CAMP, *M. Scheffler (FHI Berlin), K.-H. Schwarz (TU, Vienna), G.P. Srivastava ( Univ. Exeter),* and *A. Walker (UEA Norwich).* Additionally, recently we have also included a pointer to the WWW home page of the Solid State Theory Group at National Renewable Energy Laboratory, Golden, CO 80401 *(http://www.sst.nrel.gov).* If you maintain a home page on your activities we will be happy to include a pointer from the *Network's* home page to your home page.

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

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

|  | function |
|---|---|
| **psik-coord@daresbury.ac.uk** | messages to the coordinator & newsletter |
| **psik-management@daresbury.ac.uk** | messages to the NMB |
| **psik-network@daresbury.ac.uk** | messages to the whole Network |

Dzidka Szotek & Walter Temmerman
e-mail: psik-coord@daresbury.ac.uk

# 2  News from the Network

## 2.1  The Near-Future: After Schwäbisch Gmünd

Thank you all for making the Schwäbisch Gmünd Conference such a huge success. Our Network has now little over a year to go. In order to run down the finances I need now to plan financially the activities for the remaining part of this year and next year. Therefore, could you submit to me, by November 1, your proposals for workshops, hands-on training courses, visits costing more than 1kECU, and secondments via collaboration and training projects together with a financial estimate.

Walter Temmerman
psik-coord@dl.ac.uk

## 2.2  Conference Summary I

# Concluding Remarks about the $\Psi_k-$Network Conference at Schwaebisch Gmuend, 17 - 21 September, 1996

This is an historic occasion with over 320 band structure theorists, gathered for the first international conference for at least 25 years devoted specifically to cover all our subject. (I can remember one in Exeter, I think in the late 1960's.) A wide spread of fascinating science has been presented, and many people have commented how glad they are that they followed the advice given at the beginning, namely to attend sessions different from those relating just to their own work. The subject is certainly bubbling, and the number attending shows it is growing. Moreover the standard of the contributed papers has been excellent, which demonstrates the healthy dynamics of our field. This matter of quality is very important, and I shall return to it later.

Before commenting on the science, I want to make some remarks about this conference, and how we got here and where we are going. As you will see later, this is not just history for the sake of history: there is a crunch coming at the end. But first of all I want to pay tribute to Ole Andersen who has not only been the chairman and tireless worker for this conference, but has also been the main driving force behind it to make it happen. He has always had a particular concern for "the whole family" of European researchers in our field, and helping them to do high quality work through interaction with others, and to achieve recognition through presenting their work publicly.

The first Europe-wide organisation in our field that I know of came at the beginning of the 1980's. Before that people had met rather by random chance at semiconductor or magnetism or whatever conferences. In the United Kingdom and perhaps other countries, there was a small effort in meeting for workshops etc. but more or less only on a national basis. The effort had been mainly directed at calculating band structures for optical properties of semiconductors and Fermi surfaces of metals, and in magnetism one could go on to calculate the equilibrium magnetic moment. Then around 1980 Richard Martin who is here today and Marvin Cohen pioneered the calculation of Hellmann Feynman forces and total energies with pseudopotentials and plane waves. This was clearly going to be a major dveleopment, and in the early 1980's a few young researchers came back from the USA with these techniques. They started as isolated individuals, one (or at most two) in each of several European countries. Clearly they were not going to achieve high quality work at the forefront of research as isolated individuals, and so an annual gathering and workshop was started. That movement now embraces a much wider range of electronic structure calculation, and you have seen the next biannual 'maxi workshop' (equals 'conference') next January advertised by David Vanderbilt from Rutgers University, New Jersey. (see also this Newsletter: page 21). It is good that we do not just pay lip service to keeping contact with our American and Japanese colleagues, but make it a reality. The main point about this development was that it opened the door to calculating a wide range of properties and behaviour of solids and surfaces, and analogous developments were occurring on the transition metal and magnetism fronts.

The next development was that the ESF (European Science Foundation) started a series of research conferences patterned on the American Gordon Conferences for about 100 participants in one field. Since other branches of physics were cornering the market in some of these, it seemed wise to start an annual series on Electronic Structure of solids which would rotate around various aspects of our subject from year to year. Four very successful conferences were held, one each year from 1992 to 1995 inclusive. While the 1996 one was dropped in favour of the present $\Psi_k$−Network conference, good topics and chairmen for 1997 and 1998 were put forward, but these have been cancelled by the ESF. Most of you will have learnt of this earlier in the year, and it was helpful that some of you protested to the ESF or its national Research Council members. Unfortunately the ESF has not rescued these conferences from its own funds as had been hoped. It really is pathetic that Europe is so chaotic that it cannot even run a series of conferences successfully. After setting it all up, it falls apart after four years. The reason in this case is that ESF relied too much on the EU Commission in Brussels for financial support instead of developing stable financing of its own. It is well known that the EU Commission changes its policies and priorities about as frequently as its underpants, and unfortunately it has said to the ESF "get lost" for 1997 - 1998. I have only just seen the Brussels comments on our pair of proposals, some of which I find outrageous, because they now criticise the very things which I understood they previously endorsed, namely that the conference topic rotates around different aspects of our subject and groups of people in our community. We will of course reply but it will not help. I will try to keep you informed about developments regarding the ESF conferences; there may come a time when you might be able to help influence your national Research Council to put more money into the ESF Conference Programme to secure it properly, independent of the lottery in Brussels. I think it is a good programme which European science needs, and our

conferences have been excellent as shown by the attendence and by the reports of the attenders.

Over the same period as the ESF Conferences, there have been a few DFT (Density Functional Theory) Conferences, the next one in 1997 being advertised at this conference (and in this issue of the Newsletter: page 21). That series has originated from among chemists, and I think it is great to see their conversion to the DFT formalism.

The present $\Psi_k-$Network is funded under the HCM (Human Capital and Mobility) Programme of the European Union. It is rather anomalous, being by far the largest Network (having 40 nodes) in the physics section. It comes to an end on 31 December 1997 and there is some money left for workshops, hands-on training courses and individual collaborative visits before then. (Note applicants must be EU citizens and there must be some kind of connection with one of the 40 nodes. We tried to enlarge it to more nodes and to eastern Europe but Brussels did not allow that. Please send any proposals to Walter Temmerman, preferably by 1 November 1996 by email.) The quantum Monte Carlo people and the GW calculators succeeded in getting their own HCM networks, but the $\Psi_k-$Network is trying to provide an infrastructure for "the whole family" including running this conference. Previously there was not even an address list. We had lacked cohesion as a community because firstly we are relatively new, secondly because we tend to identify with the community such as surfaces or magnetism or semiconductors to which our calculations relate (which I consider a very positive feature), and thirdly because we do not have a central facility to organise around as the neutron scatterers do or those using synchrotron radiation.

Let me come straight out to say what I think. I believe that the very high quality of the invited and contributed papers at this conference and the general dynamic of our community are partly due to all the interaction and networking over the last 15 years which I have described. Achieving that high quality depends on knowing about the latest advances made elsewhere, especially in a rapidly developing field such as ours. When I was young there was virtually no work on electronic structure calculation in Britain or continental Europe, and all of the more important research I did at that time depended on contact with my American friends who were kind enough to invite me to visit nearly every summer. Now Europe is leading the world in this field and we have workshops and conferences through the $\Psi_k-$Network and others. The hands-on training courses on LMTO, LAPW and plane wave codes have also made an important contribution. The second benefit of our networking is the ability to make joint application for European funding. All the projects linked to the EU and ESF have grown out of the earlier informal contacts, and the EU TMR Network on surface magnetism starting in 1997 has been built on the $\Psi_k-$Network. (Note: the EU Training and Mobility of Researchers (TMR) Programme is the successor to HCM.) Thirdly personal contacts generated through the networking are important for undergraduates to find a good group if they want to do a Ph.D. in our subject, for those with Doctorates to find post-doc positions, and for more senior researchers to find long-term academic positions. I was told yesterday that someone from another European country would have no chance of getting a professorship in country X because such positions are decided by local power politics. I also believe there are many universities in Europe where someone from our community is not likely to be appointed to a professorship in theoretical physics because some people still do not rate our type of work highly because it involves computing. I think it is appalling that such things happen among our fellow scientists in condensed matter physics. This

situation is slowly changing, and we can help the change by firstly insisting such things do not happen whenever we are involved in the decision making, secondly by our forming a dynamic and publicly visible community, and thirdly by making our calculations as useful as we can to the mainstream science of our experimentalist colleagues.

I turn now to the future. The ESF Conferences are cancelled at the present and we do not know whether they will be reinstated. When the present $\Psi_k-$Network ends next year, we cannot apply to the EU for a new one because they have totally changed the rules and want small focused networks with post-docs. We are therefore applying to the ESF for what they call a 5-year "Programme" meaning a meganetwork of the type we have now, covering all of Europe, not only the EU states. We will circulate a copy of the application as an extra issue of the Newsletter as soon as it is finalised. The problem about such a Programme is that the ESF has no money for it. All the ESF can do is to suggest to the member national Research Councils to consider putting extra money into ESF specifically for this Programme. When I have more information, I will let you know so that you can make your case to your national Research Council if you wish.

Enough about organisation: let us talk science. Of course it is an impossible task to summarise about 200 invited and contributed talks and posters, although several people have kindly helped me cover the parallel sessions and areas of interest. I repeat: what most impresses me is the high scientific quality. I have a list headed "Boom Boom" of noteworthy contributions but the list is too long to start on now. Not only is the quality of the calculations high, but they are contributing to important areas of mainstream science, being closely joined with experimental results to understand "the phenomena of nature." The focus has shifted from calculating the electronic structure as an end in itself, to calculating various properties or simulating various processes. The list here is endless: magnetic dichroism, ferroelectric behaviour, electric field gradients needed for Nuclear Magnetic Resonance, defects in GaN, and so on. Even transport properties are appearing, sometimes calculated directly from the wave functions with the Kubo-Greenwood formalism. Among simulations we had, for instance, the atomistic effects in polishing a diamond surface. Our work has a growing impact on materials science, for example in the study of optoelectronic properties, semiconductors and grain boundaries. There are a growing number of applications in chemistry, where techniques based on Density Functional Theory are gaining acceptance at last. The calculations include organic materials, even including some of biological importance. There are four whole sessions in this conference devoted to surface science, with papers on such practical issues as crystal growth and surface chemical reactions.

The gap to industrial applications is closing, or rather has closed at a few points. Throughout the abstract book, with too many examples to count, one comes across little remarks that the material is being considered for making a blue laser or as a particular pigment or for opto-electronic devices. Whilst there are applications to industry, unfortunately there are very few participants from industry. I trust that will change in future.

The largest number of sessions and perhaps the greatest excitement has come from magnetism. In passing, I want to remark that magnetism, in intellectual content as a science is as large as High Energy Particle Physics: compare the number of basically different interactions (exchange, superexchange, double exchange), the number of phenomena (phase transitions, the list is end-

less), number of experimental techniques (magnetometry, neutron scattering, individual spin resonance, co-operative ferromagnetic resonance, etc.), and ramifications outside its own field (geophysics, industry from transformers to magnetic recording, ionospherics, astrophysics). Our colleagues from particle physics often want to treat condensed matter physics lumped together as one subject comparable to their own, whereas in reality it is a constellation of subjects some of which are at least as large scientifically as high energy particles. One needs to remind them of that occasionally. We have heard at this conference about magnetism at surfaces, in multilayers, as well as in bulk with non-collinear moments, and important orbital contributions to the moment as well as spin. There are novel experiments such as the circular dichroism with the new intense synchrotron sources, there are spectacular effects in which Giant Magneto Resistance is followed by Colossal Magneto Resistance (where next?), and device applications to storage media. The experiments, the analytic theory and the calculations on magnetic coupling through a gold layer reviewed by P. Bruno are very impressive indeed.

I want to emphasise that our purpose in all these calculations is usually not just to generate numbers for their own sake, although that is a legitimate objective for "computer experiments" when such quantities are important and not directly measurable. Usually as scientists and as mostly theoreticians we are concerned to understand the observed phenomena. What do we understand by the word 'understanding'? That is a non-trivial question which I have often discussed with students. It certainly does not mean calculating everything in sight, and I ask students how much understanding of the weather they would gain if they could have a computer code to calculate where and when every raindrop would fall. Well, that is too large a subject to embark on here, but suffice it to say there have been good examples at this conference of well chosen computer experiments designed to elucidate some observed phenomenon.

My predilection for applications rather than techniques is an expression of my New Zealand 'colonial' culture, but I want to mention here the Quantum Monte Carlo (QMC) calculations. I expect everyone here will know of Aesop's fable of the tortoise and the hare. If we think of QMC as the tortoise compared with the hare of DFT LDA (Local Density Approximation) calculations, then the tortoise has been growing some long legs recently. The beautiful work by Gunnarsson on the C60 compounds showed theoretically the role of degeneracy on the precise criterion for the Mott transition, backed up by convincing lattice QMC calculations. Foulkes showed how two separate finite-size effects could be eliminated, resulting in much better converged calculations with small supercells. QMC is already feeding usefully into the mainstream of our work, for example in testing the Generalised Gradient Corrections to the Local Density Approximation for exchange and correlation. At present QMC is about 1000 times slower than an LDA factor of two every year, it will only take 10 years to make up the factor of 1000. It is a stupendous thought that in ten years time, everything reported at this conference may be done by QMC.

Density functional theory is the rock on which almost all our work is built. (At this point there followed some historical and general remarks that might form the basis of a future article: Editor) The QMC results that I have seen seem to show that the Generalised Gradient Corrections (GGA) to LDA are not a universal cure: they make agreement with (almost) exact QMC calculations worse in some cases by as much as they improve the results in others. However in a restricted sphere such as interaction including hydrogen bonding in water, it can be highly effective and open the door to a whole new area of work as illustrated by Parrinello's talk. But

the conference has shown how the Density Functional tree has also sprouted some other rather stranger branches of LDA + U and LDA + SIC and LDA + (angular momentum polarisation). At first these were greeted with scepticism because they depend on the orbitals in a way not invariant under unitary transformation. These are however genuine functionals that try to give a better approximation to the correlation energy functional. For example reduction of Coulomb energy through coupling of angular momenta is the basis of Hund's second rule for atomic ground states. Finally we have heard of the success of Hardy Gross in calculating the excited states of first row atoms through a development of density functional theory, which it is now planned to extend to solids.

I promised to return to the theme of scientific excellence. There is a clear benefit to pursuing our subject at European level, rather than purely nationally. In a sense we are building, within the microcosm of our own community, the sort of Europe we want to see. It certainly does not mean everyone being required to use some "Brussels code" for their calculations!! It means finding the correct mixture of where to go our own individual ways and where to sink our differences for concerted action. In the long term such co-operation depends on trust, and trust depends on respect, and respect in a scientific community can only ultimately be built on a common pursuit of excellent science. This is non-trivial. I have seen scientists behave just as badly as we read about politicians in the way of both nationalism and local power politics. However this conference is a milestone in our particular community which I see in the co-operative work that has brought it about, in the scientific excellences of the contributions, and in how a very large fraction of the contributions carry addresses from two or more different countries or involve people whose names indicate different home countries.

Finally it remains to thank Ole Andersen as conference chairman for all his work, ably supported on left and right by his wife Sanne and secretary Gisela Schmidt, and to front and rear by Ove Jepsen and Armin Burkhardt. I have also seen others involved from the Andersen and Parrinello groups. Moreover Walter Temmerman and Dzidka Szotek spent most of June and beginning of July in Max-Planck-Institut für Festkörperforschung in Stuttgart, working full time on the Conference. They have also parachuted in from Daresbury for the last ten days of final preparations. To all these we owe great and grateful thanks.


Volker Heine

## 2.3   Conference Summary II

# $\Psi_{\vec{k}}$—Network Conference

**Ab initio (from electronic structure) calculation of complex processes in materials**

**Schwäbisch-Gmünd, 17-21 September 1996**

The $\Psi_{\vec{k}}$—Network-Conference constituting the culminating point of our EU-Human Capital and Mobility Network took place in Schwäbisch Gmünd from Tuesday 17 September to Saturday 21 September. The conference was organized by Professor O.K. Andersen and his co-workers from the Max-Planck-Institut für Festkörperforschung in Stuttgart and Daresbury Laboratory in England, and we should all be grateful to this team for the great job they have done. The Network Management Board, supported by an Overseas Advisory Committee acted as the Program Committee. The conference was attended by 322 participants, 260 participants came from EU countries, 60 from Eastern Europe and overseas. Thanks to important financial contributions from the $\Psi_{\vec{k}}$—Network, from the Max-Planck-Gesellschaft and from the EU-Commission it was possible to offer financial support not only to the 48 invited speakers, but altogether to 166 mostly young participants. To this one has to add support for HCM-activities provided out of national sources for nationals of the "new" EU-countries (Austria, Finland, Sweden), and Switzerland. The fact that so many young members of our community were able to attend has certainly contributed to the lively and active atmosphere throughout all four conference days - even during the very last sessions no decrease in the attendance could be observed. The excellent organization set up by Ole Andersen and his team, as well as the favourable arrangement of the lecture rooms in the Congress Center around the large central hall housing the posters, also contributed to the success of the conference. In think that after this conference it is fair to say that - largely due to the success of the $\Psi_{\vec{k}}$—Network - there now exists an active and intensely cooperating electronic-structure community in Europe and that this community has achieved world-wide leadership in this field. It will certainly be a very important task for the Network Management Board to find a way how these fruitful exchanges and cooperations can be supported beyong the expiration date of the HCM-Network end 1997.

In his closing remarks the chairman of our Network, Volker Heine, has described in an impressive way what we could call the scientific harvest of this conference. Without attempting to step into his footprints, I shall try to offer here my own resume - admittedly it might be slightly biased by personal interest and expertise. The cornerstone of all our work is Density Functional Theory (DFT). We are all aware of its successes, but also of its limitations. Hence it was very appropriate that a number of sessions were devoted to attempts to overcome these shortcomings: GGA, SIC, OEP, GW, LDA+U, ... . Quantum Monte Carlo techniques play an increasingly important role in providing a testing ground for theories beyond the local density approximation. These activities reflect the committment of our community to find better functionals to make DFT even more useful. Finding an accurate functional is only the first step, the second consists

in setting up efficient techniques for solving the Kohn-Sham equations of DFT and to compute total energies and forces for ever more complex systems. The papers presented at the conference demonstrate not only the tremendous progress achieved during the last few years, based on both improved computer performance and better codes (who would have thought only five years ago that we will so soon be able to describe ab-initio not only complex molecular processes at solid surfaces, but even biochemical reactions ?), but also that the development of more performant computational tools remains a very active field of research. The competition is open for a better scaling of the CPU-time with the number of degrees of freedom ($O(N)$-scaling), but we should not forget that to extend the time-scale of our simulations is as necessary as increasing the number of atoms. The development of new codes seems to be characterized by diversification - sometimes one has the impression that a new code should not only be efficient, but also as different as possible from existing codes. Future development could profit from more cooperation and syncretism. However, to make sure that the interesting elements of a code can be put into other codes in an unproblematic way, it is necessary that the codes remain - at least for academic research - within the public domain.

Our work derives a good part of its justification from the successful applications of the techniques we are developing to technologically relevant problems. In the conference applications to semiconductors (including novel carbon-based materials), magnetism, superconductors, mechanical properties and phase transitions, surfaces, interfaces and catalysis, and even biological materials were actively discussed. To select highlights among the many results is of course a highly arbitrary decision. If we just pick as an example the modelling of a chemical reaction catalyzed by a transition-metal surface or of the protonization of a molecule by the acid-sites inside a zeolite, we have certainly found convincing examples for the ability of ab-initio simulations to characterize a process in much more detail than possible in a laboratory experiment. This should be of immediate interest not only in academia, but also for industry. Similar conclusions could be drawn from the description of the microscopic magnetic structure of a noncollinear magnet or a thin film, from the modelling of solvation reactions, and from a series of other examples. However, with all the emphasis on application we should not underrate fundamental science - here the encouraging steps towards a pairing-density theory of superconductivity merit special attention.

After this successful conference, what about the future ? With the expiration of the HCM-framework, will the $\Psi_{\vec{k}}-$Network conference remain a singular event? The Network Management Board will certainly report in another place on its activities to ensure the continuity of the cooperations built up during the last three years. Among topical workshops and seminars, a regular series of triannual $\Psi_{\vec{k}}-$Conferences is certainly one of the goals to be achieved.

Jürgen Hafner

# 3    News from the Working Groups

## 3.1    Reports of Collaborative Visits

### Report on the collaborative visits of A. Bieniok (Frankfurt/M, Germany) to the Cavendish Laboratory, University of Cambridge, UK

1–13 July, 1996

Dr. Anna Bieniok visited Cambridge from Frankfurt am Main from 1st to 13 July 1996, in connection with *ab initio* calculations on zeolites in Cambridge by Dr. Mike Payne, graduate student Rajiv Shah, and others planned for the future. Zeolites containing AlOH groups catalyse various chemical reactions including dissociation of methanol in chabazite as a first step in forming more complex molecules. In such reactions, the flexibility of the zeolite framework is very important, a subject on which Dr. Bieniok is an expert and we in Cambridge are not. Zeolites are very flexible, but only in a few very specific ways. During her visit, she discussed with us the particular fexibility of chabazite and another zeolite on which it is hoped to start calculations. She also had other scientific interactions in Cambridge, so that the $\Psi_k-$Network has only been asked to contribute a small fraction, namely 142 pounds, to the costs of the visit, charged to the Cambridge node and Pseudopotential working group.

(V. Heine)

### Report on the collaborative visits of J.E. Inglesfield (University College Cardiff, UK) to the University of Nijmegen (The Netherlands)

16 August, 1996

On 16th August I visited the Electronic Structure of Materials group in Nijmegen, partially supported by the network, to discuss work on alloys by Patrick Slavenburg. Using the Augmented Spherical Wave method, Patrick Slavenburg has been studying the electronic structure of many alloy systems, particularly Ti alloys such as TiNi, TiPd and TiAu which show the shape memory effect. This effect is associated with a martensitic phase transformation, and there is a need to understand the factors which govern the transition temperature. Changes in the electronic structure through the phase transition seem to correlate with trends in transition temperature, and it has been particularly useful to define a bond-order within the ASW formalism, which shows the role of different sorts of bonding in the transition. This work is now being written up.

(J.E. Inglesfield)

# Report on the collaborative visit of J.L. Martins (Lisbon, Portugal) to V. Van Doren's Group at the University of Antwerp

June 24 and 25, 1996

We are interested in the prediction of the structure of crystals. For complicated structures we have to search a multidimensional space of the $3N - 3$ internal coordinates and the 6 lattice parameters (lengths and angles). For that, we can use a variable cell shape simulated annealing for coarse optimization, followed by a conjugate gradient minimization of the energy to find the local minima. The method is working well with model potentials (e.g. Lennard-Jones) but we still have problems for first principles calculations. Those are related to the spurious breaking of symmetry of the k-point integration mesh. The collaboration continues, and we are working on how to minimize those effects.

(J.L. Martins)

# Fe/Cr interface magnetism

*Satellite Meeting of the Symposium*
*of the E-MRS Spring Meeting '96 on:*

*Magnetic Ultrathin Films, Multilayers and Surfaces*

**(Strasbourg, 2-3 June 1996)**

Workshop supported by:

*EU–HCM $\Psi_k-$Network*
*Institut de Physique et Chimie des Matériaux de Strasbourg*
*Université Louis Pasteur de Strasbourg*

## 1. Scientific content

The aim of this two-day meeting was to take advantage of the presence of many scientists in Strasbourg, to organize a well-focused meeting on a key problem. The Fe/Cr interface is a kind of paradigm since almost all problems encountered in the study of artificial magnetic systems can be found. The purpose was to gather together experimentalists and theoreticians in an informal atmosphere for a hopefully fruitful discussion.

The workshop was organized in three sections: structural characterization, magnetic order and electronic structure, interlayer coupling, and GMR. All these subjects are closely related to each other and it was one of the main purposes of the workshop to discuss these interrelations.

Forty colleagues from outside Strasbourg took part in the workshop coming from the U.S.A. (5), Japan (5), Russia (3), Canada (1) and Europe. Including colleagues and students from the Institut de Physique et Chimie des Materiaux de Strasbourg we had an audience of 60 people. Five people were supported by the HCM. Most of the talks were given by experimentalists and the "highlights" of the workshop were:

i) atomic-scale observations of alloying in Cr/Fe(001) using scanning tunneling microscopy and other techniques;

ii) "absence of magnetism" in Cr proposed through perturbed angular correlation (PAC) experiments whereas all other types of experiments explain the absence of Cr magnetization by interface roughness;

iii) ab-initio calculations for small Cr clusters and monolayers on Fe(001). Multiple magnetic configurations with differences of energies in the order of the mRy are obtained. These different configurations can therefore being reached by modifying slightly the growth conditions;

iv) semi-empirical models in real-space are now calculating very complex geometrical configurations (steps, large adsorbed Cr(Fe) islands on Fe(Cr) with classical collinear magnetic configurations). Non-collinear magnetic configurations calculations have been presented;

v) the major point leading to the most vivid and controversial debate was about the persistance (or not) of spin density wave (SDW) in non-thick Cr spacer in Fe/Cr superlattices. The debate was essentially raging between experimentalists. There is a clear need of calculations considering the stability of the SDW in Cr slabs when the thickness is decreased.

## 2. Preprints, digest

Most of the participants had sent beforehand an "extended abstracts" of 2 pages so that a booklet was ready and distributed 2 weeks before the workshop. A few copies of this booklet remain available and people interested can contact the local organizers (H. Dreyssé, C. Demangeat). This booklet offers a quite general state-of-the-art of this interface and the related problems.

## 3. Next workshop

The idea of a satellite meeting connected to the European Material Research Society Symposium on magnetic mulilayers was unanimously judged very positive. Therefore such workshop could take place in May 1998 as a satellite to the next European-MRS on magnetic multilayers. Professor Dr. H. Zabel from the Ruhr-Universität Bochum will join the group of organizers. Any proposition is greatly welcome.

C. Demangeat, H. Dreyssé, J. A. C. Bland, G. Bayreuther

**The programme of the meeting follows!**

**PROGRAMME**

*Sunday, 2 June*

14:00   Opening Remarks

**Structural Characterization**

14:05   *B. Heinrich (Burnaby)*
"The Role of Interfaces in the Exchange Coupling of Fe/Cr/Fe(001) Systems"
14:25   Discussion
14:35   *R. Pfandzelter (Berlin)*
"Growth of Cr on Fe(100) Studied by Grazing Ion-surface-scattering"
14:45   *D.E. Bürgler (Basel)*
"Fe/Cr/Fe Triplelayer on Ag(001)/Fe/GaAs(001):
Morphology and Chemical Properties"
14:55   *A. Davies (NIST)*
"Atomic-scale Observations of Alloying in Cr/Fe(001)"
15:05   Discussion
15:25   Break
15:55   *V. Dupuis (Lyon)*
"From Superparamagnetic to Magnetic Ordered State in Systems
of Transition Metal Clusters Embedded in Matrices"
16:05   *R. Schad (Nijmegen)*
"The Interface Structure of GMR Superlattices"
16:15   Discussion

**Magnetic Order, Electronic Structure**

16:50   *S.M. Dubiel (Cracow)*
"Application of Mössbauer Spectroscopy in the Investigation
of Charge- and Spin-density Waves"
17:10   *J. Meersschaut (Leuven)*
"Perturbed Angular Correlation Spectroscopy Study
of Thin Chromium Films and Multilayers"
17:30   Discussion
17:40   *H. Zabel (Bochum)*
"Spin Density Waves in Cr(001) Epitaxial Films
and Fe/Cr(001) Superlattices: Recent Results from Synchrotron
and Neutron Scattering Experiments"
18:00   Discussion
20:00   Banquet

09:00   *F.J. Himpsel (Madison)*
"Confinement of Empty States in Cr/Fe(100) Studied by
Inverse Photoemission"

09:10   *T. Rasing (Nijmegen)*
"Nonlinear Magneto-optical Study of the Fe/Cr Interface"

09:20   *Y. Suzuki (Tsukuba)*
"Magneto-optical Properties of the Cr Wedges Grown on Fe(001)"

09:25   Discussion

09:45   *E. Kisker (Düsseldorf)*
"Magnetic Properties of Ultrathin Cr Layers on Fe(100) and Fe(110)"

10:05   Discussion

10:15   *N.I. Kulikov (Troitsk)*
"Slater-Pauling curve for Fe-Cr alloys"

10:25   *Y. Kawazoe (Sendai)*
"Phase Stability of the Sigma Phase in Fe-Cr Based Alloys"

10:35   Discussion

10:45   Break

11:15   *K. Wildberger (Jülich)*
"Ab-initio Study of Cr and Other 3d Impurities at the Fe(001)
Interface"

11:25   *S. Blügel (Jülich)*
"Magnetism, Stability and Growth Mode of Ultrathin
Cr and Mn Films on Fe(100)"

11:35   *V.M. Uzdin (St-Petersburg)*
"Cr Overlayers on Fe. Influence of the Roughness on the Distribution
of Magnetic Moments"

11:45   *G. Bayreuther (Regensburg)*
"Magnetic Moments at Stepped Fe/Cr Interfaces"

11:50   *M. Freyss (Strasbourg)*
"Non-collinear Orders in Fe/Cr Superlattices"

11:55   Discussion

12:15   *A. Vega (Valladolid)*
"Magnetic and Electronic Properties of Fe/Cr Interfaces:
FeN Cluster Impurities in the Cr Matrix and Fe(Cr) Overlayers
on Cr(Fe) Substrates"

12:25   *A. Berger (San-Diego)*
"Thermodynamic Properties of Imperfect FM/AFM-Multilayers"

12:35   Discussion

12:45   Lunch

14:30   *P. Grünberg (Jülich)*
"Bilinear and Biquadratic Interlayer Exchange in Fe/Cr
Layered Structures and its Relation to Growth and Structure"

14:50   *M.D. Stiles (NIST)*
"Oscillatory Exchange Coupling in Fe/Cr/Fe"

15:00   *S. Mirbt (Uppsala)*
"Calculated Magnetic Properties of Fe/Cr Interfaces"

15:10   Discussion

15:25   *S.N. Okuno (Kawasaki)*
"Interlayer Exchange Coupling in Fe/Cr(001) Observed
from the Fe Layer Thickness Dependence"

15:35   *J. Pflaum (Bochum)*
"Ferromagnetic Resonance Studies of the Influence of Cr
Interfaces on Fe Single Layers and Fe/Cr Multilayers"

15:45   *Th. Kleinefeld (Bochum)*
"Domain Structure and Interlayer Exchange Coupling
in Fe/Cr/Co Multilayers"

15:55   Discussion

16:10   *J. A. C. Bland (Cambridge)*
"Biquadratic Coupling in Epitaxial Fe/Cr/Fe Structures
and the Magnetism of the Fe/Cr Interface"

16:20   *D. Stoeffler Strasbourg)*
"Theoretical Study of Fe on Cr Monolayers Deposited on a Cr(001)
or Fe(001) Substrate: Role of Step Induced Defects"

16:30   Discussion

16:40   Break

17:10   *I. Mertig (Dresden)*
Ab-initio Calculations of Giant Magnetoresistance in Fe/Cr

17:20   *G. Reiss (Dresden)*
"Growth and Annealing Behaviour of Fe/Cr on SiOx Substrates"

17:30   *V.V. Ustinov (Ekaterinburg)*
"Magnetic Anisotropy and Magnetoresistance of MBE-grown Fe/Cr
Superlattices with Non-collinear Magnetic Structure"

17:40   Discussion

18:05   *S.S.P. Parkin (San-Jose)*
"Dependence of GMR and Interlayer Coupling on Fe Layer Thickness"

18:15   Discussion

18:25   Panel Discussion headed by P. Wigen (Columbus)

# 4 Conference/Workshop Announcements

## 4.1 DFT97 Conference Announcement

# DFT 97

7th International Conference on the
## 'Applications of Density Functional Theory
in Chemistry and Physics'

## September 2-6, 1997, Vienna, Austria

Chairman: *Karlheinz Schwarz*

kschwarz@email.tuwien.ac.at

(Vienna University of Technology, Austria)

Web Site:

`http://www.tuwien.ac.at/theochem/dft97/dft97.html`

*International Scientific Committee*

R.Ahlrichs (U.Karlsruhe, Germany)
R.Car (IRRMA Lausanne, Switzerland)
P.J.Durham (Daresbury, UK)
P.Fantucci (U.Milano, Italy)
A.Goursot (ENSC Montpellier, France)
W.Kohn (U.California Santa Barbara, CA, USA)
R.G.Parr (U. North Carolina, Chappel Hill, NC, USA)
D.Salahub (U.Montreal, Canada)
P.Siegbahn (U.Stockholm, Sweden)

*Local Organizing Committee*

P.Blaha (TU Vienna)
J.Hafner (TU Vienna)
P.Herzig (Univ.Vienna)
H.Lischka (Univ.Vienna)
J.Luitz (TU Vienna)
P.Mohn (TU Vienna)

E.Nusterer (TU Vienna)

K.Schwarz (TU Vienna)

P.Weinberger (TU Vienna)

*Scientific Program*

This four day symposium will be held in Vienna at TU Wien and will bring together scientists interested in DFT, the basic and methodological aspects of theory, program developments and applications in chemistry and physics. The conference will feature invited talks, poster sessions and panel discussions.

The conference begins Tuesday evening, September $2^{nd}$, with (registration and) a reception and ends on Saturday, September $6^{th}$, 1997.

The previous DFT95 conference was held in Paris in 1995 and was attended by about 250 participants.

*Sponsors*

COST-D3

**Pre-registration**

Fill in the pre-registration form using our www-page :

**http://www.tuwien.ac.at/theochem/dft97/dft97.html**

The formal registration will be made available at a later date. The second circular will be mailed to those who have pre-registered by www, email or by completing and returning the registration form below.

---

**DFT97 pre-registration form**

Name (first/initial/last):

Position/Prof./Dr./Ms./Mr./etc./:

Institution:

Address:

Zip-code:

Country:

Phone:

FAX:

Email:

Scientific contribution (tentative title):

Probability to attend: ...... %

Additional comments or questions:

---

Return this information by:

**www (preferred)**, **email** to: dft97@tuwien.ac.at, or by **regular mail** to:

DFT97 Conference
c/o Prof.Karlheinz Schwarz
Vienna University of Technology
A-1060 Vienna
Austria
Fax: +43-1-58 68 937

## 4.2 Trieste Workshop Announcement

# Total Energy and Force Workshop

*Trieste, Italy, 9-11 January, 1997*

The next *"Total Energy and Force Workshop"* will be held in Miramare, Trieste, Italy on 9–11 January 1997.

In order to minimize overlap with the $\Psi_k$–Network Conference in Schwäbisch Gmünd on 17–21 September 1996, this Workshop will focus on a cluster of topics of current interest to both chemists and physicists. These include: location of transition states and calculations of rates; treatment of excited states; electron dynamics; and reactions in solvated and confined environments. However, the traditional wide range of topics in first–principles computational condensed matter physics will also be covered.

A preliminary announcement is available at:

**HTTP://WWW.PHYSICS.RUTGERS.EDU/ DHV/TRIESTE/** .

# 4th European Summer School in Surface Science:

# "Surface Reactivity"

**August 16-22, 1997**

**Krogerup Højskole**
**Humlebæk (north of Copenhagen)**
**Denmark**

**Registration BEFORE April 1, 1997**

**Registration fee: DKR 1500**
(approx. $250)

**More information at the Web page:**

http://www.fysik.dtu.dk/summer97/

Secretary - Helle Wellejus - E-mail: summer97@fysik.dtu.dk

**The summer school is sponsored by the Danish Research Academy, Center for Surface Reactivity, and Center for Atomic-scale Materials Physics (CAMP).**

# 5 Job Announcements

## Studentships

## Queen's University of Belfast and Trinity College of Dublin

The QUEEN'S UNIVERSITY OF BELFAST in collaboration with TRINITY COLLEGE DUBLIN have two interdisciplinary studentships immediately available for theoretical projects in chemistry/physics/materials science. Applications are invited from graduates with first, or second class (upper division honours), or equivalent, in Chemistry or Physics. The first studentship, with Dr. P. Hu (QUB) in collaboration with Dr. J.C. Greer (TCD), involves the development and utilisation of *ab initio* programs for molecules, solid surfaces and the interactions between molecules and solid surfaces. The second project with Professor M.W. Finnis (QUB) and Professor S. Corish (TCD) concerns the ceramic zirconia. It has three crystal structures which are stable at different temperatures. The objective is to find why the addition of elements such as Y or Mg which introduce cation vacancies change the relative stability of the phases. The student will use novel interatomic potentials based on *ab initio* calculations, and classical simulation techniques such as molecular dynamics. Applicants should make a written application, including a CV and the names of two academic referees, to **Dr. P. Hu (School of Chemistry, email: p.hu@qub.ac.uk) or Prof. M. W. Finnis (School of Mathematics and Physics, email: m.finnis@qub.ac.uk), The Queen's University of Belfast, Belfast, BT9 5AG**. The University is a charity established in 1845 to advance education.

# *Announcement*

## OHIO UNIVERSITY - TENURE TRACK
## CONDENSED MATTER THEORY

The Department of Physics and Astronomy at Ohio University invites applications for a tenure-track faculty position in **theoretical condensed matter physics**. The position begins **September 1, 1997**, subject to administrative approval. An excellent research record, a commitment to excellence in teaching, post-doctoral experience, and strong communication skills will be required of the successful applicant. The opening is intended at the Assistant Professor level although a more senior appointment may be possible. The candidate will become a member of the interdisciplinary Condensed Matter and Surface Sciences Program (CMSS) which involves 20+ faculty members in the physics, chemistry, and geology departments as well as mechanical, electrical, and chemical engineering departments. A more complete description of the department and the program can be found via the website `http://www.phy.ohiou.edu`. Applicants should send a resume, a brief description of research plans including a proposed start-up budget, a statement of teaching experience and philosophy, and arrange for three letters of reference to be sent directly to **Prof. S. E. Ulloa, CMSS-Theory, Department of Physics and Astronomy, Ohio University, Athens, OH 45701-2979**. The deadline for completed applications is **15 January 1997**. Ethnic minorities and women are especially encouraged to apply. Ohio University is an AA/EO employer.

## *Announcement*

# Postdoctoral Research Assistant in "Electronic Structure Calculations"

*University of Bristol*

*Department of Physics*

Applications are invited to work on the flag-ship project of CCP9 (Computational Collaborative Project 9 of the EPSRC) involving calculations of surface magnetic anisotropy from first principles. Experience with LMTO and KKR band theory methods would be desirable.

The successful candidate will be member of the Bristol Theory Group but the work will entail collaboration with groups in the UK and Europe.

**Salary range: 14,317–16,628 GBP p.a.**

Informal enquires may be directed to Professor B.L. Györffy, Department of Physics on +44-(0)117-928 8704 or email B.Gyorffy@Bristol.ac.uk.

For further details telephone +44-(0)117-925 6450 (ansaphone after 5pm), minicom +44-(0)117-928 8894, e-mail Recruitment@bris.ac.uk, or write to the Personnel Office (EO), University of Bristol, Senate House, Bristol, BS8 1TH, quoting reference E217.

**The closing date for applications is 1st November 1996**.

An Equal Opportunities Employer
An International Centre for Education and Research

# *Announcement*

## Post–doctoral Position

## Technical University, Vienna, Austria

At the Institute of Theoretical Physics of the Technical University of Vienna (Austria) a postdoctoral position will be available starting November 1996 within a research project on *Ab-initio studies of adsorption processes and reactions of small molecules on transition-metal surfaces.* The position is available for one year, with a possible extension to a second year. The candidate should have a good background in electronic structure calculations and preferably also molecular dynamics, familiarity with surface physics would be appreciated. Salary is at the level of an assistant professor.

**Aplications should be sent to:**

**Juergen Hafner**
**Institut fuer Theoretische Physik**
**Technische Universitaet Wien**
**Wiedner Hauptstrasse 8-10/136**
**A-1040 Wien, Austria**
**Tel. : +43-1-58801-5676**
**FAX : +43-1-5867760**
**Email : jhafner@tph.tuwien.ac.at**

# *Announcement*

## Post–Doctoral Research Position
## Computational Materials Science Department,
## Sandia National Laboratories, Livermore, California, USA

The Computational Materials Science Department at Sandia National Laboratories, Livermore, California, USA, is looking for a highly qualified candidate for a Post-Doctoral Research Position. Candidates are sought with a background in development/application of electronic-structure-type calculations. Those with experience with multiple-scattering, Green's function (KKR) methods are especially of interest. The CMS Dept. has a variety of theoretical projects active: bulk and interphase boundary alloy thermodynamics, energetics of defects, simulations of surface (surface alloy) structural defect phenomena, dynamics of bulk defect structures (e.g., grain boundaries), electronic origins for atomic and displacive short-range order and order/disorder transformations, simulation of early stage growth of alloy microstructure, simulations for reliability of microprocessor lines, to name several. Interested parties should send Curriculum Vitae, including Citizenship, e-mail address, and research interests, to:

**Dr. Duane Johnson, MS 9161,**
**RE: POST-DOC APPLICATION**
**Computational Materials Science Dept.,**
**Sandia National Laboratories,**
**Livermore, CA 94551-0969**
**USA**
**e-mail: djohns@qed.ran.sandia.gov**

Sandia National Laboratories is an Equal Opportunity Employer.

# *Announcement*

## Post–Doctoral Research Vacancy

## Metals and Ceramics Division

## Oak Ridge National Laboratory

The Theory Group of the Metals and Ceramics Division will have one and possibly more vacancies for post doctoral researchers in first principles studies of the magnetic properties of metals and alloys. A background in LDA electronic structure calculations and preferably multiple scattering and/or LMTO techniques is required. An interest in order-N methods for large systems and massively parallel computing is desirable. Members of the theory group have expertise in many areas of materials science. The theory group is part of a large multi-displinary division engaged in materials research and development. The theory group has available a wide range of workstations and has access to state of the art massively parallel computers. Interested individuals should contact Malcolm Stocks at the address below to recieve information regarding the formal application procedure. Initial application via E-mail is preferred. An early starting date is highly desirable.

Oak Ridge National Laboratory is an equal opportunity employer.

**G. Malcolm Stocks,**
**Metals and Ceramics Division,**
**Oak Ridge National Laboratory,**
**P.O. Box 2008-6114,**
**Oak Ridge,**
**TN 37831-6114,**
**USA**
**E-mail: gms@ornl.gov**

# 6  Book Announcements

## Electronic Structure of Disordered Alloys, Surfaces and Interfaces

by

**I. Turek, V. Drchal, J. Kudrnovský, M. Šob**

*Academy of Sciences of the Czech Republic*

**P. Weinberger**

*Technical University of Vienna*

- **Comprehensive text on electronic structure calculations in complex materials**
- **General methods illustrated by applications to many specific systems**
- **Of interest to researchers and graduate students in condensed matter physics and in materials science**

The book gives a detailed and comprehensive account of the *ab initio* tight-binding linear muffin-tin orbital method for studying the electronic structure of ordered and disordered bulk alloys, their surfaces and interfaces. The emphasis is put on a unified description of both the bulk- and surface-related properties in terms of Green function methods. The effect of substitutional randomness is treated in the framework of the coherent potential approximation while the surface Green function technique is used to describe surfaces and interfaces of realistic semi-infinite systems. The presentation of selfconsistency within the local spin-density approximation includes also a non-spherical charge distribution at surfaces and interfaces. Relativistic generalization of the formalism suitable to treat both the non-magnetic and spin-polarized systems is discussed in detail. Basic numerical algorithms as well as ample applications to many of current problems in the solid state and material science theory are also presented.

**Contents**: Introduction. – Linear Muffin-Tin Orbital (LMTO) Method. – Green Function Method. – Coherent Potential Approximation (CPA). – Selfconsistency within Atomic Sphere Approximation. – Relativistic Theory. – Bulk Systems, Overlayers and Surfaces. – Magnetic Properties. – Effective Interatomic Interactions in Alloys. – Numerical Implementation.

**317 pages, 39 figures, 19 tables**         **Publication date: End of 1996**

# Proceedings of the 23rd International Conference on

## THE PHYSICS OF SEMICONDUCTORS

are in print. They are scheduled to appear in about 5 weeks. The CONTENTS of the four volumes (listing also the page numbers) can be found on:

**http://www.rz-berlin.mpg.de/th/icps23/CONTENT.html**

With best wishes from the editors,

Matthias Scheffler and Roland Zimmermann

# Proceedings of the NATO ARW - Early Stages of Oxygen Precipitation in Silicon

Edited by

**R. Jones**

*Department of Physics, University of Exeter, Exeter, EX4 4QL, UK*

This conference covered various aspects of the early stages of oxygen precipitation in silicon, with emphasis on both theoretical and experimental work.

Important new findings have emerged from experiments such as the careful monitoring of the changes in the infra-red lattice absorption spectra over long durations, the observation of the growth of new bands which are correlated with electronic infra-red data, and high resolution ENDOR studies. In addition, progress has been made in the improved control of samples containing oxygen, carbon, nitrogen and hydrogen.

In parallel with these developments, there have been great advances in modelling techniques. A large amount of modelling has already been carried out and the central role of an *overcoordinated* oxygen atom in donors has already been emphasised. Recent progress in first principles methods has, above all else, given greater confidence in predictive theory, and it is thus natural that the subject has excited the interest of so many theoreticians.

The following is a list of sections written by the key speakers from the conference; the proceedings also include many shorter articles from those who presented posters there.

## Primary Contents

1. *Oxygen-related defects in silicon: studies using stress-induced alignment,*
   G. D. Watkins

2. *The initial stages of oxygen aggregation in silicon: dimers, hydrogen and self-interstitials,*
   R. C. Newman

3. *Infrared studies of the early stages of oxygen clustering in silicon,*
   J. L. Lindström, and T. Hallberg

4. *Magnetic resonance investigations of thermal donors in silicon,*
   C. A. J. Ammerlaan, I. S. Zevenbergen, Yu. V. Martynov, and T. Gregorkiewicz

5. *Magnetic resonance on heat treatment centres in silicon,*
   J. -M. Spaeth

6. *Effect of hydrogen on oxygen-related defect reactions in silicon at elevated temperatures,*
   V. P. Markevich, I. F. Medvedeva, and L. I. Murin

7. *Passivation of thermal donors by atomic hydrogen,*
   J. Weber, and D. I. Bohne

8. *Oxygen-carbon, oxygen-nitrogen and oxygen-dimer defects in silicon,*
   C. P. Ewels, R. Jones, and S. Öberg

9. *The role of trivalent oxygen in electrically active complexes,*
   P. Deák

10. *Hydrogen-oxygen interactions in silicon,*
    S. K. Estreicher, Y. K. Park, and P. A. Fedders

11. *Oxygen diffusion in Si: the influence of hydrogen,*
    M. Ramamoorthy, and S. T. Pantelides

12. *Generation of thermal donors, nitrogen-oxygen complexes and hydrogen-oxygen complexes in Si,*
    M. Suezawa

13. *The electronic structure of the oxygen donor in Si from piezospectroscopy,*
    M. Stavola

14. *Low temperature diffusion and agglomeration processes of oxygen in silicon,*
    U. Gösele, E. Schroer, P. Werner, and T. Y. Tan

15. *Role of structural defects and contaminants in the nucleation of oxygen precipitates in silicon,*
    K. Sumino

16. *Various forms of isolated oxygen in semiconductors,*
    B. Pajot

17. *Oxygen-related luminescence centres created in Czochralski silicon,*
    E. C. Lightowlers, and G. Davies

For more details, contact Chris Ewels via e-mail: `ewels@excc.ex.ac.uk`.

# Oxygen-carbon, oxygen-nitrogen and oxygen-dimer defects in silicon

C. P. Ewels, R. Jones

*Department of Physics, University of Exeter, Exeter, EX4 4QL, UK*

S. Öberg

*Department of Mathematics, University of Luleå, Luleå, S95187, Sweden*

## Abstract

An *ab initio* local density functional cluster method, AIMPRO, is used to examine a variety of oxygen related point defects in silicon. In particular results are given for X-$O_n$ complexes where X is interstitial C, N or O. For $n = 2$, the first defect has been assigned to a P-centre giving a PL line at 0.767 eV and seen in Cz-Si annealed around 450°C, while the second has properties consistent with a nitrogen related shallow thermal donor. We have also found that a $(C-H)O_{2i}$ defect has very similar electronic properties, and this implies that shallow thermal donors do not have a unique composition. The structure and migration energy of the oxygen dimer is considered and the dimer is found to migrate very much faster than a single oxygen atom.

# Di-carbon defects in annealed highly carbon doped GaAs

J. Wagner[1], R. C. Newman[2], B .R. Davidson[2], S. P. Westwater[3], T. J. Bullough[3],
T. B. Joyce[3], C. D. Latham[4], R. Jones[4], S. Öberg[5]

## Abstract

Formation of bonded di-carbon C–C centers is deduced by the observation of Raman lines at 1742, 1798 and 1674 cm$^{-1}$ in GaAs co-doped with $^{12}$C and $^{13}$C after annealing at 850 C with concomitant loss of vibrational scattering from $C_{As}$. The frequencies agree with results of *ab initio* theory for a C–C split interstitial (deep donor) formed by the trapping of a mobile interstitial C (displaced $C_{As}$ acceptor. Other mechanisms of carrier loss are inferred since a weaker Raman triplet is detected at 1859, 1824 and 1788 cm$^{-1}$ from a different C–C complex.

[1]   Fraunhofer-Institut für Angewandte Festkürperphysik, Tullastrasse 72, D-71908 Freiburg, Germany.
[2]   Interdisciplinary Research Centre for Semiconductor Materials, The Blackett Laboratory,
Imperial College of Science, Technology and Medicine, London, SW7 2BZ, UK.
[3]   Department of Materials Science and Engineering, P.O. Box 147, Liverpool University, L69 3BX, UK.
[4]   Department of Physics, University of Exeter, Exeter, EX4 4QL, UK.
[5]   Department of Mathematics, University of Luleå, S-951 87 Luleå, Sweden.

# Dynamic Properties of Interstitial Carbon and Carbon-Carbon Pair Defects in Silicon

P. Leary, R. Jones

*Department of Physics, University of Exeter, Exeter, EX4 4QL, UK*

S. Öberg

*Department of Mathematics, University of Luleå, Luleå, S95187, Sweden*

V. J. B. Torres

*Departamento de Física, Universidade de Aveiro, 3810 Aveiro, Portugal*

## Abstract

Interstitial carbon, $C_i$, defects in Si exhibit a number of unexplained features. The $C_i$ defect in the neutral charge state of gives rise to two almost degenerate vibrational modes at 920 and 931 cm$^{-1}$ whose 2:1 absorption intensity ratio naturally suggests a trigonal defect in conflict with uniaxial stress measurements. The di-carbon, $C_s$-$C_i$, defect is bi-stable, and the energy difference between its A and B forms is surprisingly small even though the bonding is very different. In the B-form appropriate to the neutral charge state, a silicon interstitial is believed to be located near a bond centered site between two $C_s$ atoms. This must give rise to vibrational modes which involve the motion of both C atoms in apparent conflict with the results of photoluminescence experiments. We use an *ab initio* LDF cluster method, AIMPRO, to calculate the structure and vibrational modes of these defects and find that the ratio of the absorption intensities of the local modes of $C_i$ is in reasonable agreement with experiment even though the structure of the defect is not trigonal. We also show that modes in the vicinity of those detected by PL for the B-form of the di-carbon center involve independent movements of the two C atoms. Finally, the trends in the relative energies of the A and B-forms in three charge states are investigated.

# Effects of band structure and spin-independent disorder on conductivity and giant magnetoresistance in Co/Cu and Fe/Cr multilayers

E.Yu.Tsymbal and D.G.Pettifor

*Department of Materials, University of Oxford,*

*Parks Road, Oxford OX1 3PH, UK*

## Abstract

We develop a tight-binding model for calculating conductivity in multiband spin-dependent systems within the Kubo-Greenwood formalism. The model includes spin-independent disorder in the on-site atomic energies, representing intrinsic defects in real systems, and realistic spin-polarised electronic band structure. The model is applied to calculating conductivity in elemental 3d metals and giant magnetoresistance (GMR) in magnetic Co/Cu and Fe/Cr multilayers. We find that for disorder, producing a realistic resistivity of the multilayers, the values of GMR are in quantitative agreement with those observed experimentally. We demonstrate how the conductivity and GMR depend on the features of the electronic band structure and degree of disorder in the system. In particular, we show that (i) the d electrons make an important contribution to the current in magnetic 3d metals and multilayers, (ii) the sp-d hybridisation is crucial for GMR, (iii) increasing disorder causes a decrease of the spin-asymmetry of conductivity in magnetic metals and a drop of GMR in multilayers, (iv) GMR for the current-perpendicular-to-plane geometry is typically a factor of two higher than that for the current-in-plane geometry and (v) the semiclassical treatment of conductivity applied to magnetic multilayers results in overestimated values of GMR due to the neglect of interband transitions.

# Multilayer systems and symmetry

P. Weinberger

*Institut für Technische Elektrochemie, Technical University of Vienna,*
*and Center for Computational Materials Science, Vienna, Austria*

## Abstract

In this paper concepts such as lattices and translational and rotational invariance are critically reviewed as far as their applications for infinite and semi-infinite multilayer systems are concerned. It turns out that new terms such as *parent three-dimensional lattices* and *colloquial lattices* have to be defined. Particular attention is given to the consequences of these new concepts as well as to a spin-polarized fully relativistic description for magnetic multilayers within the local density functional approximation.

# Lattice distortion in Cu-based dilute alloys: a first-principles study by the KKR Green function method

N. Papanikolaou, R. Zeller, and P. H. Dederichs

*Institut für Festkörperforschung, Forschungszentrum Jülich,*
*D-52425 Jülich, Germany*

N. Stefanou

*Section of Solid State Physics, University of Athens,*
*GR-15784 Zografos, Athens, Greece*

## Abstract

The full-potential Korringa-Kohn-Rostoker Green function method is extended to treat the lattice distortion in the vicinity of a point defect. The method is applied to predict the atomic positions in the neighborhood of $d$ and $sp$ substitutional impurities in Cu. Both the total energy and the Hellmann-Feynman force are used for the calculation of the ground state configuration while the semicore states of the impurities are treated as valence states. Our results for the atomic displacements are in very good agreement with the experimental data from extended X-ray-absorption fine-structure and lattice-parameter measurements.

# A density functional study of polythiophene derivatives

G. Brocks

*Philips Research Laboratories,*
*Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands*

## Abstract

Density functional calculations within the Car-Parrinello framework are used to obtain self-consistently the electronic and the geometrical structures of polythiophene derivatives. The relation between the electronic states and quinoid vs. aromatic structures is studied on a series of substituted polythiophenes (PTh) and polyisothianaphtenes (PITN). Excellent agreement is found with experimental data, where these are available. Some short-comings of semi-empirical methods in describing $\pi$ bonds with hetero-atoms are revealed. A unique minimal energy structure is obtained for each of the polymers; no other local minima are found. The general rule is that a polymer adapts the structure which leads to the largest possible band gap, which for PTh-like polymers is the aromatic structure and for PITN-like polymers is the quinoid structure. Substitutions do not change the basic geometry and electronic structure of either PTh or PITN, but can alter the band gap by several tenths of an eV.

# Theory of the Electronic and Magnetic Structure of Cerium Pnictides under Pressure

A. Svane[†], Z. Szotek[‡], W.M. Temmerman[‡], and H. Winter[§]

[†]*Institute of Physics and Astronomy, University of Aarhus,*
*DK-8000 Aarhus C, Denmark*
[‡]*Daresbury Laboratory, Warrington WA4 4AD, United Kingdom*
[§]*Forschungszentrum Karlsruhe, INFP, Postfach 3640, Karlsruhe, Germany*

## Abstract

The electronic structures of the cerium pnictides CeN, CeP, CeAs, CeSb and CeBi are calculated within the self-interaction corrected local-spin density approximation. This method allows a description of the Ce $f$−electrons as either localized or delocalized. We find that the isostructural phase transition in CeP is associated with the delocalization of the $f$−electron under pressure. Similar structural phase transitions in CeAs, CeSb and CeBi are also well described by this theory. Moreover, in agreement with recent experiments we obtain a very low carrier type−I antiferromagnetic groundstate for CeP and CeSb.

# Influence of the Orbital Polarization on the Magnetic X-ray Dichroism of Transition Metals

H. Ebert
*Institut für Physikalische Chemie, Universität München,*
*Theresienstr. 37, D-80333 München, Germany*

## Abstract

Using the fully relativistic Korringa-Kohn-Rostoker (KKR) band structure method, the consequences of the orbital polarization mechanism, as described by the formalism of Brooks and coworkers, for the circular magnetic dichroism in X-ray absorption (MCXD) has been investigated for the $L_{2,3}$- and K-edges of pure Fe. For the $L_{2,3}$-edge only small changes for the dichroic spectrum has been found, while the corresponding spectrum of the K-edge shows an appreciable enhancement. These apparently paradox results are explained on the basis of the so-called MCXD sum rules.

# Magneto-optical effects in transition metal systems

H. Ebert

*Institut für Phys. Chemie, Univ. München,*
*Theresienstr. 37, D-80333 München*

## Abstract

A theoretical description of magneto-optical effects in metallic transition metal systems on the basis of an itinerant description for the underlying electronic structure is presented and applications to the magneto-optical Kerr effect and the circular dichroism in X-ray absorption are discussed. Simple arguments based on symmetry considerations as well as electronic excitation schemes are given that magneto-optical effects are caused by the interplay of magnetic ordering and spin-orbit coupling. The various band structure techniques developed to deal with this situation are reviewed with an emphasize on fully relativistic methods based on the Dirac equation. The theoretical framework to calculate magneto-optical spectra on the basis of the underlying band structure is outlined in some detail. In addition a number of sum rules derived by various authors are presented that allow to estimate spin and orbital magnetic moments of an absorbing atom from its magnetic X-ray dichroism spectra. For the magneto-optical Kerr effect as well as the magnetic X-ray dichroism application of the theoretical formalism is presented for a great variety of systems, i.e. pure elements, compounds, alloys, and multilayer systems. For both kind of spectroscopies it is demonstrated that model calculations, that allow to manipulate the exchange splitting and the spin-orbit coupling strength give valuable information for a better understanding of the rather complex spectra. Concerning the sum rules this technique together with the direct calculation of the dichroism spectra allow for a stringent test of the various assumptions on which these rules are based.

# The atomic and electronic structure of the diamond (100) surface: reconstructions and rearrangements at high hydrogen coverage

M. D. Winn[1], M. Rassinger, and J. Hafner

*Institut für Theoretische Physik, Technische Universität Wien,*

*Wiedner Hauptstraße 8 - 10, A-1040 Wien, Austria*

## Abstract

The atomic and electronic structure of the diamond (100) surface has been investigated theoretically via a semi-empirical Tight-Binding model for a range of hydrogen coverages. Model parameters for C–C interactions have been taken from the work of Goodwin (J.Phys.: Condens. Matter **3**, 3869 (1993)), while new parameter sets have been determined for C–H and H–H interactions. The model gives results for the clean and monohydrogenated surfaces in good agreement with previous studies, but novel features have been identified for higher H-coverages. When the H-coverage is sufficiently high, the substrate lattice is found to distort in order to reduce steric repulsions between dihydride units. As an important example, we obtain two novel structures for the dihydrogenated surface which are significantly more stable than those proposed previously. For H-coverages intermediate between the monohydrogenated and dihydrogenated surfaces, stable geometries consisting of monohydrogenated dimer units and dihydride units are found. In contrast, geometries which include isolated monohydride units, such as have been previously investigated, are found to be thermodynamically and kinetically unstable. Tight-Binding Molecular Dynamics is used to illustrate a mechanism for the rapid removal of isolated monohydride units. The electronic structure of the surfaces are described via the total and partial electronic densities of state, which are obtained directly from the Tight-Binding Hamiltonian. For the monohydrogenated surface and higher coverages, the stable geometries are found to yield no states in the bulk band gap.

[1] *Present address: Daresbury Laboratory, Daresbury, Warrington, WA4 4AD, England.*

*Email: m.d.winn@dl.ac.uk*

# Atomic and Electronic Structure of Decagonal Al-Pd-Mn Alloys and Approximant Phases

M. Krajčí[1] and J. Hafner

*Institut für Theoretische Physik, Technische Universität Wien,*

*Wiedner Hauptstraße 8-10/136, A-1040 Wien, Austria*

M. Mihalkovič

*Institute of Physics, Slovak Academy of Sciences,*

*it Dúbravská cesta 9, SK 84228 Bratislava, Slovakia*

## Abstract

The electronic structure of the decagonal phase $Al_{70}Pd_{13}Mn_{17}$ and related crystalline phases has been calculated using the self-consistent tight-binding linear-muffin-tin-orbital TB-LMTO technique. The electronic densities of states and the spectral functions have been calculated via the real-space recursion technique. The structural models are based on the decagon-pentagon-hexagon (DPH) tiling. Chemical short-range order is optimized using the information about the local densities of states. The pentagonal columnar clusters (identified by Hiraga et al) exhibit structural stability and play the role of a characteristic structural unit of all the discussed phases. Formation of a pseudogap in the Al-sp-band is observed and its origin and role in the stabilization of the decagonal phase is discussed.

[1] *Permanent address: Institute of Physics, Slovak Academy of Sciences,*

*SK 84228 Bratislava, Slovakia*

# Propagating and localized elementary excitations in decagonal quasicrystals

J. Hafner[a], M. Krajčí[a,b], and M.Mihalkovič[b]

[a] *Institut für Theoretische Physik, Technische Universität Wien,*
*Wiedner Hauptstr. 8-10, A-1040 Wien, Austria*
[b] *Institute of Physics, Slovak Academy of Sciences,*
*SK 84226 Bratislava, Slovakia*

## Abstract

We have studied the properties of elementary excitations in decagonal (d) quasicrystals at the example of vibrational eigenstates in a model d-AlMn alloy. We show that the presence of a periodic direction leads to marked differences compared to icosahedral (i) quasicrystals: distinctly higher eigenvalues, a much more structured density of states, a stronger tendency towards the localization of certain eigenstates. These effects are related to the lower dimensionality of the quasiperiodicity, and in particular to the coupling between longitudinal modes propagating along the periodic direction and transverse modes in the quasiperiodic plane, but polarized parallel to the periodic axis.

# Elementary Excitations in Quasicrystals

M. Krajčí and J. Hafner

*Institut für Theoretische Physik and Center for Computational Materials Science*
*Technische Universität Wien, Wiedner Hauptstraße8 − 10, A-1040 Wien, Austria*

## Abstract

We present detailed ab–initio investigations of electron- and phonon spectra in realistic models for icosahedral and decagonal quasicrystals. We show that the hierarchical dense structure of quasi–Brillouin–zone centers and boundaries in wave–number space explains both the spiky nature of the density of states and the existence of both propagating and stationary (localized) eigenstates. The consequence of the character of the eigenstates for the anomalous electronic transport and magnetic properties are discussed.

# Hydrogen adsorption on the (100) surfaces of rhodium and palladium: The influence of nonlocal exchange-correlation interactions

A. Eichler, J. Hafner, and G. Kresse

*Institut für Theoretische Physik and Center for Computational Materials Science*
*Technische Universität Wien, Wiedner Hauptstraße8 – 10, A-1040 Wien, Austria*

## Abstract

We report *ab-initio* investigations of the adsorption of atomic hydrogen on the (100) surfaces of $Rh$ and $Pd$ in the local-density-functional and generalized-gradient approximations. Our calculations have been performed in a plane-wave basis, using optimized ultrasoft pseudopotentials for describing the electron-ion interactions. Detailed results are reported for the adsorption energies, the stability of various adsorption geometries, the adsorption-induced changes in the surface-relaxations and in the work functions. We find that the adsorption of a monolayer of hydrogen changes the inward-relaxation of the top-layer of the substrate into an outward-relaxation. However, the change of the substrate-relaxation has only a very small influence on the adsorption-energy and geometry. On both metals the stable adsorption sites are the fourfold hollows. The site-preference has its origin in a maximum gain of covalent bonding energy resulting from the overlap of the hydrogen-s and the metal-$d_{x^2-y^2}$ orbitals and from a minimal Pauli repulsion. Nonlocal exchange-correlation corrections have only a small influence on the atomic adsorption process and on the relaxation of the substrate, but influence the adsorption energy through corrections to the binding energy of the hydrogen molecule. Relativistic effects, however, turn out to be quite important.

# Reaction Path for the Dissociative Adsorption of Hydrogen on the (001) Surfaces of Face-Centered-Cubic Transition Metals

A. Eichler, J. Hafner, and G. Kresse

*Institut für Theoretische Physik and Center for Computational Materials Science*
*Technische Universität Wien, Wiedner Hauptstraße8 – 10, A-1040 Wien, Austria*

**Abstract**

Detailed *ab-initio* local-density-functional studies of the potential-energy surfaces for the dissociative adsorption of hydrogen molecules on the (100) surfaces of face-centred-cubic transition- and noble metals are presented. We show that the energetically most favourable reaction path is determined by quantum-mechanical steering effects arising from the formation and modification of covalent metal-hydrogen bonds. Variations of the local chemical reactivity with the filling of the d-band are discussed at the example of rhodium, palladium, and silver surfaces.

# Hydrogen adsorption on the (100) surfaces of rhodium, palladium and silver

A. Eichler, J. Hafner, and G. Kresse

*Institut für Theoretische Physik and Center for Computational Materials Science*
*Technische Universität Wien, Wiedner Hauptstraße8 – 10, A-1040 Wien, Austria*

**Abstract**

The adsorption of atomic hydrogen on the (100) surfaces of face-centred-cubic rhodium, palladium and silver has been studied using *ab-initio* density-functional calculations (including generalized gradient corrections). At the example of Rh(100) we present detailed investigations of the influence of the nonlocal corrections to the exchange-correlation functional on the stable geometries and the energies of adsorption. We also study the influence of the adsorbate on the relaxation of the substrate. Chemical trends are studied along the series Rh-Pd-Ag.

# Ab-initio MD studies of the structure of C(111):$n$H surfaces

G. Kern, J. Hafner and G. Kresse

*Institut für Theoretische Physik and Center for Computational Materials Science*

*Technische Universität Wien, Wiedner Hauptstraße8 – 10, A-1040 Wien, Austria*

### Abstract

We present *ab-initio* local-density functional investigations of clean and hydrogen-covered one- (1db) and three-dangling-bond (3db) diamond (111) surfaces, the geometries of the reconstructed surfaces and their stabilities at different values of the hydrogen chemical potential. Then preliminary molecular-dynamic results of reconstruction and graphitization for the 1db surface at elevated temperatures are reported.

# Theory of bilinear and biquadratic exchange interactions in iron: bulk and surface

D. Spišák[1] and J. Hafner

*Institut für Theoretische Physik and Center for Computational Materials Science*

*Technische Universität Wien, Wiedner Hauptstraße8 – 10, A-1040 Wien, Austria*

### Abstract

We present a torque-force approach to the calculation of bilinear and biquadratic exchange interactions in itinerant magnet. Detailed calculations within a real-space tight-binding framework are presented for iron and the (001)-surface of iron.

[1] *Permanent address: Department of Experimental Physics,*

*Šafárik University, SK 041 54 Košice, Slovak Republic*

# Strained tetragonal states and Bain paths in metals

P. Alippi[1], P.M. Marcus[1,2], and M. Scheffler[1]

[1]*Fritz-Haber-Institut der Max-Planck-Gesellschaft,*
*Faradayweg 4-6, D-14 195 Berlin-Dahlem, Germany*
[2]*IBM Research Center, Yorktown Heights, N.Y. 10598, USA*

### Abstract

Paths of tetragonal states between two phases of a material, such as bcc and fcc, are called Bain paths. Two simple Bain paths can be defined in terms of special imposed stresses, one of which applies directly to strained epitaxial films. Each path goes far into the range of nonlinear elasticity and reaches a range of structural parameters in which the structure is inherently unstable. In this paper we identify and analyze the general properties of these paths by density functional theory. Special examples include vanadium, cobalt and copper, and the epitaxial path is used to identify an epitaxial film as related uniquely to a bulk phase.

# Ab initio molecular dynamics study of the desorption of $D_2$ from Si(100)

Axel Gross, Michel Bockstedte, and Matthias Scheffler
*Fritz-Haber-Institut der Max-Planck-Gesellschaft,*
*Faradayweg 4-6, D-14 195 Berlin-Dahlem, Germany*

### Abstract

*Ab initio* molecular dynamics calculations of deuterium desorbing from Si(100) have been performed in order to monitor the energy redistribution among the various $D_2$ and silicon degrees of freedom during the desorption process. The calculations show that a considerable part of the potential energy at the transition state to desorption is transferred to the silicon lattice. The deuterium molecules leave the surface vibrationally hot and rotationally cold, in agreement with experiments; the mean kinetic energy, however, is larger than found in the experiment. We discuss possible reasons for this discrepancy.

# Steering and isotope effects in the dissociative adsorption of H$_2$/Pd(100)

Axel Gross and Matthias Scheffler

*Fritz-Haber-Institut der Max-Planck-Gesellschaft,*

*Faradayweg 4-6, D-14 195 Berlin-Dahlem, Germany*

**Abstract**

The interaction of hydrogen with many transition metal surfaces is characterized by a coexistence of activated with non-activated paths to adsorption with a broad distribution of barrier heights. By performing six-dimensional quantum dynamical and classical molecular dynamics calculations using the same potential energy surface derived from *ab initio* calculations for the system H$_2$/Pd(100) we show that these features of the potential energy surface lead to strong steering effects in the dissociative adsorption dynamics. The adsorption dynamics shows only a small isotope effect which is purely due to the quantum nature of hydrogen.

# Diffusivity of Ga and Al adatoms on GaAs(001)

A. Kley and M. Scheffler

*Fritz-Haber-Institut der Max-Planck-Gesellschaft,*

*Faradayweg 4-6, D-14 195 Berlin-Dahlem, Germany*

**Abstract**

The diffusivity of Ga and Al adatoms on the (2×4) reconstructed GaAs(001) surface are evaluated using detailed *ab initio* total energy calculations of the potential energy surface together with transition state theory. A strong diffusion anisotropy is found, with the direction of fastest diffusion being parallel to the surface As-dimer orientation. In contrast to previous calculations we identify a short–bridge position between the two As atoms of a surface dimer as the adsorption site for Al and Ga adatoms.

# Ab-initio study of the anomalies in the
# He atom scattering spectra of H/Mo (110) and H/W (110)

Bernd Kohler, Paolo Ruggerone, and Matthias Scheffler

*Fritz-Haber-Institut der Max-Planck-Gesellschaft,*

*Faradayweg 4-6, D-14 195 Berlin-Dahlem, Germany*

## Abstract

Helium atom scattering (HAS) studies of the H-covered Mo (110) and W (110) surfaces reveal a twofold anomaly in the respective dispersion curves. In order to explain this unusual behavior we performed density functional theory calculations of the atomic and electronic structure, the vibrational properties, and the spectrum of electron-hole excitations of those surfaces. Our work provides evidence for hydrogen adsorption induced Fermi surface nesting. The respective nesting vectors are in excellent agreement with the HAS data and recent angle resolved photoemission experiments of the H-covered alloy system $Mo_{0.95}Re_{0.05}$ (110). Also, we investigated the electron-phonon coupling and discovered that the Rayleigh phonon frequency is lowered for those critical wave vectors. Moreover, the smaller indentation in the HAS spectra can be clearly identified as a Kohn anomaly. Based on our results for the susceptibility and the recently improved understanding of the He scattering mechanism we argue that the larger anomalous dip is due to a direct interaction of the He atoms with electron-hole excitations at the Fermi level.

# Role of defects and impurities in doping of GaN

[1]Jörg Neugebauer and [2]Chris G. Van de Walle

[1]*Fritz-Haber-Institut der Max-Planck-Gesellschaft,*
*Faradayweg 4-6, D-14 195 Berlin-Dahlem, Germany*
[2]*Xerox Palo Alto Research Center,*
*3333 Coyote Hill Road, Palo Alto, CA 94304, USA*

## Abstract

We have calculated formation energies and position of the defect levels for all native defects and for a variety of donor and acceptor impurities employing first-principles total-energy calculations. An analysis of the numerical results gives direct insight into defect concentrations and impurity solubility with respect to growth parameters (temperature, chemical potentials) and into the mechanisms limiting the doping levels in GaN. We show how compensation and passivation by native defects or impurities, solubility issues, and incorporation of dopants on other sites influence the acceptor doping levels.

# Thermal Expansion of Ag(111) and other Metal Surfaces

Shobhana Narasimhan and Matthias Scheffler

*Fritz-Haber-Institut der Max-Planck-Gesellschaft,*

*Faradayweg 4-6, D-14 195 Berlin-Dahlem, Germany*

## Abstract

We develop a model to study the thermal expansion of surfaces, wherein phonon frequencies are obtained from *ab initio* total energy calculations. Anharmonic effects are treated exactly in the direction normal to the surface, and within a quasiharmonic approximation in the plane of the surface. We apply this model to the Ag(111) and Al(111) surfaces, and find that our calculations reproduce the experimental observation of a large and anomalous increase in the surface thermal expansion of Ag(111) at high temperatures [1]. Surprisingly, we find that this increase can be attributed to a rapid softening of the *in-plane* phonon frequencies, rather than due to the anharmonicity of the out-of-plane surface phonon modes. This provides evidence for a new mechanism for the enhancement of surface anharmonicity. A comparison with Al(111) shows that the two surfaces behave quite differently, with no evidence for such anomalous behavior on Al(111).

[1] P. Statiris, H.C. Lu and T. Gustafsson, Phys. Rev. Lett. **72**, 3574 (1994).

# Theory of alkali induced reconstruction of the Cu(100) surface

Sven Quassowski and Klaus Hermann

*Fritz-Haber-Institut der Max-Planck-Gesellschaft,*

*Faradayweg 4-6, D-14 195 Berlin-Dahlem, Germany*

## Abstract

LEED experiments show that Li adsorbed at Cu(100) surfaces at room temperature induces a (2×1) missing row substrate reconstruction while adsorption at lower temperatures, $T$=180 K, results in an unreconstructed Cu(100)+c(2×2)–Li overlayer structure. Substrate reconstruction has not been observed for Na nor for K adsorption. In order to study the specific reconstruction behavior of the Li adsorbate ab initio DFT calculations have been performed on Cu(100)+Ad, Ad = Li, Na, K systems at coverages $\Theta_{Ad} = 0.25 - 0.5$ with and without reconstruction. The calculations show that the (2×1) MR reconstructed surface lies energetically above the ideal (1×1) surface by 0.2 eV per unit cell. However, alkali binding is stronger in the MR geometry as compared to that of the ideal surface where the increase in bond strength becomes smaller in going from Li to Na to K. As a result, the MR reconstructed and the overlayer adsorbate systems are energetically very close for Cu(100)+Li while for Na and K the overlayer geometry is always favored.

# Half-space Jellium and Its Natural Occupation Numbers: Generalized Neutrality Sum Rule and Correlation Entropy

Paul Ziesche

*c/o Max Planck Institute for Physics of Complex Systems,*
*Bayreuther Str. 40, D - 01187 Dresden, Germany*

Peter Gersdorf[1]

*c/o Institut für Organische Chemie, Technische Universität Dresden,*
*it Mommsenstr. 13, D-01062 Dresden, Germany*

## Abstract

A conceptional analysis of half-space jellium in terms of its one-particle density matrix (diagonalized by natural orbitals and natural occupation numbers as eigenfunctions and eigenvalues) is presented. This allows to apply the concept of correlation entropy as a measure of correlation strength. Exact expressions for the electron density, the kinetic energy density and the correlation entropy density are given. A generalized Sugiyama-Langreth neutrality sum rule for the phases which describe the bulk asymptotics of the natural orbitals is derived. Kinetic surface energy and correlation surface entropy depend on these phases and on the bulk momentum distribution of the uniform electron gas.

[1] *Present address: Luchbergstr. 6, D-01237 Dresden, Germany*

# Correlation Entropy of the He Isoelectronic Series and the Hooke Law Model

S.P. Rudin

*Department of Physics, Ohio State University,*

*Columbus, OH 43210 - 1168, USA*

Peter Gersdorf[1]

*c/o Institut für Organische Chemie, Technische Universität Dresden,*

*it Mommsenstr. 13, D-01062 Dresden, Germany*

M. Taut

*Technische Universität Dresden, Abteilung Physik, Max-Planck-Arbeitsgruppe*

*'Theorie komplexer und korrelierter Elektronensysteme', D-01060 Dresden, Germany*

Paul Ziesche

*c/o Max Planck Institute for Physics of Complex Systems,*

*Bayreuther Str. 40, D - 01187 Dresden, Germany*

## Abstract

The recently developed concept of a correlation entropy as a quantitative measure of the correlation strength present in a correlated quantum many-body state is applied to the ground states (singlets) of the He isoelectronic series $He(Z)$ and of the Hooke law model $HLM(\omega)$ with varying oscillator frequency $\omega$. The correlation entropy — constructed with the natural occupation numbers, *i.e.*, the eigenvalues of the one-particle density matrix — increases monotonically with decreasing coupling constants $Z$ or $\omega$.

# Full charge density scheme with kinetic energy correction: Application to the ground state properties of cubic 4d elements

L. Vitos and J. Kollár

*Research Institute for Solid State Physics, H-1525 Budapest, P.O.Box 49, Hungary*

H. L. Skriver

*Center for Atomic-scale Materials Physics and Department of Physics,
Technical University of Denmark, DK-2800 Lyngby, Denmark*

### Abstract

We present a full charge-density technique to evaluate total energies from the output of self-consistent linear muffin-tin orbitals (LMTO) calculations in the atomic-sphere approximation (ASA). The Coulomb energy is calculated exactly from the complete, nonspherically symmetric charge density defined within nonoverlapping, space-filling Wigner-Seitz cells, the exchange-correlation energy is evaluated by means of the local density approximation or the generalized gradient approximation applied to the complete charge-density, and the ASA kinetic energy is corrected for the nonspherically symmetric charge-density by a gradient expansion. The technique retains most of the simplicity and the computational efficiency of the LMTO-ASA method, and calculations of atomic volumes and elastic constants of the $4d$ elements show that it has the accuracy of full-potential methods.

# Effect of localization on the $\alpha$-phase atomic volumes of the light actinides

J. Kollár*, L. Vitos*, and H. L. Skriver**

*Research Institute for Solid State Physics, H-1525 Budapest, P.O.Box 49, Hungary*
**Center for Atomic-scale Materials Physics and Physics Department,
Technical University of Denmark, DK-2800 Lyngby, Denmark*

### Abstract

We have carried out a full charge density calculation for the equilibrium atomic volumes of the $\alpha$-phase light actinide metals using LDA and GGA exchange-correlation energy functional. The deviation between the experimental and GGA values never exceeds 2% and, on average, it is less than 1%. The comparison of the LDA and GGA results show that the unexpectedly large atomic volume for $\alpha$-Pu can be ascribed to the presence of low co-ordinated sites in the structure where the $f$-electrons are close to the onset of localization and the charge density is very low in the interstitial region. In this case the LDA is not able to describe properly the exchange-correlation effects, while the accuracy of the GGA is satisfactory for this system as well.

# 'Giant' magnetoresistance in uranium intermetallics: *ab-initio* calculations for $U_2Pd_2In$ and $U_2Pd_2Sn$

Manuel Richter[a], Peter Zahn[b], Martin Diviš[c,a], and Ingrid Mertig[b]

[a] *MPG Research Group 'Electron Systems', University of Technology,*
*D-01062 Dresden, Germany*
[b] *Institute of Theoretical Physics, University of Technology,*
*D-01062 Dresden, Germany*
[c] *Department of Metal Physics, Charles University,*
*Ke Karlovu 5, 121 16 Prague 2, Czech Republic*

### Abstract

Among the magnetic uranium intermetallic compounds, a considerable number is exhibiting field induced magnetic phase transitions. Such transitions are frequently accompanied by 'giant' magnetoresistance (GMR) effects. On the basis of density functional calculations we predict GMR to be present in the recently discovered ternary compounds $U_2Pd_2In$ and $U_2Pd_2Sn$. In particular, it is shown by this exemplary calculation that GMR in 5f intermetallics can be produced by topological changes of the Fermi surface even if the size of the Brillouin zone is invariant under the metamagnetic transition. The possibility of an inverse GMR effect is demonstrated without assuming any spin dependence in the scattering. No qualitative changes of the results are found if a moderately spin dependent scattering is introduced.

# Magnetism and Magnetocrystalline Anisotropy of $Np_2T_2X$ (T = Co, Ni, Ru, Rh, Pd, Ir, Pt; X = In, Sn) compounds derived from Density Functional Calculations

Martin Diviš[1,2], Manuel Richter[2] and Helmut Eschrig[2]

[1]*Department of Metal Physics, Charles University,*
*Ke Karlovu 5, 121 16 Prague 2, Czech Republic*
[2]*MPG Research Group 'Electron Systems', University of Technology,*
*D-01062 Dresden, Germany*

## Abstract

*Ab initio* electronic structure calculations for $Np_2T_2X$ intermetallic compounds were performed using an optimized linear combination of atomic orbitals method based on the local density approximation. Thus, we are aiming at a theoretical description of magnetic properties in the normal metallic state. The 5f-states of Np were assumed itinerant and treated as band states. The particular composition dependent electronic structure results from the interplay between two main ingredients: first, the band filling of the free electron background (s-, p- and neptunium d-electrons) and the transition metal bonding bands and second, covalency (hybridization) between bonding predominantly d-states of T atoms and antibonding predominantly f-states of Np atoms. Spin and orbital moments were obtained from fully relativistic spin-polarised calculations. A quantitative study of the magnetocrystalline anisotropy is provided on the basis of calculated differences of eigenvalue sums for different orientations of the magnetic moment. We show that the results of our approach agree with the observed experimental trends in the magnetic properties of $Np_2T_2X$.

# Electronic structure of Eu and Yb graphite intercalation compounds

S.L. Molodtsov[1], C. Laubschat[1], M. Richter[2], Th. Gantz[1],
and A.M. Shikin[3]

[1] *Institut für Oberflächenphysik und Mikrostrukturphysik,*
*TU Dresden, D-01062 Dresden, Germany*
[2] *Max-Planck-Arbeitsgruppe "Elektronensysteme", TU Dresden,*
*D-01062 Dresden, Germany*
[3] *Institute of Physics, St. Petersburg State University,*
*198904 St. Petersburg, Russia*

## Abstract

An angle-resolved photoemission (PE) study is performed on graphite intercalation compounds (GIC's) with Eu and Yb prepared *in situ* by deposition of the pure metals onto single-crystalline graphite(0001) surfaces and subsequent annealing. The low-energy-electron-diffraction patterns reveal a sharp $(\sqrt{3} \times \sqrt{3})R30°$ overstructure as observed for other rare-earth (RE) and alkali GIC's. The PE data are in excellent agreement with local-density-approximation band-structure calculations for stage-2 GIC's that indicate charge transfer of about 0.5 electrons per RE atom into graphite-derived states of $\pi$ symmetry. This charge transfer is caused by an energetical lowering of the graphite-derived $\pi$ bands and leads to the appearance of an intense Fermi-level structure in the PE spectra taken around the $K(\Gamma')$ point of the Brillouin zone. Admixtures of rare-earth-derived d states are found close to the Fermi energy in the region of the $\Gamma$ and the $M'$ points.

# Self Interaction Correction and Relativistic Exchange on the Core States and Core Hyperfine Fields in Fe, Co and Ni

L. Severin

*Institut für Festkörperphysik, Technische Hochschule Darmstadt*

*D-64289 Darmstadt, Federal Republic of Germany*

M. Richter and L. Steinbeck

*MPG, Research Group 'Electron Systems', University of Technology*

*D-01062 Dresden,Federal Republic of Germany*

**Abstract**

For the core states, self interaction corrected local density calculations are reported for the transition metal ferromagnets Fe, Co and Ni. The hyperfine field matrix elements have been computed. Good agreement with measurements is obtained for Co, whereas for Fe and Ni the discrepancy between local density theory and experiment remains also in the self interaction corrected calculation. Possible changes in the core states due to relativistic exchange corrections are also discussed and found to be of minor importance.

# Calculation of extended electronic states in simple liquids and plasmas

Pierre Dallot

*Commissariat a l'Energie Atomique, Centre d'Etude de Limeil-Valenton,*

*94195, Villeneuve St. Georges, France*

**Abstract**

The calculation of some electronic processes, such as bound-free transitions in plasmas, require a description of the free electron wave function that is consistent with that of the bound state. Because the plasma is a disordered media, such a description is difficult. In this paper, we first propose that the one-electron expectation values $< \Psi_E|A|\Psi_E >$ can be considered as self averaging quantities when $|\Psi_E >$ is delocalized. Using this, we give a description of the eigenstate that is consistent with the disorder, and that permits us to calculate $< \Psi_E|A|\Psi_E >$ in the thermodynamic limit. Finally, we test the method by calculating an electron-ion correlation function in liquid sodium.

# Non–collinear magnetism in distorted perovskite compounds

I.V. Solovyev[1], N. Hamada[2] and K. Terakura[3]

[1]*Joint Research Center for Atom Technology, Angstrom Technology Partnership,*
*1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan*
[2]*Science University of Tokyo, 2641 Yamasaki, Noda, Chiba 278, Japan*
[3]*Joint Research Center for Atom Technology,*
*National Institute for Advanced Interdisciplinary Research,*
*1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan*

## Abstract

Using results of the band structure calculations in the local-spin-density approximation we demonstrate how the crystal distortions affect the magnetic structure of orthorhombically distorted perovskites leading to a non-collinear spin arrangement. Our results suggest that the non-collinearity of the spin magnetic moments, being generally small in La$MO_3$ series with $M$=Cr-Fe, is large in $SrRuO_3$.

# Electron energy loss spectroscopy as a tool to probe the electronic structure of intermetallic alloys

G.A. Botton[1], G.Y. Guo[2], W.M. Temmerman[2], C.J. Humphreys[1]
[1] *Dept of Materials Science and Metallurgy, Univ. of Cambridge,*
*Pembroke St, Cambridge, CB2 3QZ, U.K.*
[2] *Daresbury Laboratory, Warrington, WA4 4AD, U.K.*

## Abstract

A combination of theoretical calculations using the LMTO and KKR methods and EELS experiments has been used to probe the electronic structure of transition metal aluminides. We investigate the bond differences between the late transition metal aluminides (FeAl, CoAl and NiAl) and TiAl. We also study the sensitivity of the combined theory and experiment approach to dopants (Co and Cu) in the NiAl system where we demonstrate that EELS can clearly detect changes in the density of states (DOS) and the position of the Fermi level within the DOS. Preliminary results are then shown for high spatial resolution analyses on a grain boundary in NiAl.

# Preprints from
# Center for Atomic-scale Materials Physics (CAMP)

- P. Murray, I. Stensgaard, E. Lægsgaard, and F. Besenbacher:
  *Growth and structure of Pd alloys on Cu(100)*,
  Surf.Sci. accepted

- J. Schiøtz, T. Rasmussen, O.H. Nielsen, and K.W. Jacobsen:
  *Mechanical deformation of nanocrystalline materials*,
  submitted

- A. Ruban, B. Hammer, P.Stoltze, H.L. Skriver, and J.K. Nørskov:
  *Surface electronic structure and reactivity of transition and noble metals*,
  J.Mol.Catal. in print

- P. Kratzer, B. Hammer, and J.K. Nørskov:
  *A theoretical study of $CH_4$ dissociation on pure and gold-alloyed Ni(111) surfaces*,
  submitted

- P.T. Sprunger, E. Lægsgaard, and F. Besenbacher:
  *Growth of Ag on Cu(110) studied by STM: From surface alloying to Ag superstructures*,
  Phys.Rev.B. accepted

- P.W. Murray, S. Thorshaug, I. Stensgaard, F. Besenbacher, E. Lægsgaard, A. Ruban,
  K.W. Jacobsen, G. Kopidakis, and H.L. Skriver:
  *New mechanisms for interlayer mixing: Pd on Cu(110) and Ag(110)*,
  submitted

- J. Jacobsen, K.W. Jacobsen, and J.K. Nørskov:
  *Simulations of homoepitaxial growth of Pt(111): Island shapes and the growth mode*,
  submitted

- F. Besenbacher:
  *Scanning tunnelling microscopy studies of metal surfaces*,
  "Reports on Progress in Physics" accepted

- J.J. Mortensen, B. Hammer, O.H. Nielsen, K.W. Jacobsen, and J.K. Nørskov:
  *Density functional theory study of self-diffusion on the (111) surfaces of Ni, Pd, Pt, Cu,
  Ag and Au*,
  Springer Series on Solid State Physics, Ed. A. Okiji

- M.R. Sørensen, K.W. Jacobsen, and H. Jónsson:
  *Thermal diffusion processes in metal tip-surface interactions: Contact formation and
  adatom mobility*,
  submitted

- A.C. Egsgaard Madsen, P. Stoltze, K.W. Jacobsen, and J.K. Nørskov:
  *Comment on "Cs-induced relaxation of the Cu(110) surface",*
  submitted

- I. Alstrup, I. Chorkendorff, and S. Ullmann:
  *The dissociative chemisorption of nitrogen on iron(111) at elevated pressures,*
  Zeitschrift für Physikalische Chemie, NF, accepted

- H. Brune, K. Bromann, K. Kern, J. Jacobsen, P. Stoltze, K. Jacobsen, and J. K. Nørskov:
  *Fractal and dendritic growth of surface aggregates,*
  MRS-proceedings from fall meeting 1995 in Boston, accepted

- M. Brandbyge, K.W. Jacobsen, and J.K. Nørskov:
  *Scattering and conductance quantization in 3 dimensional metal nano-contacts,*
  submitted

- G. Caldarelli, F.D.Di Tolla, and A. Petri:
  *Self organization and annealed disorder in fracturing process,*
  submitted

More information can be obtained from helle@fysik.dtu.dk

Helle Wellejus
CAMP and Department of Physics
Building 307, Technical University of Denmark

# 8 HIGHLIGHT OF THE MONTH

# Electronic Structure using Wavelets

James F. Annett

University of Bristol, H.H. Wills Physics Laboratory,

Royal Fort, Tyndall Avenue, Bristol BS8 1TL, UK

E-mail: James.Annett@Bristol.ac.uk

## 8.1 Introduction

In July of this year J. Bernholc and I organised a workshop at CECAM with the theme of "Grid, Multigrid and Wavelet Methods in Electronic Structure Computation." About 25 researchers from Europe, USA and Japan came to discuss new approaches to electronic structure calculations based upon these ideas. The goal was to develop a next generation of DFT codes for total energy and molecular dynamics calculations which would work entirely in real-space. Rather than traditional real-space quantum chemistry basis sets, such as Gaussians, the workshop focussed entirely on grid based methods. The motivation being that such methods retain complete flexibility in the form of the wave functions. Many of the methods discussed are well known in other numerically intensive computing fields, such as finite elements, multigrids and wavelets, but so far have not been widely used in electronic structure. From the progress reported at the workshop it seems clear that some of these methods will indeed play an important role in the future.

In this article I intend to give a brief overview of the motivation behind this work. Then I shall describe in more detail one particular approach, based on the elegant mathematics of wavelet theory. Hopefully this article will highlight some of the advances which have been made, as well as the difficulties which have yet to be overcome.

## 8.2 Motivation

The readers of this newsletter will, of course, be well aware of the capabilities of modern electronic structure algorithms. Using the Car Parinello algorithm together with a plane wave basis set and separable norm-conserving pseudoptentials accurate ab initio calculations are now possible for very complex systems with several hundred inequivalent atoms. The impressive examples shown by Parinello and others at the $\Psi_k$ network conference included direct simulation of liquids, reaction dynamics of large molecules, and determining the structure of biological molecules.

The plane wave basis sets used in these calculations have many advantages, in particular:

1. The speed of the Fast Fourier Transform (FFT).

2. The ability to compute the Hellman Feynman forces on the ions.

3. The plane wave cut-off can be easily adjusted to ensure convergence.

These have made plane wave pseudopotential methods very popular because they are fairly simple to implement, fast, and relatively straightforward to run.

However, despite these advantages the plane wave basis set also has several disadvantages or factors which limit potential applications. These problems include (in no particular order):

1. Each basis state extends throughout the whole unit cell.

2. The FFT requires a uniform spacing of grid points everywhere in the unit cell.

3. The boundary conditions must be periodic and hence the unit cell must be charge neutral.

4. The FFT is not convenient for massively parallel computation.

5. 'Hard pseudopotential' atoms, such as transition metals, are expensive to include.

Problems 1-3 are specifically due to the nature of plane waves and of the FFT. In particular, problem 1 means that plane wave basis sets are not useful for O(N) algorithms, for which the computational time is proportioal to system size. Standard plane wave algorithms, such as Car Parinello, scale with $N^3$ for large systems because of the time to keep the occupied wave functions orthogonal to each other. The various O(N) algorithms build in the 'near-sightedness' of the total energy by working with real-space representations of the density-matrix. Real space bases are thus essential.

Problem 4, the difficulty of parallelization, is a consequence of 1, the global nature of the plane wave basis. Of course parallel FFTs do exist, however, unless each computer node has enough memory to store the whole FFT grid for all the occupied states for a given k point, significant data communication between nodes is inevitable. In contrast the O(N) algorithms are naturally parallel since the near-sightedness implies that distant regions of space are quite independent, and so can be handled in parallel. In fact any real-space basis set makes parallelization relatively simple by domain decomposition, reducing communication to only the data associated with the boundaries between domains.

Problem 5, the hard pseudopotential problem, is difficult to surmount with any completely general basis set. Of course LMTO and LAPW methods are very successful for transition metals. However, forces are difficult for molecular dynamics applications. Soft pseudopotential methods are now making some transition metal systems quite feasible with Car Parinello type methods. To some extent the real problem with these systems is the requirement of a uniform grid spacing (problem 2 above). The higher cut off involved in adding even one transition metal atom to a system requires a denser grid everywhere throughout the cell. On the other hand, this problem would be overcome by using finite elements, adaptive grids or wavelets. These methods allow the program to (automatically) allocate more grid points where needed so reducing to a minimum the computationl cost ascociated with hard pseudopotential atoms.

Why are grid methods to be preferred over other real space basis sets such as Gaussian orbitals? Gaussian basis sets are ubiquitous in quantum chemistry, and are also well known in solid state calculations. Tight binding LMTO and screened KKR methods also provide ab initio real-space basis sets. The main motivation for the grid based methods is their complete flexibility. The calculation will be gauranteed to converge to the exact answer for all atomic geometries without user input based on 'physical intuition'. Physical intuition may help in choosing 'good' basis sets, but can also be misleading if the intuition is wrong! For those of us who have difficulty in visualizing wave functions in 100 atom non-periodic systems it is very helpful to have a single parameter, say a grid spacing $h$, and know that $h \to 0$ is always the exact answer. Standardized Gaussian basis sets are certainly useful to obtain 'chemical accuracy' $\sim 0.01 - 0.1 \mathrm{eV/atom}$, but for problems requiring higher precision (e.g. energy differences between polytypes, magnetic coupling, testing DFT functionals) it can be important to ensure that basis set error is negligible. To some extent grids methods and Gaussians can be useful as complimentary methods, for example using accurate grid calculations to benchmark Gaussian basis sets, or using novel grid methods to improve the speed of Gaussian based calculations.

At the CECAM workshop several different grid based methods were discussed. These included real-space finite difference methods [1, 2], adaptive curvilinear coordinate methods [3, 4], finite element methods [5], multigrid methods, [6] interpolets [7], and wavelets [8, 9, 10, 11]. The limited space here does not allow me to describe them all. Below I shall focus entirely on the wavelet approach. Wavelets are a simple and elegant mathematical concept, as I shall try to show below. Applying wavelet ideas to electronic structure calculations is far from complete at the present time (although several groups are working on development), however I shall try to give some general ideas about how wavelet ideas can be applied in practical electornic structure calculations.

## 8.3 The Wavelet Concept

'Wavelet theory' became a substantial field of mathematics following some key developments in the early 1980's. The original ideas built on physics concepts, such as scaling transfomations and localized wave packets, developing a powerful mathematical formalism from these concepts [12, 13]. Very quickly the wavelet ideas were applied in signal analysis and image compression problems. Work on a variety of ordinary and partial differential equations also developed. The first application of wavelet concepts to electronic structure calculation was by Cho et al. [8]

.and more recently by Wei and Chou [9].

The central idea is the concept of a multi-resolution analysis. Normally in signal analysis one samples a signal $f(x)$ at a constant rate, corresponding to a uniform set of points, $f(x_n)$, $x_n = nh$. Obviously $h$ defines a fixed resolution and Fourier components of $f(x)$ can be found up to $\pm\pi/h$. The similarity with plane wave pseudopotential calculations is clear. To do better than this one would like to adjust the resolution $h$ depending on whether $f(x)$ is slowly or quickly varying in a given place. In a **multiresolution analysis** one divides $f(x)$ into component parts, where each component contains the data expressed as well as possible at a given resolution length scale.

The multiresolution analysis process is remarkably similar to the Kadanoff block spin transformation in phase transition theory. The idea is to develop a nested sequence of Hilbert spaces corresponding to coarser and coarser length scales. Suppose there are $N$ function values $f_0(x_n)$, $x_n = nh = nL/N$. The set of all possible function values is an $N$ dimensional vector space, $V_0$. Using a block-spin idea we can easily imagine transfomations where we eliminate 'fast modes' and define $N/2$ new function values $f_1(x_n)$, $x_n = nh$ for even values of $n$. The space of such functions $f_1$ obeys

$$V_0 > V_1 \tag{1}$$

Repeating the process to decimate again and again we can generate a sequence of spaces on coarser and coarser scales

$$V_0 > V_1 > V_2 > V_3 > \dots. \tag{2}$$

Space $V_p$ has dimension $N/2^p$. The sequence obvously ends when there is only a single data point left. A specific example of such scaling transfomation might be an average or sum of adjacent points

$$f_{p+1}(x_n) = f_p(x_n) + f_p(x_{n+d}) \tag{3}$$

where $d = 2^p$ the spacing of points in function $f_p$ is $2^p h$. For simplicity I assume periodic boundary conditions, $n + N \equiv n$. The coarse grained functions $f_p$ contain all of the information present in the function at the given scale of resolution.

The above scaling transformation 'coarse grains' the function onto longer and longer length scales. However it is not invertible, since we have not yet defined a way to go back form the coarse grained data to a finer scale. The wavelet transformation does that, making an invertible (and in some cases unitary) transform. What is needed is to retain information about the high frequency components. For example to invert Eq. 3 we obviously need to retain information about the differences:

$$h_{p+1}(x_{n+d}) = f_p(x_n) - f_p(x_{n+d}), \tag{4}$$

with $d = 2^p$. This defines a new sequence of functions $h_p$ $p = 1, 2, \dots$ containing only the high frequency data. In terms of the Hilbert spaces, the $N/2^p$ dimensional space $V_p$ has been divided into two spaces of half the size:

$$V_p = V_{p+1} \oplus W_{p+1} \tag{5}$$

where $W_p$ is the space of possible functions $h_p$. Scaling several times, the original function N dimensional space $V_0$ has been divided into spaces of dimension $N/2$, $N/4$, $\dots$

$$V_0 = W_1 \oplus W_2 \oplus \dots \oplus W_P \oplus V_P. \tag{6}$$

The final space $V_P$ can contain as little as one point.

The 'fast wavelet transform' (FWT) of a function $f_p(x_n)$ in this example is a band matrix multiplication:

$$
\begin{pmatrix}
f_{p+1}(x_0) \\
h_{p+1}(x_d) \\
f_{p+1}(x_{2d}) \\
h_{p+1}(x_{3d}) \\
\dots \\
\dots
\end{pmatrix}
=
\begin{pmatrix}
1 & 1 & 0 & 0 & \dots\dots \\
1 & -1 & 0 & 0 & \dots\dots \\
0 & 0 & 1 & 1 & \dots\dots \\
0 & 0 & 1 & -1 & \dots\dots \\
\dots & \dots & & & \\
\dots & \dots & & &
\end{pmatrix}
\begin{pmatrix}
f_p(x_0) \\
f_p(x_d) \\
f_p(x_{2d}) \\
f_p(x_{3d}) \\
\dots \\
\dots
\end{pmatrix} .
\tag{7}
$$

This is obviously unitary, apart from an overall factor of $1/\sqrt{(2)}$. The inverse transform is thus also simply a matrix multiply, using the transpose of the above matrix. To scale from the original function from $f_0$ to $f_P$ requires repeating the above matrix multiplication to $p = 0$, $p = 1$, $p = 2$, ... $p = P - 1$. If the original data has $N$ points, the CPU time to do this is of order $N + N/2 + N/4 + \dots \approx 2N$. The FWT is thus an $O(N)$ algorithm, rather than the $O(N \log N)$ FFT. The particular form for the matrix in Eq. 7 is called the Haar wavelet transform. The Daubechies wavelet transforms are also unitary band matrix multiplications, only with a longer bandwidth of 4, 6 or higher. Coding subroutines to do these transforms is simple. Examples are given in Numerical Recipes (2nd Edition only!) [13] or are available form the author. [11]

What is the physical meaning of the coefficients $h_p(x_n)$? They are the coefficients of the function expanded in a new basis, the wavelet basis. This is just like Fourier coefficients which are expansion coefficients of a function in a basis of plane waves. Hence there exist functions $\psi_1(x_n)$, $\psi_2(x_n)$ etc. such that

$$
\begin{aligned}
f(x_n) = \quad & \sum_m h_1(x_m)\psi_{1m}(x_n) + && (8) \\
& \sum_m h_2(x_m)\psi_{2m}(x_n) + && (9) \\
& \dots + && (10) \\
& \sum_m h_P(x_m)\psi_{Pm}(x_n) + && (11) \\
& \sum_m \phi_{Pm}(x_n)f_P(x_m). && (12)
\end{aligned}
$$

The function has thus been decomposed by the FWT into its components on the different basis functions $\psi_{1m}$, $\psi_{2m}$ .... At the longest lengthscale there is a wavelet $\psi_{Pm}$, and also a second function, $\phi_{Pm}$, usually called the scaling function. (Another more picturesque name is the 'mother wavelet' $\psi_{Pm}$ and the father wavelet $\phi_{Pm}$. The smaller scale wavelets $\psi_{pm}$ are then 'daughter' wavelets. There are no sons!) Figure 1 shows the father wavelet, mother wavelet and some daughters for the Daubechies D-4 wavelet transform.

For the Haar and Daubechies wavelet transforms these basis functions are orthonormal. This follows simply because the wavelet transform is unitary. (Recall that unitary transformations, such as Hermitian matrix diagonalization, always preserve the orthonormality of basis vectors). Thus the vectors $\psi_{pm}(x_n)$ and $\psi_{p'm'}(x_n)$ are orthogonal to each other under translation, $m \neq m'$, and under changes of scale, $p \neq p'$. The wavelets, $\psi_{pm}(x_n)$, are also orthogonal to the scaling function $\phi_{Pm}$ on the longest scale.
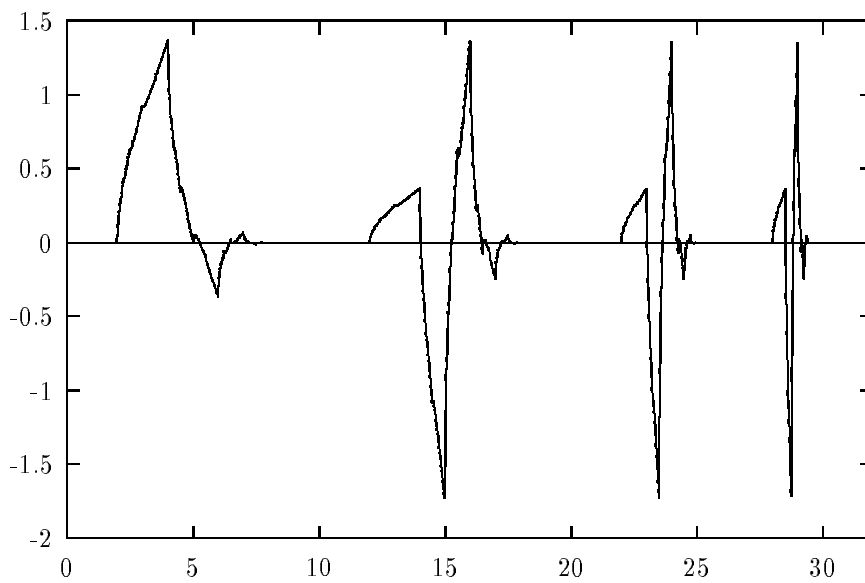
Figure 1: Daubechies D-4 wavelets and scaling function. From left to right: the scaling function (or father wavelet), $\phi_{Pm}(x)$, the longest scale wavelet (or mother wavelet), $\psi_{Pm}(x)$, and two smaller scale (daughter) wavelets, $\psi_{pm}(x)$. The heights have been rescaled for clarity in the plot.

This orthogonality persists after **any** number of scaling transforms. An amazing consequence of this is that there is a continuum limit $N \to \infty$ in which the Daubechies wavelet is defined for all $x$, $\psi_{pm}(x)$, not just on a set of discrete points. These continuum functions are compact (vanish exactly outside a finite interval), and are again orthonormal under all integer translations and scaling by powers of 2:

$$\int \psi_{pm}(x)\psi_{p'm'}(x) = \delta_{mm'}\delta_{pp'} \tag{13}$$

with

$$\psi_{pm}(x) = 2^{-p/2}\psi(2^{-p}x - m). \tag{14}$$

The Daubechies wavelets (plus the scaling functions) defined in this way form a complete orthonormal set of functions. Using the Haar wavelet transform of Eq. 7 the base wavelet turns out to be just:

$$\psi(x) = \begin{cases} +1 & 0 < x < 1/2 \\ -1 & 1/2 < x < 1 \\ 0 & otherwise \end{cases}. \tag{15}$$

It is easy to see that this function obeys the orthogonality relations 13 under scaling by any power of two, or under translation by any integer. The Daubechies D-4 wavelets in Fig. 1 do not have a simple analytic formula, but can also be proved to be orthonormal under scaling and translation. Unlike the Haar wavelet they are also continuous functions, but unfortunately are not differentiable. Higher order Daubechies wavelets (D-6, D-8 , ...) exist and are smoother, at the expense of being wider in their range of support.

These wavelet bases are useful because of the way they separate contributions from different length scales. If a function is smooth then the high frequency components ($h_p(x_m)$ for small $p$) will be negligible. However, unlike simple Fourier filtering of the high frequencies the wavelets also retain spatial information. If $f(x)$ has rapid variation in some region, say near $x_0$, and is

smooth elsewhere then the wavelet coefficients $h_p(x)$ will be negligible except near $x_0$. Retaining the big coefficients near $x_0$ and dropping the others one can represent $f(x)$ very compactly. Because high frequencies are retained where needed the function retains its sharp fetures, while saving storage by eliminating high frequenciy components where the function is smooth. It is for this reason that wavelets have found important applications in image compresson algorithms. One minimizes storage by efficiently representing the regions where the image varies slowly, while still retaining sharp edges where the function varies rapidly. Typically wavelet methods can effectively reduce image data set sizes to of order 1%. In the electonic structure context the analog is clear. One wants to represent the regions where the wave function is smooth using relatively few coefficients, while retaining high frequency components where the wave function has rapid variation, e.g. near the atomic cores.

## 8.4 Cubic B-spline Wavelets

There are many different types of wavelet optimized for various properties. The Daubechies wavelets have the advantage of compactness (vanishing exactly outside some interval) and orthonormality. However the Daubechies wavelets are not very smooth, as Fig. 1 shows for the D-4 wavelets. The higher order Daubechies wavelets are smoother, but at the expense of extending over a longer range. Wei and Chou recently applied D-6 wavelets to electronic structure calcualtions.

I have chosen to work with wavelets derived from cubic B-splines [14]. These are a good compromise between smoothness and compactness. They are not orthogonal, but this is not necessarily a problem in quantum mechanics applications. A B-spline (basis-spline) is a localized function made out of smoothly joined polynomials [15]. For evenly spaced points (called spline knots), spacing h, and using cubic polynomials the basic B-spline is simply

$$
b_0(x) = \begin{cases}
(2 + x/h)^3/6 & -2h < x \le -h \\
(4 - 6(x/h)^2 - 3(x/h)^3)/6 & -h < x \le 0 \\
(4 - 6(x/h)^2 + 3(x/h)^3)/6 & 0 < x \le h \\
(2 - (x/h))^3/6 & h < x \le 2h.
\end{cases} \tag{16}
$$

By construction $b_0(x)$ is compact and twice differentiable. Making a set of $N$ functions by translation (again with periodic b.c.),

$$
b_{0m}(x) \equiv b_0(x - x_m)) \tag{17}
$$

for $x_m = mh$, yields an N dimensional Hilbert space. A function in this space is of the form

$$
f(x) = \sum_m f_m b_{0m}(x). \tag{18}
$$

Any such function is obviously a cubic polynomial between the knots, $x_m$, and is continuous and smooth at the knots. I.e the function is a spline function, such as those found by spline fits interpolation of $N$ evenly spaced data points, $f(x_m)$). The Hilbert space spanned by the B-splines is the space of all such spine functions.

This Hilbert space is convenient for doing quantum mechanics since all functions in the space are necessarily twice differentiable. Furthermore smooth wave functions are well represented in

this basis set because they are locally close to polynomial. A simple estimate of the error in such a basis comes from calculating the kinetic energy of a plane wave $\psi(x) = \exp(ikx)$ represented in the basis. The energy is $\epsilon(k) = k^2/2 + O(k^6 h^8)$, showing a very rapid convergene as $h \to 0$, similar to that of a high order finite difference scheme.

The cubic B-splines can be made into a wavelet basis set by considering changes of scale. Defining

$$b_1(x) = b_0(x/2) \tag{19}$$

gives a function exending over range wider by a factor of 2, from -4h to +4h. This function has spline knots at at the even numbered points $x = 2nh$. Translating this function, $b_{1m} = b_1(x - x_m)$ for $n = 0, 2, 4, \ldots$, gives a Hilbert space of dimension $N/2$. This space is exactly contained in the original $N$ dimensional space, since any spline function defined at $N/2$ evenly spaced knots is obviously a special case of splines defined at $N$ knots. We thus have a situation exactly like Eq. 1. In fact one can easily verfy that the B-splines obey the 'scaling equation'

$$b_1(x) = \frac{b_0(x - 2h)}{8} + \frac{b_0(x - h)}{2} + \frac{3b_0(x)}{4} + \frac{b_0(x + h)}{2} + \frac{b_0(x + 2h)}{8}. \tag{20}$$

Taking a function defined on the original $N$ basis functions $b_{0m}$, and projecting a function onto the $N/2$ dimensional space defined by the $b_{1m}$ is exactly analogous to the coarse graining in Eq. 3. The corresponding wavelets represent the high frequency information not included in the coarse graining. In this case a suitable compact, smooth and symmetric wavelet is

$$w_1(x) = -\frac{b_0(x - h)}{2} + b_0(x) - \frac{b_0(x + h)}{2}. \tag{21}$$

Repeating the scaling proceeduce produces wavelets on longer and longer length scales $w_2$, $w_3$ etc, similar to the Daubechies wavelets. After a B-spline wavelet transform the original function, Eq. 18 is thus expanded in terms of this wavelet basis as follows:

$$f(x) = \qquad \sum h_{1m} w_{1m}(x) +$$
$$\sum h_{2m} w_{2m}(x) + \ldots$$
$$+ \sum h_{Pm} w_{Pm}(x) + \sum f_{Pm} b_{Pm}(x) \tag{22}$$

quite analogously to Eq. 12. The B-spline functions $b_{Pm}(x)$, are $w_{pm}(x)$ are shown in Fig. 2.

One can also scale the other way, to finer and finer scales. This defines wavelelts $w_{0m}$, $w_{-1m}$, $w_{-2m}$.... Since $w_{pm}$ corresponds to a spatial resolution $h = 2^p L/N$ this is equivalent to adding points giving higher and higher resolution in the wave function. The basis set is clearly complete in this $h \to 0$ limit.

## 8.5    Electronic Structure with Wavelets

Applying these wavelet bases to electronic structure problems is simple in principle, but not so easy in practice. The first change from a plane wave pseudopotential method into a wavelet basis is to replace the usual FFT evaluation of the Bloch wave functions

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} c_{\mathbf{G}nk} \exp\left[i(\mathbf{k} + \mathbf{G}).\mathbf{r}\right] \tag{23}$$
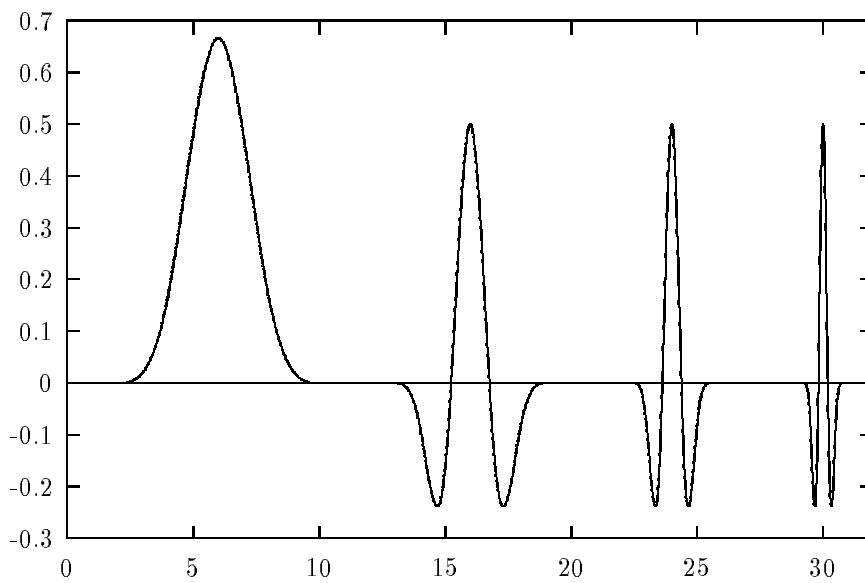
Figure 2: Cubic B-spline scaling function and wavelets of increasing resolution.

with a corresponding fast wavelet transform. In the case of B-spline wavelets this is

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \left( \sum_{\mathbf{pm}} h_{\mathbf{pm}n\mathbf{k}} w_{\mathbf{pm}}(\mathbf{r}) + \sum_{\mathbf{m}} f_{\mathbf{Pm}n\mathbf{k}} b_{\mathbf{Pm}}(\mathbf{r}) \right). \tag{24}$$

where $P$ is the coarsest scale of wavelets included in the basis set. Here for brevity $\mathbf{p} \equiv (p_1, p_2, p_3)$ and the three dimensional wavelets are just products of 1-d wavelets

$$w_{\mathbf{pm}}(\mathbf{r}) \equiv w_{p_1 m_1}(r_1) w_{p_2 m_2}(r_2) w_{p_3 m_3}(r_3). \tag{25}$$

For general unit cells it is convenient to change variables so that

$$\mathbf{r} = r_1 \mathbf{a}_1 + r_2 \mathbf{a}_2 + r_3 \mathbf{a}_3 \tag{26}$$

where $\mathbf{a}_1$ etc. are the Bravais lattice vectors. In terms of the $r_i$ the unit cell is then just the unit cube $0 \le r_i < 1$.

Instead of the FFT one uses the wavelet transform Eq. 7 (actually the inverse of Eq. 7) to expand out the long scales and hence evaluate $\psi_{n\mathbf{k}}(\mathbf{r})$ in real space. From $\psi_{n\mathbf{k}}(\mathbf{r})$ one can obtain the charge density $n(\mathbf{r})$, Coulomb potential and so on. Since the wavelet fransform is similar in speed to the the FFT (actually $N$ not $N \log N$)) this is clearly a competitive method. Furthermore the wavelet transform can be made even faster is one can make use of the fact that most of the wavelet expansion coefficients (the $h_{pm}$ in Eq. 12) will be negligible. Thus with a wavelet basis one can hope to save in terms of memory used (only non-zero $h_{pm}$ need be stored) as well as CPU time.

Several groups are now working on wavelet methods in electronic structure [8, 9, 10, 11]. Other closely related approaches, such a multi-grid methods, finite elements and interpolets are also under development. In principle these efficient basis sets can also be combined with the advantages of massively parallel and/or order N algorithms. It will be exciting to see just what sort of physics problems will be solvable in the future with these powerful combinations of techniques!

# References

[1] J.R. Chelikowsky, N. Troullier and N. Saad, Phys. Rev. Lett. **72**, 1240 (1994).

[2] A.P. Seitsonen, M.J. Puska and R. Nieminen, Phys. Rev. B **51** 14057 (1995).

[3] F. Gygi, and G. Galli, Phys. Rev. B **52**, R2229 (1995).

[4] G. Zumbach, N.A. Modine and E. Kaxiras, Solid State Communications, **99**, 57 (1996).

[5] E.Tsuchida and M.Tsukada, Solid State Commun. **94**, 5 (1995); E.Tsuchida and M.Tsukada, Phys.Rev.B **52**, 5573 (1995).

[6] E.L. Briggs, D.J. Sullivan and J. Bernholc, Phys. Rev. B **52**, R5471 (1995).

[7] T. Arias and M. Teter, unpublished.

[8] K. Cho, T. Arias, J.D. Joannopoulos and P.K. Lam, Phys. Rev. Lett. **71**, 1808 (1993).

[9] S. Wei and M.Y. Chou , Phys. Rev. Lett. **76**, 2650 (1996).

[10] R.M. Martin and V. Rao, unpublished.

[11] J.F. Annett, 'Wavelets and Applications', Lectures from the College on Computational Physics, ICTP Trieste, 1995, unpublished.

[12] The are many books and articles on wavelet theory. Among the more accessible are: I. Daubechies, *'Ten Lectures on Wavelets'* , (SIAM, Philadelphia, 1992); C.K. Chui, *'An Introduction to Wavelets'*, (Academic Pressm San Diego, 1992); Y. Meyer, *Wavelets and Operators'*, (Cambridge 1994).

[13] W.H. Press, S.A. Teukolsky, W.T. Vetterling, and B.P. Flannery, *'Numerical Recipes'*, 2nd Ed., Cambridge 1992).

[14] J.F. Annett, in *'Toward Teraflop Computing, the New Grand Challenges*, (Nova Scientific Publishers, 1995).

[15] P.M. Prenter, *'Splines and Variational Methods'* (Wiley 1975).