Ψ_k Newsletter

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

Number 60 December 2003

Editor: Z. (Dzidka) Szotek
E-mail: psik-coord@dl.ac.uk

Contents

1 Editorial

This last newsletter of the current year is rather large, over 190 A4 pages. It is mostly due to a number of extended reports on past workshops organized either within the ESF Psi-k Programme or one of the RT Networks. In particular, both RTN1 (”Computational Magnetoelectronics”) and RTN2 (”f-electrons”) contain one report each, while the ESF Psi-k section contains three reports. Nearly all the reports include detailed abstracts of presented papers. In addition, the RTN2 section contains also its first annual report with short scientific highlights of main research projects. Workshop/Conference announcements can be found both in the ESF, and a general section dedicated to events organized without financial support of either the Psi-k Programme or either of the RTNs. Position announcements and abstracts of newly submitted papers are in their usual sections. In this newsletter we also have a short book announcement. The book is by Mike Finnis (Queen's University, Belfast) on ”Interatomic Forces in Condensed Matter”. As usually, the newsletter is finished with the scientific highlight which is by Mike Towler (Cambridge, UK) on **”Quantum Monte Carlo and the CASINO program: highly accurate total energy calculations for finite and periodic systems”**. Please see table of contents for further details.

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

http://psi-k.dl.ac.uk/

The above contains information on the Psi-k 2003 workshops and hands-on courses (subject to funding). In these pages you can also find information on how to apply for funding to make collaborative visits.

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

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

	function
psik-coord@daresbury.ac.uk	**messages to the coordinators, editor & newsletter**
psik-management@daresbury.ac.uk	**messages to the NMB of all Networks**
psik-network@daresbury.ac.uk	**messages to the whole Ψ_k community**

Dzidka Szotek and Walter Temmerman
e-mail: psik-coord@dl.ac.uk

2 General News

2.1 Psi-k Web Pages

-o-o-o-o-o-o-o-o-o-o-o-o-

Recently, the web pages of the Psi-k Programme and RT Networks, associated with our community, have been revamped to provide a more user-friendly interface. Note that from now on only the pdf-files of the newsletters and highlights will be available on our web pages

http://psi-k.dl.ac.uk.

Your comments and feedback on the present state and possible improvements of the web pages would be most welcome.

2.2 Call for Scientific Highlights for 2004

-o-o-o-o-o-o-o-o-o-o-o-o-

At the end of this calendar year we would like to renew our call for contributing scientific highlights to the Psi-k newsletters of next year. We do realize the effort involved, but this is an effort spent for our community and the benefits are invaluable to all of us. If you want more people to be aware of your field and perhaps even start new collaborations this way, then please do contribute a highlight. We published already 60 Psi-k Newsletters and almost all of them contained scientific highlights. We are very gratefull to all members of our community who contributed scientific highlights over the past 10 years. We need six scientific highlights for the next year, but at the moment have only one in the pipeline. Therefore, once again we would like to appeal to all our readers for contributions. The highlights are freely available on our web pages and can be referenced in scientific journals, as much as the cond-mat papers are. If you would like to contribute a highlight, we would need to know it at least two months before the date of your submission to be able to plan accordingly for the whole year. All the contributions to the subsequent newsletters need to reach us at least a few working days before the end of the months preceeding the publication months of the newsletters, i.e., a few days before the end of January for the February issue, a few days before the end of March for the April issue, a few days before the end of May for the June issue, a few days before the end of July for the August issue, a few days before the end of September for the October issue, and a few days before the end of November for the December issue.

3 News from the Research Training Network 1 (RTN1)

COMPUTATIONAL MAGNETOELECTRONICS

3.1 Reports on RTN1 Workshops

3.1.1 Report on the Annual Meeting of the RTN "Computational Magnetoelectronics"

MPI of Microstructure Physics, Halle, October 9-11, 2003

Sponsors :

- ESF Ψ_k Programme "Towards Atomistic Materials Design"
- EU RT-Network "Computational Magnetoelectronics"

Organisers :

- Patrick Bruno, Max Planck Institute of Microstructure Physics, Halle
- Ingrid Mertig, Fachbereich Physik, Martin-Luther-Universität Halle-Wittenberg, Halle

Aim : The purpose of the meeting was to provide an overview on the activities of all the partners of the network during the last year.

The workshop took place at the Max Planck Institute of Microstructure Physics in Halle. It was organized by the Halle node, i.e. people from the MPI of Microstructure Physics and Halle University. The lectures took place in the big lecture hall of the MPI in the IAMO building, whereas the poster session was organized in the lecture hall in the MPI building. The meeting was attended by 84 participants from 8 European countries.

Every session started with an invited talk (1 hour), three of them devoted to experimental work and two to theoretical concepts. In the experimental talks Wolfgang Kuch spoke about magnetic interface coupling, Henri Jaffrés about spin dependent transport and Klaus Kern about STM investigations of nanostructures. The invited theoretical talks have been devoted to electronic transport in molecular nanostructures (G. Seifert) and SIC-LSD for correlated electrons (Walter Temmerman). Members of the network reported their actual results in contributed talks (20' length each). All together 23 contributed talks have been given.

Beside the talks we have had 34 poster presentations in the fields : dilute magnetic semiconductors; surfaces, interfaces, nanostructures; oxides; transport properties; exchange interactions and miscellaneous.

We have had very active discussions to each talk, but also during the poster session and the conference dinner.

You can find the information about the workshop also online :
`http://www.physik.uni-halle.de/RTN/`

W. Hergert

Programme

			page
Thursday, 09.10.2003			
Afternoon Session (lecture hall IAMO)			
14.00 - 15.00	I1	**W. Kuch** (*MPI Halle*) Experimental study of magnetic interface coupling in single-crystalline FM–AF bilayers and FM–AF–FM trilayers	10
15.00 - 15.20	C1	**S. Khmelevskyi** (*Vienna University of Technology*) Anomalous spontaneous volume magnetostriction in Fe-based fcc and bcc alloys: Electronic origin of the Invar effect.	12
15.20 - 15.40	C2	**A. Perlov** (*Munich University*) Ab initio calculation of the optical and magneto-optical properties of moderately correlated magnetic solids	12
15.40 - 16.00	C3	**A. A. Kovalev** (*Delft University of Technology, Netherlands*) Magnetovibrational magnetization dynamics	13
16.00 - 16.20	C4	**J. Manschot** (*Delft University of Technology, Netherlands*) Magnetization dynamics of magnetic multilayers	13
16.30 - 19.00	*Poster Session* (lecture hall MPI), *Coffee, refreshments*		

continued on next page

continued from previous page

Friday, 10.10.2003

Morning Session (lecture hall IAMO)

09.00 - 10.00	I2	**H. Jaffrès** (*Unité Mixte de Physique CNRS-THALES*) Spin-dependent transport in *GaMnAs*-based heterostructures	11
10.00 - 10.20	C5	**L.M. Sandratskii** (*MPI Halle*) Electronic structure, exchange interactions and Curie temperature in III-V and II-VI DMS	13
10.20 - 10.40	C6	**Rajeev Ahuja** (*Uppsala University, Sweden*) Ferromagnetism above room temperature in bulk and transparent thin films of Mn-doped ZnO	14
10.40 - 11.00	C7	**V. Drchal** (*AS CR, Praha, Czech Republic*) Energetics of Mn atoms in diluted magnetic semiconductors	14
11.00 - 11.30	*Coffee*		
11.30 - 11.50	C8	**O.Eriksson** (*Uppsala University, Sweden*) Magnetic semiconductors, from first principles theory to Monte Carlo simulations	14
11.50 - 12.10	C9	**F. Máca** (*Praha, Czech Republic*) Interstitial Mn in (Ga,Mn)As	15
12.10 - 12.30	C10	**I. Turek** (*Brno, Czech Republic*) Residual resistivity of (Ga,Mn)As alloys	15
12.30 - 14.00	*Lunch* (lecture hall MPI)		

Afternoon Session (lecture hall IAMO)

14.00 - 15.00	I3	**K. Kern** (*MPI Stuttgart*)	12
15.00 - 15.20	C11	**Gustav Bihlmayer** (*FZ Jülich*) Rashba-effect at (magnetic) metal surfaces	16
15.20 - 15.40	C12	**J. Minár** (*Universität München*) Magnetic and spectroscopic properties of free and supported transition metal clusters	16

continued on next page

continued from previous page

15.40 - 16.00	C13	**I. A. Abrikosov** (*Linköpings University, Sweden*) Unexpected magnetism: the effect of low dimensionality	17
16.00 - 16.30	*Coffee*		
16.30 - 18.30	*Discussion*		
20.00	*Conference Dinner* (restaurant Diebels)		

Saturday, 11.10.2003

Morning Session (lecture hall IAMO)

09.00 - 10.00	I4	**G. Seifert** (*Technical University of Dresden*) Calculations for the electronic transport in molecular nanostructures	12
10.00 - 10.20	C14	**J. Fransson** (*Stockholm, Sweden*) Theory of negative differential conductance in double quantum dots	17
10.20 - 10.40	C15	**A. Bagrets** (*MPI Halle*) Conductance through single atoms: an *ab initio* approach	18
10.40 - 11.00	C16	**T. Dziekan** (*Uppsala University, Sweden*) Conductance as a tool of structure analysis	19
11.00 - 11.30	*Coffee*		
11.30 - 11.50	C17	**V. S. Stepanyuk** (*MPI Halle*) Structure, quantum effects and magnetism in atom-sized contacts	19
11.50 - 12.10	C18	**G. Brocks** (*University of Twente, Netherlands*) Conductance calculations for quantum wires, wave function matching or Green functions?	20
12.10 - 12.30	C19	**Jürgen Henk** (*MPI Halle*) Bias-voltage dependence of the magneto-resistance in ballistic vacuum tunneling: Theory and application to planar Co(0001) junctions	20
12.30 - 13.30	*Lunch* (lecture hall MPI)		

continued on next page

continued from previous page

Afternoon Session (lecture hall IAMO)

13.30 - 14.30	I5	**W. Temmerman** (*Daresbury Laboratory Warrington, UK*) SIC-LSD for Correlated Electrons	12
14.30 - 14.50	C20	**S. Mankovsky** (*Universität München*) Incorporation of the rotationally scheme into invariant LDA+U the SPR-KKR formalism: Application to disordered alloys	21
14.50 - 15.10	C21	**D. Wortmann** (*FZ Jülich*) Spin-dependent ballistic electron transport through interfaces from ab-initio FLAPW Green function embedding	21
15.10 - 15.30	C22	**Ph. Mavropoulos** (*FZ Jülich*) The effect of the spin-orbit coupling on the band gap of half-metals	21
15.30 - 15.50	C23	**L. Udvardi** (*Budapest University, Hungary*) First principles relativistic study of spin–waves in thin magnetic films	22
15.50 - 16.00	*Concluding remarks*		
16.00	*Coffee, refreshments*		

Abstracts

Invited Talks

I1 Experimental study of magnetic interface coupling in single-crystalline FM–AF bilayers and FM–AF–FM trilayers

W. Kuch
Max Planck Institut für Mikrostrukturphysik,
Weinberg 2, D-06120 Halle, Germany

Single-crystalline bilayers and trilayers containing $Fe_{50}Mn_{50}$ as antiferromagnetic layer are ideal systems to study the coupling between an antiferromagnetic and a ferromagnetic film at well-defined interfaces. Because of the low lattice mismatch ($\approx 0.4\%$), fcc FeMn can be grown epitaxially on Cu(001), as well as on Co/Cu(001). Structure and morphology of the films were characterized by medium and low energy electron diffraction (MEED, LEED) and scanning tunneling microscopy (STM), while magnetic properties were investigated using magneto-optical Kerr effect (MOKE) and x-ray magnetic circular dichroism photoelectron emission microscopy (XMCD-PEEM). All systems show pronounced layer-by-layer growth, as confirmed by medium energy electron scattering during evaporation and by scanning tunneling microscopy. This layer-by-layer growth provides the unique opportunity to tune the interface roughness in a controlled way by changing the atomic layer filling.

Characteristic changes in the domain pattern of a ferromagnetic Co layer in contact with an FeMn layer are observed at the transition of the FeMn layer between paramagnetic and antiferromagnetic. These include a drastic reduction in domain size of as-grown Co–FeMn bilayers, and a change in the magnetization direction from $\langle 110\rangle$ to $\langle 100\rangle$ in-plane directions. This is discussed as being due to monoatomic steps at the interface which lead to magnetic frustrations at topological 90° domains in the antiferromagnetic FeMn layer if one assumes a non-collinear spin structure similar to bulk FeMn. The presence of such a non-collinear spin structure in ultrathin FeMn films is indeed supported by measurements of the linear dichroism in x-ray absorption spectroscopy.

A pronounced influence of the interface roughness on the coercivity as a measure of the magnetic interface coupling in Co/FeMn bilayers was detected. Furthermore, the interlayer coupling between two ferromagnetic layers across an antiferromagnetic FeMn layer was studied for double-wedged samples by layer-resolved domain imaging using XMCD-PEEM. An oscillatory coupling between parallel and antiparallel alignment of the two ferromagnetic layers as a function of FeMn spacer layer thickness was observed with a period of two ML. The influence of the interface roughness, as experimentally set by the atomic layer filling of the bottom FM layer, on the interlayer coupling across an FeMn layer is clearly manifest as a shift in the phase of this oscillatory coupling. This result is qualitatively discussed with the help of a simple model in which part of the deposited FeMn at the interfaces does not take part in the interlayer coupling across the AF layer.

I2 Spin-dependent transport in GaMnAs-based heterostructures.

H. Jaffrès, R. Mattana, J.-M. George, F. Nguyen Van Dau, A. Fert(1), B. Lépine, A. Guivarch́ and G. Jézéquel(2)

(1) *Unité Mixte de Physique CNRS-THALES, Domaine de Corbeville, 91404 Orsay Cedex, France and Université Paris Sud, 91405 Orsay Cedex, France*

(2) *Equipe de Physique des Surfaces et Interfaces, Unité Mixte de Recherche CNRS-Université 6627 "PALMS", Université Rennes I, 35042 Rennes Cedex, France*

We will present our last experiments of spin-dependent transport across heterostructures integrating the ferromagnetic semiconductor *GaMnAs*. We will first emphasize on the magnetoresistance (TMR) of *GaMnAs/AlAs/GaAs/AlAs/GaMnAs* double tunnel junction accounted in terms of sequential tunneling without spin relaxation and associated to the occurrence of spin accumulation in the *GaAs* quantum well. We will discuss i) the conditions to obtain such TMR effects by comparing the dwell time of spin-polarized holes injected in the well to the characteristic spin-lifetime and ii) show to what extend TMR measurements can be used as a probe of spin-lifetime in semiconducting nanostructures. In this mind, we will comment the strong dependence of the TMR vs. temperature associated to the thermal activation of the different spin-flip mechanisms in p-type *GaAs* quantum wells. In the second part, we will present results of spin-dependent tunneling in junctions constituted of a *GaAs* spacer playing the role of barrier for holes injected from *GaMnAs*. Comments will be given on the thermal and bias dependence of the TMR signal together with the key issues of spin-dependent transport in such structures.

I3 K. Kern
MPI for Solid State Research, Stuttgart, Germany

I4 **Calculations for the electronic transport in molecular nanostructures**
G. Seifert
Technical University of Dresden, Dresden, Germany

The basic ideas for calculations of electronic transport in molecular structures will be explained briefly. The specific realization within a method, based on the joint use of a density functional tight binding (DFTB) and of a Green's function technique will be discussed. Applications will be shown for the calculation of currents through various structures, as nanotubes and molecular nanostructures.

I5 **SIC-LSD for Correlated Electrons**
W. Temmerman
Daresbury Laboratory Warrington, UK

A review will be given of the application of the Self-Interaction-
Corrected Local-Spin-Density (SIC-LSD) to the study of correlated d and f electron systems. In particular, the valency of the rare earths will be discussed, and issues concerning the metal/insulator transition in transition metal oxides.

Contributed Talks

C1 **Anomalous spontaneous volume magnetostriction in Fe-based fcc and bcc alloys: Electronic origin of the Invar effect.**
S. Khmelevskyi and P. Mohn
Center for Computational Materials Science, Vienna University of Technology, Getreidemarkt 9/134, 1060 Vienna, Austria

We show that the spontaneous volume magnetostriction in Fe-based alloys can be calculated from first-principles in good agreement with experiment. Our results are obtained by modelling the paramagnetic state above the magnetic ordering temperature as a state with disordered local moments. Studing bcc Fe-Co and fcc Fe-Pt(Pd) alloys, which have a large value of the volume magnetostriction in a certain range of chemical compositions and there show an anomalously low thermal expansion (Invar effect), we found that this a behaviour is due to dynamical changes in the electronic structure induced by effects of magnetic disorder. These changes result in the repopulation of the minority and majority spin bands and thus lead to changes of the values of the local atomic moments in the paramagnetic state. This effect is found to be strongly enhanced in Invar alloys and is due to peculiar features of the density of states.

C2 **Ab initio calculation of the optical and magneto-optical properties of moderately correlated magnetic solids**

A. Perlov[1], S. Chadov[1], H. Ebert[1], L. Chioncel[2], A.I. Lichtenstein[2] and M.I. Katsnelson [3]

[1] *Munich University, Butenandtstr. 5-13, D-81377, Munich, Germany*

[2] *University of Nijmegen,NL-6525 ED Nijmegen, The Netherlands*

[3] *Uppsala University, SE-751 21, Uppsala, Sweden*

An approach for the calculation of the optical and magneto-optical properties of solids based on the one-particle Green Function is introduced in the framework of the LMTO method. The approach keeps all advantages of the more accurate KKR scheme as the possibility to account for many-body effects in terms of the nonlocal energy dependent self energy but is numerically much more efficient. In particular an incorporation of the single site self energy coming from the dynamical mean-field theory (DMFT) is implemented. An application of the approach to bulk Ni and Fe showed rather good agreement with the experimental data, in contrast with the results of standard local spin density approximation (LSDA) computations.

C3 Magnetovibrational magnetization dynamics

A. A. Kovalev[1], G. E. W. Bauer[1], and A. Brataas[2]

[1] *Department of NanoScience, Delft University of Technology,*
Lorentzweg 1, 2628 CJ Delft, The Netherlands.

[2] *Department of Physics, Norwegian University of Science and Technology, N-7491 Trondheim, Norway*

We present an example of a system (a small cantilever with a magnet) which can display a coherent motion of magnetic and mechanical degrees of freedom. The coupling of both fields leads to splittings in FMR spectra. Applications for sensors and actuators should be possible as well as for microwave field generation.

C4 Magnetization dynamics of magnetic multilayers

J. Manschot[1,2], A. Brataas[2] and G. E. W. Bauer[1]

[1] *Department of NanoScience, Delft University of Technology,*
Lorentzweg 1, 2628 CJ Delft, The Netherlands.

[2] *Department of Physics, Norwegian University of Science and Technology, N-7491 Trondheim, Norway*

Magnetization dynamics as function of bias current and external magnetic field is studied of thin film pillars with two magnetic layers. Magnetic layers are assumed to be monodomain magnets. Spin flip processes are disregarded. Comparison is made with experimental observations.

C5 Electronic structure, exchange interactions and Curie temperature in III-V and II-VI DMS

L.M. Sandratskii and P. Bruno

Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany

A wide row of the diluted magnetic semiconductors of III-V and II-VI types is studied. (Some of the results presented can be found in Refs. [1-4]).

We begin with the discussion of the electron structure focusing on the properties of the impurity band. We estimate the value of the exchange interaction between the Mn 3d electrons and the states of the semiconductor matrix (J_{pd}) and calculate the spatial distribution of the hole states. We show how these characteristics of the system determine the values of the effective interatomic exchange interaction between magnetic impurities J_{dd}. The Curie temperature of all systems is calculated as a function of the number of carriers. LDA and LDA+U schemes are used in the calculations.

We show that under certain conditions large J_{pd} exchange can coexist with negligible J_{dd}. These are the paramagnetic systems showing giant Zeeman splitting in applied magnetic field.

We provide a first-principles theory of the high-T_C II-VI DMS (ZnCr)Te.

We discuss the properties of (GaMn)N which is a subject of much controversy.

[1] L. Sandratskii and P. Bruno, PRB 66, 134435 (2002)

[2] L. Sandratskii and P. Bruno, PRB 67, 214402 (2003)

[3] L. Sandratskii Exchange interactions in (ZnMn)Se (submitted)

[4] L. Sandratskii and P. Bruno, J.Phys.: CM 15, L1 (2003)

C6 Ferromagnetism above room temperature in bulk and transparent thin films of Mn-doped ZnO

Rajeev Ahuja
Department of Physics, Uppsala University, P.O. Box 530, SE 751 21 Uppsala, Sweden

The search for ferromagnetism above room temperature in dilute magnetic semiconductor has been intense in recent years. We report the first observations of ferromagnetism above room temperature for dilute (¡4 at%) Mn-doped ZnO.The Mn is found to carry an average magnetic moment of 0.16 Bohr Magneton per ion. Our ab initio calculation find a valence state Mn(2+) and that the magnetic moments are ordered ferromagnetically, consistent with the experimental findings.

C7 Energetics of Mn atoms in diluted magnetic semiconductors

V. Drchal(1), J. Kudrnovský(1), I.Turek(2) and P. Weinberger(3)
(1) *Institute of Physics, AS CR, Praha, Czech Republic*
(2) *Institute of Physics of Materials, AS CR, Brno, Czech Republic*
(3) *Center for Computational Materials Science, TU Vienna, Austria*

We examine the energetics of diluted ferromagnetic III-V semiconductors on an *ab initio* level using the tight-binding linear muffin-tin orbital method combined with the coherent-potential approximation. Magnetic disorder is treated within the disordered local moment method. Based on total energies calculated as functions of alloy composition and on energies of selected clusters, we analyze the local environment effects on formation energies of antisite defects and substitutional and interstitial Mn atoms. The theory is illustrated on the $Ga_{1-x}Mn_xAs$ alloy system, a possible aggregation of Mn atoms and its consequences are discussed.

C8 Magnetic semiconductors, from first principles theory to Monte Carlo simulations

O.Eriksson

Department of Physics, Ångström laboratory, Uppsala University, Box 530 Sweden

The electronic structure and magnetic properties of dilute magnetic semiconductors, especially Mn in GaAs, will be reported. The importance of defects for the magnetic properties will be discussed and recent experimental and theoretical results on Mn and As defects will be reviewed. First principles calculations as well as Monte carlo simulations have been used to evaluate the importance of randomness and clustering on the critical temperature of dilute magnetic semiconductors, and the connection between structural arrangement and magnetism is found to be strong. A few examples of novel ferromagnets, that under certain alloying conditions may become semi-conducting, will be given.

C9 Interstitial Mn in (Ga,Mn)As

F. Máca and J. Mašek

Institute of Physics ASCR, Na Slovance 2, 182 21 Praha 8, Czech Republic

We used the FPLAPW method to obtain total energies of supercells simulating various geometric and magnetic configurations of Mn atoms in (Ga,Mn)As. In absence of other defects, the ground state of the Mn interstitials is the tetrahedral T(As_4) position. The energy of the T(Ga_4) position, however, is almost the same. The situation changes in the p-type material where the T(Ga_4) position has a lower energy. The hexagonal interstitial position has much higher energy and represents a barrier for diffusion of Mn from one to another interstitial site.

The exchange coupling J_{pd} of Mn interstitials with the holes in the valence band is, for both T(As_4) and T(Ga_4), close to the value of J_{pd} obtained for the substitutional Mn. This can be well explained by the hybridization of the Mn d-states with the close next-nearest neighbors of $\mathrm{Mn_{int}}$ which are shown to be important for understanding the properties of the interstitial Mn.

The Mn interstitials are attracted to the substitutional Mn and form stable and magnetically inactive pairs. The density-functional estimate for both binding energy of the pair and for the energy of the antiferromagnetic coupling is of order of 0.3 eV. This fits well with the present day notion of the interstitial Mn in (Ga,Mn)As (K. M. Yu et al., PRB **65** (2002) 201303 (R) and J. Blinowski, P. Kacman, PRB **67**, (2003) 121204). In contrary to the general opinion, however, we found that the efficient pairing is not restricted to $\mathrm{Mn_{int}}$ in the T(Ga_3Mn) position and we showed the importance of the close next-nearest neighbors for the properties of the interstitial Mn.

C10 Residual resistivity of (Ga,Mn)As alloys

I. Turek$^{1)}$, J. Kudrnovský$^{2)}$, V. Drchal$^{2)}$ and P. Weinberger$^{3)}$

$^{1)}$*Institute of Physics of Materials AS CR, Brno, Czech Republic*

$^{2)}$*Institute of Physics AS CR, Prague, Czech Republic*

$^{3)}$*Center for Computational Materials Science, TU Vienna, Austria*

Residual resistivity of diluted (Ga,Mn)As magnetic semiconductors is calculated from first principles using the Kubo-Greenwood linear response theory [I. Turek et al., Phys. Rev. B 65 (2002) 125101]. The electronic structure is described within the local spin density

approximation using the tight-binding linear muffin-tin orbital method in the atomic sphere approximation. The chemical and magnetic disorders of the alloys are treated in the coherent potential approximation. Particular attention is paid to the role of native defects like As-antisites and Mn-interstitials as well as of the local moment disorder of Mn atoms.

The order of magnitude of the calculated resistivities compares reasonably well with available experimental data [K.W. Edmonds et al., Appl. Phys. Lett. 81 (2002) 4991]. The calculated resistivity of alloys with a fixed concentration of As-antisites decreases with increasing Mn-content, in clear contrast to conventional metallic alloys. This effect is due to the increase of number of carriers. For the same reason, the resistivity of alloys with a fixed Mn-content increases with increasing number of As-antisites as well as with increasing number of Mn-interstitials. The resistivities differ significantly for the cases with parallel and antiparallel orientations of magnetic moments of the substitutional and interstitial Mn atoms. In qualitative agreement with experiment, the calculated resistivities are strongly correlated with the alloy Curie temperatures evaluated in the mean field approximation for a classical Heisenberg Hamiltonian [J. Kudrnovský et al., J. Superconductivity 16 (2003) 119].

C11 Rashba-effect at (magnetic) metal surfaces

Gustav Bihlmayer
Institut für Festkörperforschung des Forschungszentrums Jülich,
D–52425 Jülich

In semiconductor heterostructures the Rashba effect allows the manipulation of spin-polarized electrons in a 2DEG by an electric field. Using photoemission the Rashba effect can be observed directly as spin-orbit splitting of surface states on some metal surfaces. First-principles calculations of the closed packed surfaces of 5d and 4f-metals show, why the splitting is observed for some surface states while it is negligible for others. On the Gd(0001) surface we have additionally a spin-spitting, that allows also experimental (spin-resolved) observation. We can manipulate the strength of the Rashba effect by adsorption of O on this surface, as has also been shown experimentally. We compare our calculations with experimental data, where available, and find overall good agreement. Criteria that determine the strength of the Rashba-effect can be inferred from an analysis of the data.

C12 Magnetic and spectroscopic properties of free and supported transition metal clusters

J. Minár$^{1)}$, H. Ebert$^{1)}$, S. Bornemann$^{1)}$, O. Sipr$^{2)}$, I. Cabria$^{3)}$,
R. Zeller$^{3)}$ and P.H. Dederichs$^{3)}$
$^{1)}$*Department Chemie / Physikalische Chemie, Universität München, Butenandstr. 5-13, D-81377 München, Germany*
$^{2)}$*Czech Academy of Science, Prague*
$^{3)}$*Inst. für Festkörperforschung, Forschungszentrum Jülich, Postfach 1913, D-52425 Jülich, Germany*

1ex The fully relativistic spin-polarized KKR method has been used to study the magnetic and spectroscopic properties for free and supported clusters. For free Fe clusters a strong enhancement of the spin and orbital magnetic moments is found for the surface atoms.

This is directly reflected by the pronounced magnetic circular dichroism (MCXD) found for the corresponding $L_{2,3}$-absorption spectra. In spite of the discrete eigenvalue spectrum for the finite free clusters the enhancement is comparable in magnitude to that found for the (001) surface of bcc-Fe. For clusters supported on a transition metal substrate it is shown that the magnetic properties depend on many different parameters as substrate type, cluster size and shape and so on. In line with recent experimental findings a very pronounced magnetic circular dichroism in X-ray absorption is found for Co-clusters on Pt(111). The results for the MCXD spectra and their connection with the spin, orbital and spin dipolar moments will be discussed on the basis of the so-called sum rules.

C13 Unexpected magnetism: the effect of low dimensionality

I. A. Abrikosov1), W. Olovsson2), E. Holmström2), L. V. Pourovskii2), A. V. Ponomareva3), E. A. Smirnova3), E. I. Isaev3) and O. Eriksson2)
1) *Department of Physics and Measurement Technology (IFM),*
Linköpings University, SE-581 83 Linköping, Sweden,
2) *Condensed Matter Theory Group, Physics Department,*
Uppsala University, Box-530, S-75121 Uppsala, Sweden,
3) *Theoretical Physics Department, Moscow Steel and Alloys Institute,*
117419, 4 Leninskii pr., Moscow, Russia

Due to an importance of magnetic devices for the modern technology there is a constant need for new magnetic materials. This leads to discoveries of new magnetic phenomena, and also new classes of magnetic materials are synthesized. One avenue for the search for artificial magnetic materials is a possibility of altering magnetic properties of a system via reducing its dimensionality. Indeed, it is well established theoretically that by reducing a number of the nearest neighbors for a given atom one may increase magnetic moment in the system. Therefore, low-dimensional systems like nanoclusters, thin films and surfaces represent an attractive class of objects for the search of new magnetic materials. Several unexpected effects that occur in different systems upon reducing their dimensionality will be discussed. In particular, results of *ab initio* calculations of magnetization of the unsegregated and segregated (100) surface of MoV binary alloy will be presented. We will also describe stabilities and peculiar magnetic properties of Ni and Fe-Ni alloys grown at Cu (100) substrate. We will discuss the problem of characterization of non-equilibrium systems that often occurs during the preparation of magnetic thin films. In particular, we will show that a combination of experimental measurements and theoretical calculations of the core-level shifts can be used as a reliable tool for the determination of metastable structures at surfaces and interfaces.

C14 Theory of negative differential conductance in double quantum dots

J. Fransson1,2) and O. Eriksson2)
1) *Physics Department, Royal Institute of Technology (KTH),*
SE-106 91 Stockholm, Sweden
2) *Physics Department, Uppsala University, Box 530,*
SE-751 21 Uppsala, Sweden

An explanation for the negative differential conductance in a double quantum dot system attached to metallic external contacts is proposed, based on a diagrammatic technique for non-equilibrium many-body operator Green functions. The theory suggests that tunneling between the states in the double quantum dot suppress the total current dynamically as the bias voltage is increased. The effect is especially evident in systems where the double quantum dot states are asymmetrically coupled to the left and right contacts. Our theory is consistent with recent experimental data on double quantum dots, see Fig. 1. In addition, the theory explains the asymmetries in experimental current-voltage characteristics of mesoscopic quantum systems. Further, we investigate the influence on the resonant peak from spin-splitting the levels in the double quantum dot.

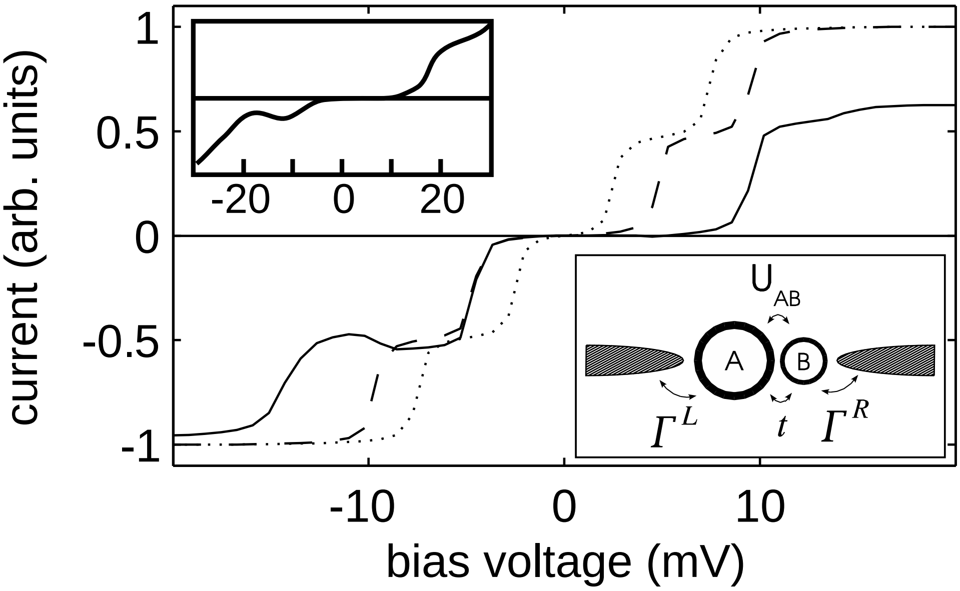

Figure 1: $J-V$ characteristics of the DQD system calculated within the HIA (dotted), with the renormalised transition energies (dashed) and with the full loop correction (solid). For the computations we used the left/right coupling strength $\Gamma^{L/R} = 0.375$ meV and conduction electron band width 2 eV symmetrically around the equilibrium chemical potential $\mu = 0$ at $T = 1$ K. The upper inset shows a drawing of the experimental $J-V$ results on the DQD reported in *Appl. Phys. Lett*, **79**, 1864 (2001). The lower inset displays the geometry of the DQD system.

C15 **Conductance through single atoms: an *ab initio* approach**

A. Bagrets$^{1,2)}$, N. Papanikolaou $^{3)}$ and I. Mertig$^{2)}$
$^{1)}$*Max-Planck-Institut für Mikrostrukturphysik,*
D-06120 Halle, Germany
$^{2)}$*Martin-Luther-Universität, Fachbereich Physik,*
D-06099 Halle, Germany
$^{3)}$*Institute of Materials Science, NCSR "Demokritos",*
GR-15310 Athens, Greece

We present a theoretical study of the conductance through single atoms using an *ab initio* screened Korringa-Kohn-Rostoker Green's function method based on density functional theory. We have simulated atomic-sized contacts, which are usually prepared by the mechanically controllable break junction (MCBJ) technique, considering fcc Cu [001] semi-infinite leads and a cluster of few atoms embedded between the Cu electrodes such a way that a contact is formed by a single atom only. We consider this atom to be (i) Cu; (ii) an *sp*-atom (Na, Mg, Al, Si, P, S, and Zn), or (iii) a $3d$ ferro- or paramagnetic atom (Sc, Ti, V, Cr, Mn, Fe, Co, and Ni). We assume that the case of a single impurity atom at the contact position can be realized in the MCBJ experiments by using a dilute Cu alloy as the wire material. We show that the conductance G of such systems is determined essentially by the electronic properties of the particular atom forming the single-atom contact. In spite of the value of G is sensitive to the geometrical arrangement of the atoms, similar trends in the behaviour of G along the *sp*- and $3d$-series are observed. The interpretation of these results is given by analyzing the local density of states (LDOS) at the contact atom and using the conclusions of the simplified tight-binding models [J.C. Cuevas *et al.*, Phys. Rev. Lett. **80** (1998) 1066]. The pure Cu nanocontacts accept three conducting channels: one sp_z and a twofold degenerate p_xp_y channel. For the *sp*-series ($Z = 11 \ldots 16$) conductance has a maximum at $Z = 14$ (Si) and correlates with the p_xp_y-LDOS, so that the increase and decrease of G are due to opening and closing of p_xp_y conducting channels. In the case of the $3d$-series three orbitals of the contact atom, d_{xz}, d_{yz} and d_{z^2}, forming the sharp resonances in the LDOS, can lead to additional conducting channels if these resonances are pinned or close to the Fermi energy. The transmission always increases in the case of d_{xz}, d_{yz} resonances, however, at particular atomic configurations the d_{z^2} resonance can be superimposed with the van Hove-like singularity of the s-LDOS of the contact atom and thus does not necessarily lead to a larger transmission.

C16 Conductance as a tool of structure analysis

T. Dziekan and S. Mirbt
Department of Physics, Uppsala University, Box 530 Uppsala, Sweden

Recent work done on the stability of gold nanowires has given strong evidence that the gold atoms in the chain are separeted by hydrogen atoms. To fortify this idea we are calculating the conductance of several wire setups containing Au and H and comparing it with available experimental data.

Furthermore these calculations are thought to be a test for the program package which we are using. It should help us to discover shortcomings and restricions and open the way for extending the code.

Beside a short description of the experimental situation the talk will briefly present the applied physical methods in the code. (DFT pseudopotentials, Landauer formalism, Greens function formalism)

I am looking forward for the discussion and remarks after the talk.

C17 Structure, quantum effects and magnetism in atom-sized contacts

A.L. Klavsyuk$^{1)}$, A. N. Baranov$^{1)}$, W. Hergert$^{1)}$, I. Mertig$^{1)}$,
V. S. Stepanyuk$^{2)}$ and P. Bruno$^{2)}$
$^{1)}$*Fachbereich Physik, Martin-Luther-Universität,*
Von-Seckendorff-Platz 1, 06120 Halle, Germany
$^{2)}$*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2,*

D-06120 Halle, Germany

Quantum point contacts are structures in which a neck of atoms just a few atomic diameters wide bridges two electrodes. Our approach is based on density functional theory and the Korringa-Kohn-Rostoker Green's function method. Atomic relaxations of nanocontacts and electrodes are calculated with ab initio based many body potentials for low-dimensional systems. We concentrate on Cu, Fe, Co, Rh and Pd atomic bridges. Our calculations reveal the interplay between, stress and electronic states of nanocontacts. The quantum size effect is found to be dominated by unoccupied electronic states and leads to an enhancement of the LDOS at the Fermi level as the number of atoms in the contact increases. We show that the atomic bridges constructed from non-magnetic in bulk Rh and Pd can be magnetic.

C18 Conductance calculations for quantum wires, wave function matching or Green functions?

G. Brocks, P. A. Khomyakov, M. Zwierzycki and P. J. Kelly

Computational Materials Science, Faculty of Science and Technology, and MESA+ Research Institute, University of Twente, P. O. Box 217, 7500 AE Enschede, the Netherlands.

In the linear response regime the conductance of a quantum wire comprising two ideal leads and a scattering region is related using Landauer's formula to a total transmission probability. The latter can be calculated from the scattering wave functions obtained by matching the wave functions in the ideal leads to those in the scattering region using an elegant technique as formulated by Ando [1]. In this contribution we will discuss this method and show that it is related in a simple way to more complicated Green function techniques [2,3]. The method can be used in combination with any localized basis set. However, here we will focus upon an implementation that does not rely on a basis set, but instead uses a representation on a real space grid. Results will be presented of transport calculations on simple atomic wires.

[1] T. Ando, Phys. Rev. B **44**, 8017 (1991).
[2] C. Caroli, R. Combescot, P. Nozières, and D. Saint-James, J. Phys. C **4**, 916 (1971).
[3] P. S. Krstić, X.-G. Zang, and W. H. Butler, Phys. Rev. B **66**, 205319 (2002).

C19 Bias-voltage dependence of the magneto-resistance in ballistic vacuum tunneling: Theory and application to planar Co(0001) junctions

Jürgen Henk and Patrick Bruno

Max Planck Institute of Microstructure Physics
Weinberg 2, D-06120 Halle, Germany

Motivated by first-principles results for jellium and by surface-barrier shapes that are typically used in electron spectroscopies, the bias voltage in ballistic vacuum tunneling is treated in a heuristic manner. The presented approach leads in particular to a parameterization of the tunnel-barrier shape, while retaining a first-principles description of the electrodes. The proposed tunnel barriers are applied to Co(0001) planar tunnel junctions. Besides discussing main aspects of the present scheme, we focus in particular on the absence of the zero-bias anomaly in vacuum tunneling.

C20 Incorporation of the rotationally invariant LDA+U scheme into the SPR-KKR formalism: Application to disordered alloys

S. Mankovsky, A. Perlov and H. Ebert
Department Chemie / Physikalische Chemie, Universität München, Butenandstr. 5-13, D-81377 München, Germany

An incorporation of the LDA+U formalism into the spin-polarized relativistic Korringa-Kohn-Rostoker (SPR-KKR) method of band structure calculations is presented. This new approach accounts for one-particle relativistic effects in a proper way when applying the LDA+U method to get an improved description of correlation effects compared to plain LDA-based calculations. In addition, it allows to deal straight forwardly with disordered systems by a combination with the Coherent Potential Approximation (CPA) alloy theory. These features are demonstrated by results obtained for fictitious ferromagnetic fcc-Uranium and the disordered alloy system $\mathrm{Fe}_x\mathrm{Co}_{1-x}$.

C21 Spin-dependent ballistic electron transport through interfaces from ab-initio FLAPW Green function embedding

Daniel Wortmann, Gustav Bihlmayer and Stefan Blügel
Institut für Festkörperforschung, Forschungszentrum Jülich, D–52425 Jülich, FRG

A current key issue is the understanding of the spin-dependent electron transport properties through atomically sharp interfaces and atomic scale contacts. This requires a transport description based on the detailed electronic structure which depends on the realistic atomic scale geometry and arrangement of the system at hand. Transport properties are most naturally described using a Green-function method. Of increasing importance are systems containing both transition-metals and oxides or semiconductors, materials with open and complex structures as well as low-symmetry. The treatment of these systems combined with the capability of performing structural optimizations is a strength of the FLAPW method. This motivated us to develop in collaboration with Prof. H. Ishida, an efficient method for calculating the conductance of ballistic electrons through an interface from first-principles using the embedding approach of Inglesfield. In our method the Landauer-Büttiker formula for ballistic transport is expressed in terms of quantities that are available in the embedded Green function calculations. The embedding approach is implemented within the full-potential linearized augmented plane method (FLAPW) as realized in the FLEUR code. We present results for the spin-dependent ballistic electron transport through a Fe/MgO/Fe junction, a model system for tunnel-magneto-resistance (TMR) devices.

C22 The effect of the spin-orbit coupling on the band gap of half-metals

Ph. Mavropoulos(1), K. Sato(1), R. Zeller(1), P. H. Dederichs(1), V. Popescu(2) and H. Ebert(2)
(1) *Institut für Festkörperforschung, Forschungszentrum Jülich,*
D-52425 Jülich, Germany
(2) *Department Chemie/Physikalische Chemie, University of Munich,*
Butenandtstr. 5-13, D-81377 Munich, Germany

We have performed first-principles calculations in order to investigate the effect of the spin-orbit coupling to the existence of the spin-down band gap of half-metals. Due to spin-orbit coupling the spin is not a good quantum number, so that a 100% spin polarisation cannot exist. As typical half-metallic systems, we have chosen the Heusler alloy NiMnSb, the ordered zinc-blende alloys CrAs, CrSb, and MnBi, and the diluted magnetic semiconductors (Ga,Mn)As and (Ga,Mn)N. We find that the majority-spin states are partly reflected into the minority band gap. The intensity of the DOS for minority electrons in this energy region depends mainly on the strength of the spin-orbit coupling, heavier *sp* elements resulting in a higher ratio of minority/majority spin DOS. Thus we see a trend of increasing min./maj. DOS ratio in the middle of the gap as we go from CrAs (0.2%) to CrSb (0.7%) and finally to MnBi (13%). In NiMnSb we find a ratio of 0.2%.

Also, it is important how deep the Fermi level lies within the gap, since majority states close to the gap edges can be easier spin-flipped than states deep in the gap. This results in high minority-spin DOS ratio 4.2% for (Ga,Mn)As where E_F is very close to the valence band edge. We have also explained these effects by first-order perturbation theory.

For transport applications in spintronics we conclude that even in compounds with strong spin-orbit effect (MnBi or (Ga,Mn)As) the majority DOS at E_F dominates the behaviour. Even in MnBi the DOS ratio is only 13%, meaning a spin polarisation of 77%.

Available on-line: cond-mat/0308146

C23 First principles relativistic study of spin–waves in thin magnetic films

L. Udvardi$^{1,2)}$, L. Szunyogh$^{1,2)}$, K. Palotás$^{2)}$ and P. Weinberger$^{2)}$

$^{1)}$*Department of Theoretical Physics, Budapest University of Technology and Economics, Budafoki út 8, H-1111, Budapest, Hungary*

$^{2)}$*Center for Computational Materials Science, Technical University Vienna, Gumpendorfer Str. 1a, A-1060 Vienna, Austria*

Within the adiabatic approach we have developed a relativistic treatment of the low energy magnetic excitation spectrum of thin magnetic films. The method can be considered as a relativistic generalization of the well known torque method by Lichtenstein. The formalism clearly makes possible to identify the different type of generalized exchange interactions, namely, the isotropic exchange, the anisotropic symmetric exchange and the Dzyaloshinsky-Moriya interactions as well as the on-site magnetic anisotropy.

The method is demonstrated for a few atomic layers of Fe and Co on (001) and (111) surfaces of Cu and Au. In particular, the gap which is the consequence of the spin–orbit coupling is calculated. The magnetic anisotropy energies provided by the present method for the Fe$_n$/Cu(001) system are in excellent agreement to those obtained as band energy differences. We point out that in the case of in–plane magnetized thin films, such as Co/Cu(001), the Dzyaloshinsky-Moriya interaction results in an asymmetry of the magnon spectrum.

Posters

Dilute magnetic semiconductors

P1 Exchange interactions and spin waves in diluted magnetic semiconductors

K. Sato and P. H. Dederichs

IFF, Forschungszentrum Juelich, D-52425 Juelich, Germany

Magnetic properties of diluted magnetic semiconductors (DMS) are calculated from first-principles by mapping the ab-initio results on a Heisenberg model. The electronic structure of DMS is calculated by using the Korringa-Kohn-Rostoker coherent potential approximation (KKR-CPA) method within the local density approximation. Effective exchange coupling constants Jij's are evaluated by embedding two impurities i and j in the CPA medium and using the Jij formula of Liechtenstein et al. [1]. Curie temperatures (Tc) of several DMS are estimated from calculated exchange coupling constants by using the mean-field approximation (MFA) and the random phase approximation (RPA). Both approximations give the same chemical trends, i.e., Tc is proportional to the square root of Mn concentration c for (Ga, Mn)N in which the double exchange interaction dominates, on the other hand Tc is linear to c in (Ga, Mn)Sb where the p-d exchange interaction dominates. Since the extended valence hole states mediate the ferromagnetic coupling between localized Mn magnetic moments in (Ga, Mn)Sb (p-d exchange), the exchange interaction is long range leading to a flat spin wave dispersion relation. As a result, MFA gives similar results as the RPA and becomes practically exact in the very dilute limit where the screening of the interaction by others can be neglected. On the other hand, in (Ga, Mn)N impurity bands appear in the band gap and due to the broadening of the impurity bands the ferromagnetic state is stabilized (double exchange). Since the wave function of the majority Mn d-states in the gap are well localized, the exchange interaction is short range leading to dispersive magnon bands. As a result, the MFA values deviate from the RPA values already for low concentrations and Tc in MFA is about more higher than in RPA systematically.

[1] A. I. Liechtenstein et al., J. Magn. Magn. Mater. 67 (1987) 65.

P2 Exchange interactions in III-V and group-IV diluted magnetic semiconductors

J. Kudrnovský$^{1)}$, V. Drchal$^{1)}$, I. Turek$^{2)}$, P. Weinbeger$^{3)}$ and P. Bruno$^{4)}$

$^{1)}$*Institute of Physics AS CR, Prague*

$^{2)}$*Institute of Physics of Materials AS CR, Brno*

$^{3)}$*Computational Materials Science, Technical University, Vienna*

$^{4)}$*Max Planck Institute of Microstructure Physics, Halle*

Effective exchange pair interactions between Mn-atoms in diluted GaMnAs/GaMnN and GeMn diluted magnetic semiconductors are obtained by mapping total energies associated with rotations of the corresponding magnetic moments onto an effective classical Heisenberg Hamiltonian. The electronic structure is described in the framework of the local spin density approximation by including the substitutional disorder in the coherent potential approximation. A detailed study of the behavior of pair exchange interactions as a function of the distance between Mn-atoms as well as a function of Mn-concentration is presented. We have found that pair exchange interactions are exponentially damped with increasing distance between Mn-atoms due to disorder, the half-metallic character of the system, and the width of the gap of the host semiconductor. The knowledge of pair exchange interactions allows to understand the stability of the ferromagnetic phase in the presence of As-antisites in GaMnAs.

P3 A first principles study of diluted magnetic semiconductors

B. Sanyal and S. Mirbt

Condensed Matter Theory Group, Department of Physics, Uppsala University, Sweden

Mn doped diluted magnetic semiconductors are studied extensively nowadays due to their novel magnetic properties. Mn doped GaAs is a prototype belonging to this class of materials. Despite extensive theoretical and experimental investigations, understanding of many aspects of these materials is not clear. We here present results from first principles electronic structure calculations using a plane-wave pseudopotential method for several Mn and Cr doped diluted magnetic semiconductors. III-V, IV, II-VI semiconductor hosts have been considered. We have studied structural and magnetic aspects of these materials in absence and presence of defects. Also, formation energies have been calculated for neutral and charged systems. The results show good agreement with previous theoretical and experimental results, wherever applicable.

P4 Spin-dependent conductance in nonmagnetic InGaAs asymmetric double barrier system

C. Moyses Araujo$^{2)}$, A. Ferreira da Silva$^{1)}$, C. Persson$^{2)}$, R. Ahuja$^{2)}$ and E. A. de Andrada e Silva$^{3)}$

$^{1)}$*Instituto de Fisica, Universidade Federal da Bahia,40210-340 Salvador, Bahia, Brazil*

$^{2)}$*Department of Physics, Uppsala University, P.O. Box 530, SE 751 21 Uppsala, Sweden*

$^{3)}$ *Intistuto Nacional de Pesquisas Espaciais, CP515, Sao Jose dos Campos, Sao Paulo, Brazil*

The spin dependence of the conductance of an asymmetric double-barrier InGaAs system is studied within the multiband kp and envelope function approximations. The spin-dependent transmission probability for electrons across the structure is obtained using transfer matrices and the low bias conductance per unit area is calculated as a function of fermi energy (or doping) in the contacts. The possibility to obtain spin polarized currents in such system is demonstrated, however, the resulting degree of polarization is rather small (a few percent) in the specific InGaAs structure considered here.

Surfaces, Interfaces, Nanostructures

P5 Surface States of Cobalt Nanoislands on Cu(111)

A. N. Baranov$^{1)}$, V. S. Stepanyuk$^{2)}$, P. Bruno$^{2)}$, L. Diekhöner^{13},
M. A. Schneider$^{3)}$ and K. Kern$^{3)}$

$^{1)}$*Fachbereich Physik, Martin-Luther-Universität,*
Von-Seckendorff-Platz 1, 06120 Halle, Germany

$^{2)}$*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany*

$^{3)}$ *Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*

The electronic structure of thin Co monolayers has been investigated below and above the Fermi level by using of Korringa-Kohn-Rostoker (KKR) Green's function method. Two surface related electronic states are found: a strong localized peak at 0.4 eV below Fermi level and a mainly unoccupied dispersive state, giving rise to quantum interference patterns of standing electron waves on the Co surface. An analysis of charge density distribution reveal that the electronic states are spin polarized, originating from $d_{3z^2-r^2}$-minority and *sp*-majority bands respectively.

P6 Spin polarization of the L-gap surface states on Au(111)

Jürgen Henk, Arthur Ernst and Patrick Bruno
Max Planck Institute of Microstructure Physics
Weinberg 2, 06120 Halle, Germany

The electron spin polarization (ESP) of the L-gap surface states on Au(111) is investigated theoretically by means of first-principles electronic-structure and photoemission calculations. The surface states show a large spin-orbit induced in-plane ESP which is perpendicular to the in-plane wavevector, in close analogy to a two-dimensional electron gas with Rashba spin-orbit interaction. The surface corrugation, i. e., the in-plane asymmetry of the surface potential in the (1×1) unit cell, leads to a small ESP component normal to the surface, being not reported so far. The surface-states ESP can be probed qualitatively and quantitatively by spin- and angle-resolved photoelectron spectroscopy, provided that the initial-state ESP is retained in the photoemission process and not obscured by spin-orbit induced polarization effects. Relativistic photoemission calculations provide detailed information on what photoemission set-ups allow to conclude from the photoelectron ESP on that of the surface states.

P7 Stability of magnetic phases in FeAs

S. Mirbt, B. Sanyal and F. Bultmark
Condensed Matter Theory Group, Physics Department, Uppsala University, Sweden

The magnetic properties of the interface between the As-terminated surface of a GaAs crystal and a Fe layer is analyzed with the help of a zincblende FeAs crystal, and the stability of the magnetic phases is investigated by calculation of the total energy as a function of unit cell volume. All calculations have been done using ab-initio calculations of a supercell of four Fe-atoms and four As-atoms. The only stable solution is a non-magnetic cell with a lattice parameter of 5.24 Å, but if the lattice parameter is forced to be larger we find both ferromagnetic and anti-ferromagnetic solutions. The ferromagnetic solutions are always less stable than at least one of the other solutions, while the most stable solutions for crystals with a lattice parameter larger than 5.4 Å will be the antiferromagnetic configuration.

The development of the magnetic moment of the individual iron atoms is investigated for both the magnetic solutions, and the behaviour of the total energy is partly explained by an investigation of the density of states for the different solutions at certain lattice parameters. Also tetragonal crystals are examined and the magnetic phases investigated. The magnetic behaviour of FeAs in the two structures is compared and the results are explained by examining the density of states.

P8 Interface intermixing on the atomic scale

R. C. Longo(1,2), V. S. Stepanyuk(3), W. Hergert(1), L. J. Gallego(2),
A. Vega(4) and J. Kirschner(3)
(1)*Fachbereich Physik, Martin-Luther-Universität,*
Von-Seckendorff-Platz 1, 06120 Halle, Germany

[2]*Departamento de Física de la Materia Condensada, Facultad de Física, Universidad de Santiago de Compostela, E-15782, Santiago de Compostela, Spain*
[3]*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany*
[4]*Departamento de Física Teórica, Atómica, Molecular y Nuclear, Universidad de Valladolid, E-47011 Valladolid, Spain*

We reveal the main mechanism of interface intermixing in the early stages of heteroepitaxy. Performing atomic scale calculations with *ab initio*-based many body potentials, we show that submonolayer inclusions of Fe atoms in the topmost layer of Cu(001) observed in experiments are caused by a collective process of atomic exchanges near small embedded Fe islands. We demonstrate that mesoscopic relaxations in the substrate depend on the size of embedded islands and drastically affect site exchanges.

P9 **How sharp are the interfaces of metallic multilayers ?**

E. Holmström, L. Bergqvist, B. Skubic, B. Hjörvarsson, L. Nordström, I. Abrikosov, P. Svedlindh and O. Eriksson
Department of Physics, Uppsala University,Box 530, SE-75121, Uppsala, Sweden

We show that the three most relevant magnetic properties (magnetic moment, critical temperature and interlayer exchange coupling) of metallic multilayers can be reproduced with good accuracy by first principles theory, provided the picture of atomically sharp interfaces is abandoned and one allows instead for both interface alloying and interface roughness. The interface of a metallic multilayer (exemplified by the Fe/V system) is demonstrated to, at best, have interdiffusion essentially over 2-3 atomic layers on each side of the interface. Our conclusions are the result of combining experimental work with theoretical modeling, and we argue that this approach is the best avenue to obtain accurate information about the interface quality of metallic multilayers.

P10 **On magnetically dead layers at interface between Co and a non-magnetic metal**

Š. Pick(1), H. Dreyssé (2) and I. Turek(3)
(1)*J. Heyrovský Institute of Physical Chemistry ASCR,*
Prague 8, Czech Republic
(2)*Institut de Physique et Chimie des Matériaux de Strasbourg, France*
(3)*Institute of Physics of Materials ASCR, Brno, Czech Republic*

Recently, a series of experimental papers has indicated presence of magnetically dead Co or Fe layer at the interface with Nb. These systems are of interest in magnetic-system applications as well as due to new phenomena at the interface with superconducting Nb. By using TB-LMTO method in the ASA (atomic sphere) approximation, we address two problems: 1) which transition metals can suppress effectively the Co magnetization, and, 2) how the effect depends on the structure of the Nb-Co interface. As a consequence, rather lucid results are obtained: To study question sub 1), capping of the hexagonal surface of Co with metal M=Ti, Nb, Mo, Re, Os, Ir or Pt, or corresponding M-Co 1:1 surface alloy are considered. The local reduction of the Co magnetization by Ti, Nb, Mo and Re, respectively, is marked, whereas the effect of Os is of an intermediate importance. To the problem sub 2), a number of ordered or disordered one-layer or two-layer interface alloys $\mathrm{Nb}_x\mathrm{Co}_{1-x}$ are studied. If an Co atom has about five or more Nb nearest neighbours,

its magnetic moment becomes very small.

P11 Effect of atomic relaxations on magnetic properties of adatoms and small clusters

Š. Pick$^{1)}$, V. S. Stepanyuk$^{2)}$, A. N. Baranov$^{3)}$, W. Hergert$^{3)}$ and
P. Bruno$^{4)}$
$^{1)}$ *J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic,*
Dolejškova 3, CZ-18223 Prague-8, Czech Republic
$^{2)}$ *Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany*
$^{3)}$ *Fachbereich Physik, Martin-Luther-Universität,*
Von-Seckendorff-Platz 1, 06120 Halle, Germany
$^{4)}$ *Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany*

Ab initio and tight-binding calculations has been done to demonstrate an effect of atomic relaxations on magnetic properties of Co adatom and Co$_9$ island on Cu(001) surface. A perpendicular magnetization of Co adatom in unrelaxed position was obtained in the tight-binding model with parameters fitted to *ab initio* results. We show that the relaxations leads to the reduction of the spin and orbital magnetic moments and stabilize the in-plane magnetization of Co adatom.

P12 *Ab initio* study of the magnetic structure of fcc Fe grown on a Cu(001) substrate

B. Yu. Yavorsky and I. Mertig
Martin-Luther-University Halle-Wittenberg, Department of Physics,
Von-Seckendorff-Platz 1, 06120 Halle, Germany

First-principle total energy study of Fe films on a Cu (001) substrate is presented. The films are modeled by symmetric 6Fe/8Cu/6Fe slab. Both collinear and noncollinear magnetic configurations are considered. The effect of the surface relaxation on the total energy of the system is discussed. It was found that the energy difference between the favored collinear double-layered antiferromagnetic state and noncollinear configurations is reduced by contraction in the Fe sublayer but still remains positive. The possibility of the stable noncollinear magnetic configuration in the system is discussed.

P13 Calculated Electronic, Magnetic and structural properties of Fe/GaAs(001) junction

N. Baadji, M. Alouani and H. Dreyssé
Institut de Physique et de Chimie des Matériaux de Strasbourg, UMR 7054 du CNRS, 23, Rue de Loess, F-67034 Strasbourg, France.

We studied the electronic and magnetic properties of Fe/GaAs(100) interface and the effect of the atomic relaxation and diffuson at the interface by means of a first principle full-potential linear augmented plane-wave FP-LAPW. We show that the electronic and the magnetic properties depend strongly on the interface details and the so-called dead magnetic layer can be explained by the interface reconstraction (exchange of Fe and As atoms at the interface). We computed the X-ray magnetic circular dichroism (XMCD) spectra for the iron atoms at the interface to investigate the magnetic anisotropy. Another important feature in the spin-dependent transport properties of this system is the direction

of magnetization which is found to be dependent also on the details of the interface (type of semiconductor atoms at the interface and atomic relaxation). **Oxides**

P14 FERROMAGNETIC INSULATING $La_{1-x}Bi_xMnO_3$ THIN FILMS

M. Gajek[1,2], C. Ferrater[3], M. Bibes[1], F. Sanchez[2], M. Varela[3],
A. Barthelemy[1] and J. Fontcuberta[2]
[1] *Unité mixte de physique CNRS/Thales, Domaine de Corbeville, 91404 Orsay, France*
[2] *Institut de Ciència de Materials de Barcelona, Consejo Superior de Investigación Científica, E-08193 Bellaterra, Catalunya, Spain*
[3] *Department de Física Aplicada i Òptica, Universitat de Barcelona, Avinguda Diagonal 647, 08028 Barcelona, Catalunya, Spain*

An attracting approach to realize highly spin polarized electron sources, is to make the electrons tunnel through a ferromagnetic barrier material which acts as a spin filter. Recent work have shown that highly spin-polarized currents could be achieved using EuS barrier [1]. Nevertheless the low Tc of this compound (16.8 K) and the lack of sufficiently spin-polarized compatible electrodes hampers the development of this type of devices. Magnetic manganese oxides represent an interesting alternative to be integrated in such structures because of their high Tc, and nearly half metallic behaviour. Belonging to the latter family of materials, La1-xBixMnO3 perovskites are promising compounds to be used in spin filter devices as they show simultaneously a ferromagnetic and insulating behaviour over a large range of La concentrations [2]. The pristine BiMnO3 compound can only be prepared (in bulk form) under high pressures. In this paper we shall report on the growth of La1-xBixMnO3 epitaxial films on SrTiO3 single crystal substrates. La doping (¡10the material under normal conditions. We note that these substrates induce a compressive strain in the film that is likely to provide the artificial pressure necessary to stabilize the required phase [3]. In a further step towards the required device architecture, we will also report on the growth of La1-xBixMnO3 film onto an epitaxial electrode of the metallic ferromagnetic SrRuO3 perovskite.

[1] P. Leclair et al, Appl. Phys. Lett, 80, 625 (2002)
[2] Troyanchuk JETP 78 (2), 214 (1994)
[3] E. Ohshima et al. Solid State Communications 116, 73 (2000)

P15 Electronic structure of 3d-transition-metal monoxides: surfaces and bulk-point-defects

D. Ködderitzsch[1], W. Hergert[1], Z. Szotek[2], W.M. Temmerman[2]
[1] *Fachbereich Physik, Martin-Luther-Universität Halle-Wittenberg, Friedemann-Bach-Platz 6 Halle, Germany 06099*
[2] *Daresbury Laboratory, Daresbury, Warrington WA4 4AD, United Kingdom*

Transition-metal oxides (TMO) are potential candidates for application in the new field of spintronics. Density-functional-theory using the local-spin-density approximation (DFT-LSD) is not able to provide the correct electronic structure of these materials due to the strongly correlated nature of interactions in these substances. Self-interaction corrected (SIC) DFT-LSD improves strongly the description of TMO.

We have studied the magnetic interactions in NiO and the NiO(001)-surface in the framework of SIC-LSD-DFT. We characterise the magnetic interactions by extracted exchange-interaction constants of a Heisenberg-Hamiltonian. We have been able to describe the modification of the exchange-interaction constants when going from bulk to the surface.

Further we have investigated in detail the influence of cation vacancies in MnO and NiO. We found vacancy induced half-metallic behaviour in both substances. In particular, for NiO we found a vanishing macroscopic magnetisation ("half-metallic antiferromagnet") which might have technological importance.

P16 Cobalt substituted ZnO for spintronic applications

K. Rode, A. Anane, F. Petroff, V. Cros, and J-.P. Contour

Unité Mixte de Physique C.N.R.S. Thales, Domaine de Corbeville, 91404 Orsay, France et Université Paris-Sud, 91405 Orsay, France

We have grown Co-doped ZnO on $c - Al_2O_3$ films by pulsed laser deposition (PLD) using stochiometric sintered targets containing 25% of Co. Deposition parameters have been optimized to obtain ferromagnetism. Ferromagnetic films have to be grown at low oxygen pressure (typically less than $5 \cdot 10^{-7} Torr$). Ferromagnetism is characterized by an open hystresis cycle that subsists even at room temperature. Curie Temperature is well above our experimental range (350K). In some films an out-of-plane easy magnetization axis has been observed. In order to rule out the possibility of cobalt clustering as the source of the observed ferromagnetic signal, we have performed Auger micro imaging down to $10nm$ resolution, which rules out large clusters. This result, together with the magnetic zero field cooled experiment more sensitive to small clusters, make us confident in the intrinsic nature of the ferromagnetism in $Zn_{1-x}Co_xO$. We have carried out XAS and XMCD measurements on the Co $L_{2,3}$ edges as well as EXAFS. Neither XAS nor EXAFS indicate Co clustering. The XAS spectra are those of Co^{2+} as predicted by theory and we observe a dichroic signal. By comparison against thecalculated spectra we can conclude that the magnetic signal is due to the diluted Co atoms. We have elaborated magnetic tunnel junctions and measured the magnetic field dependent electronic transport. These measurements and results will be discussed.

P17 First-principle calculations of Fe-, Co-, and Ni-doped ZnO

A. Ernst(1), M. Bouhassoune(1), M. Lüders(2), L. Sandratskii(1), P. Bruno(1), Z. Szotek(2), W. M. Temmerman(2) and B. Györfy(3)

(1) *Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany*

(2) *Daresbury Laboratory, Warrington, Cheshire, WA4 4AD, UK*

(3) *HH Wills Physics Laboratory, University of Bristol, UK*

We present a first-principle study of the electronic structure of ZnO-based diluted magnetic semiconductors doped with Fe, Ni and Co. The calculations were obtained in the framework of the Korringa-Kohn-Rostoker (KKR) coherent potential approximation (CPA) within the local density approximation (LDA). Because 3d-electrons of the transition metals in oxides become strongly localized, we applied the self-interaction correction (SIC). We demonstrate both the LDA and the LDA+SIC calculations and discuss the electronic and magnetic properties of the systems.

P18 Orientation-dependent ELNES of TiO_2: a comparison of Theory and Experiment

C. Heiliger[1,2], F. Heyroth[1], F. Syrowatka[1], W. Hergert[2] and I. Mertig[2]

[1] *Center of Materials Science, Martin-Luther-University Halle-Wittenberg, Hoher Weg 8, 06120 Halle, Germany*

[2] *Martin-Luther-University Halle-Wittenberg, Department of Physics, Von-Seckendorff-Platz 1, 06120 Halle, Germany*

In this poster we present a spectroscopic investigation of titanium oxid (TiO_2). The usage of the ultra high vacuum STEM (scanning transmission electron microscope) VG HB 501 equipped with a Gatan Enfina PEELS detector gives the opportunity to detect EELS (electron energy loss spectra) with a high energy resolution. For that reason one can observe characteristic differences in the spectra between the 3 phases of TiO2: rutile, anatase and brookite. In addition it is possible to investigate the orientation dependence of the samples.

Apart from the experimental discussion a comparison to theoretical calculations is presented. The calculation is based on DFT (density functional theory) within the LDA (local density approximation) using the Stuttgart-LMTO-47 (linearized muffin tin orbitals) package. Taking into account the core hole effect in the Z+1 or Z+2 approximation a very good agreement in the peak positions is observed. The peak intensities however are not correctly reflected.

P19 First-principles calculations of Co doped $\mathbf{TiO_2}$

J. M. Osorio-Guillén[1], R. Ahuja[1] and B. Johansson[1,2]

[1] *Condensed Matter Theory Group, Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden*

[1] *Applied Materials Physics, Department of Materials Science and Engineering, Royal Institute of Technology, SE-100 44, Stockholm, Sweden*

We report a density functional theory calculation of the magnetic properties for $\mathrm{Ti}_{1-x}\mathrm{Co}_x\mathrm{O}_2$. The calculted magnetic moment per formula unit for different Co concentrations is found to be in reasonable agreement with the experiemental values.

P20 Half-Metallicity of LSMO

G.Banach and W.M.Temmerman

Daresbury Laboratory Warrington, UK

Self-interaction corrected local spin density approximation calculations were performed for $\mathrm{La}_{(1-x)}\mathrm{Sr}_{0.7}\mathrm{Mn})_3$ (LSMO) ($0.0 < x < 0.5$). The influence and inter-relationship of Sr doping, magnetic structure, O displacements and phase segregation on the Mn charge state were studied. A half-metallic state was obtained for LSMO with manganese configuration Mn^{3+}, whilst Mn^{4+} gave rise to a metallic state with a negligible spin polarisation at the Fermii level. Elongating the MnO_6 octahedron led to static mixed valence $\mathrm{Mn}^{3+}/\mathrm{Mn}^{4+}$ configuration. In the mixed valence state the total energy was minimised by an ordered array of Mn^{4+} and Mn^{3+} MnO_2 planes which showed charge ordered stripes.

Transport Properties

P21 Channel decomposition of interface scattering

M. Zwierzycki$^{1)}$, M. Talanana$^{1)}$, K. Xia$^{2)}$, P.J.Kelly$^{1)}$ and G.E.W. Bauer$^{3)}$
$^{1)}$ *University of Twente, Enschede, The Netherlands*
$^{2)}$ *State Key Laboratory for Surface Physics, Beijing, China*
$^{3)}$ *Delft University of Technology, The Netherlands*

Because the scattering states are explicitly calculated in our TB-MTO transport formalism, we are able to perform "channel decomposition" of the scattering induced by specular interfaces, interface disorder etc. As an example, we show below how the states on the single Fermi surface sheet of Cu are scattered into the multiple sheets of minority spin Co at a clean (111) interface. The calculation of the scattering matrices scales linearly with the number of principal layers L in the scattering region and as the cube of the number of atoms N in the lateral supercell. For metallic systems for which the required Brillouin zone sampling decreases as N increases, the final scaling goes as N^2L. In practice, the efficient basis set allows us to handle scattering regions for which N^2 L $\sim 10^6$. Examples are discussed where lateral supercells containing as many as 20 × 20 atoms were used.
see also Fig 2

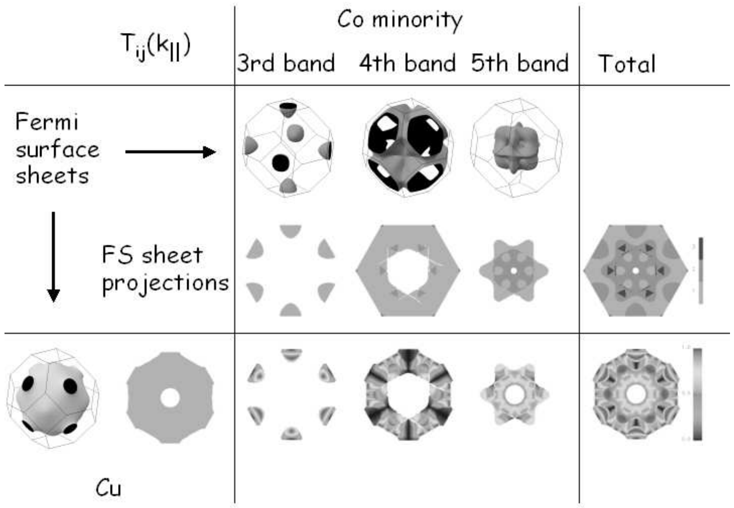

Figure 2: The specular transmission probability from Cu into the minority spin states of Co is decomposed into contributions from the different Fermi surface sheets of Co

P22 Magnetoresistance of magnetic nanojunctions with domain walls

V.K. Dugaev$^{1)}$, J. Berakdar$^{1)}$ and J. Barnaś$^{2)}$
$^{1)}$ *Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany*
$^{2)}$ *Adam Mickiewicz University, Department of Physics, Umultowska 85, 61-614 Poznań, Poland*

We calculate the magnetoresistance of magnetic nanojunctions with domain walls. Our main assumption is that the magnetic domain wall is sharp, and the wall width is of the order or smaller than the wavelength of the electrons. We use the basis of scattering states for spin up and spin down electrons. This approach corresponds to the ballistic regime, in which the interaction of electrons with the domain wall is calculated exactly, and all characteristic lengths are much smaller than the mean free path of electrons in the bulk.

In the limit of a sharp domain wall, we performed analytical calculations. We used a model of spin-flip tunneling barrier and calculated the transmission amplitudes taking into account spin-flip processes. In the case when the domain-wall width is of the order of the electron wavelength, we made numerical simulations. We found that the magnetoresistance due to the domain wall is about 70% for the ferromagnet with a large spin polarization of the electron gas (90%). We also calculated the magnetoresistance for a one-dimensional skyrmion (double domain wall) in the magnetic nanoconstriction.

We analyzed the effect of Coulomb interaction for the one-dimensional magnetic wire with the domain wall. Using the renormalization-group equations for the transmission coefficients, we calculated the critical exponents. We show that due to the Coulomb interaction, in the limit of small voltage, the magnetoresistivity diverges like in the case of a nonmagnetic one-dimensional metal with the potential barrier.

P23 Relativistic Effects in the Transport Properties of Ferromagnetic-Semiconductor-Ferromagnetic (FM/SC/FM) Trilayer Systems

V. Popescu[1), H. Ebert[1), R. Zeller[2), N. Papanikolaou[3)
and P.H. Dederichs[2)
1) *Department Chemie/Physikalische Chemie, University of Munich,*
Butenandtstr. 5-13, 81377 Munich, Germany
2) *Inst. für Festkörperforschung, Forschungszentrum Jülich,*
Postfach 1913, D-52425 Jülich, Germany
3) *Institute of Materials Science, NCSR “Demokritos”,*
GR-15310 Ag. Paraskevi, Athens, Greece

1ex We report results of calculations on the electronic, magnetic and transport properties of As-terminated Fe/GaAs/Fe trilayer systems that have been obtained on the basis of Spin-Polarised Relativistic Multiple Scattering Theory (TB-SPR-KKR).

The transport properties of this system are investigated by means of the Landauer-Büttiker formalism. The tunneling conductance and the magneto-resistance are calculated on a relativistic level.

Model calculations allowed us to gradually manipulate the strength of the spin-orbit coupling and to investigate in detail its quantitative and qualitative influence on the spin-dependent transport, especially on what spin-flip processes are concerned.

Our investigations include also a set of spin-spiral structures, which allowed us to extract averaged interlayer exchange parameters and their dependence on the width of the semiconductor spacer. The dependence of the conductance and magnetoresistance on the width of the semiconductor spacer and the relative angle between the moments of adjacent Fe-layers enabled us to determine a qualitative dependence of the electronic transport on an external magnetic field.

P24 Magnetic and Transport Properties of Fe /GaAs/Fe (001) Magnetic Tunnel Junction

P. Vlaic1), N. Baadji1), M. Alouani1), H. Dreyssé1), O. Bengone2) and I. Turek3)

1) *Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7054 du CNRS, 23, rue du Loess, F-67037 Strasbourg, France*

2) *Condensed Matter Theory Group, Physics Department, Uppsala University, S-75121 Uppsala, Sweden*

3) *Institute of Physics of Materials, Academy of Science of the Czech Republic, CZ-616 62 Brno, Czech Republic*

The electronic structure and magnetic properties of Fe/GaAs/Fe (001) tunnel junction have been studied by using a first principle Green's function technique, based on tight-binding linear muffin-tin orbital method in the atomic sphere approximation, in conjunction with the coherent potential approximation to describe the disorder effects such as interdiffusion at interface. The results show that at the Fe/GaAs interface there is a net charge transfer from iron to the semiconductor region and an enhancement of Fe magnetic moment. The charge transfer is localised almost at the first layer in the magnetic slab but is less localised in the semiconductor region. Metal-induced gap states are evidenced in the semiconductor spacer. Small magnetic moments are induced on the Ga and As atoms near the interfaces. The electronic and magnetic properties are found to be sensitive to the type of the semiconductor extremities. Thus, the charge transfer is higher at the Ga extremity and a higher value of the iron magnetic moment is obtained at the Fe/GaAs interface compared with the Fe/AsGa one. The magnetic properties are influenced also, by the interdiffusion at the interfaces. A phase transition from the ferro- to the antiferromagnetic state was obtained for an interdiffusion concentration c$\approx$28%(15%) for Ga(As) terminations. The conductance and tunnelling magnetoresistance ratio, in the current perpendicular-to-the plane geometry, are calculated by means of transmission matrix formulation of Kubo-Landauer formalism. In the ferromagnetic state the conductance is dominated by the minority-spin electrons that have a transmission coefficient higher than the majority-spin ones. For both spin channels, the conductances seem to be dependent on the type of the semiconductor spacer extremities.

P25 Electronic and Transport Properties of M/Cu/M Multilayer Systems with M=Fe,Co and Ni

P. Vlaic1), H. Dreyssé1), M. Alouani1) and O. Bengone2)

1) *Institute de Physique et Chimie des Matériaux de Strasbourg, 23, rue du Loess, F-67034 Strasbourg, France*

2) *Condensed Matter Theory Group, Physics Department, Uppsala University, S-75121 Uppsala, Sweden*

A first principle self-consistent Green's function technique based on the tight-binding linear muffin-tin orbital method in its atomic sphere approximation, in conjunction with the coherent potential approximation to describe the disorder effects such as interdiffusion at interfaces, was used to investigate the electronic structure and magnetic properties of /(semi-infinite) Cu (001)/nM/mCu/nM/Cu (001) (semi-infinite)/ multilayers systems with M=Fe, Co or Ni. (n, m=integer numbers). All calculations are based on Cu fcc-type lattice. Due to the small misfitting between the bulk Fe, Co and Ni lattice constants on one side and the Cu lattice parameter on another side, the theoretical equilibrium lattice parameters were determined. For all systems, we obtained a decrease of the lattice spacing in agreement with previous experimental and theoretical results. In case of Fe and Co systems, the iron and cobalt magnetic moments at the Fe(Co)/Cu interfaces are dependent on the lattice parameter, increasing with almost 10%(8%) when the lattice constant changes from theoretical equilibrium value to the experimental value of fcc Cu, suggesting that the lattice relaxations are important in establishing the electronic and magnetic properties of these systems. In case of 1Ni/nCu/1Ni systems, no magnetic solutions were found, the Ni layer being magnetically dead while for 2Ni/nCu/2Ni systems the magnetic states are higher in energy compared with the nonmagnetic one. In case of Ni systems, stable magnetic states were found only for systems with n^{3}3. Also, the results show that at the Fe/Cu interface there is a net charge transfer from iron to the nonmagnetic copper spacer and an enhancement of the Fe magnetic moment while in case of Ni systems, at the Ni/Cu interface, the nickel magnetic moment is reduced compared with the bulk value. Magnetic behaviour of the Fe, Co and Ni at the M/Cu interfaces may be viewed as the result of the competition between two effects: narrowing of the density of states at the Fermi level due to the reduced coordination number and the decrease of the exchange splitting between 3d majority- and minority-spin sub-bands due to the hybridisation between Cu and M states at M/Cu interfaces. Interlayer exchange coupling was studied. An oscillatory behaviour between ferro- and antiferromagnetic configurations with respect to the Cu spacer layer thickness was evidenced for all systems. The interlayer exchange coupling is influenced by the interdiffusion at M/Cu interfaces. Thus, in case of 1Fe/3Cu/1Fe system, a transition from antiferromagnetic state to the ferromagnetic one was obtained at the interdiffusion concentration $c = 4\%$ while for 1Co/3Cu/1Co system the ferromagnetic state remain more stable in the whole composition range. For 3Ni/5Cu/3Ni system, a transition from ferromagnetic to antiferromagnetic state was obtained for $c = 26\%$. The conductance and giant magnetoresistance ratio are calculated in the ballistic limit, in the current perpendicular-to-the plane geometry by means of transmission matrix formulation of Kubo-Landauer formalism. For all systems, in the ferromagnetic state, the conductance is determined by the majority-spin electrons whose transmission amplitude is higher than the minority-spin one. The oscillations of giant magnetoresistance ratio that are damped with increasing Cu spacer thickness are observed for all systems. They originate mostly from the oscillations of partial minority-spin conductance in the ferromagnetic state.

P26 **Electronic, magnetic and transport properties of ferromagnet-semiconductor heterostructure systems**

M. Košuth1), V. Popescu1), H. Ebert1), R. Zeller2) and P.H. Dederichs2)

1) *Department Chemie / Physikalische Chemie, Universität München, Butenandstr. 5-13, D-81377 München, Germany*

2) *Inst. für Festkörperforschung, Forschungszentrum Jülich,*
Postfach 1913, D-52425 Jülich, Germany

The electronic and magnetic properties of ferromagnet-semiconductor heterostructure systems have been studied using the fully-relativistic TB-KKR band structure method. Concerning the resulting magnetisation profiles of multilayer and trilayer (FM/SC/FM) systems the most important features are that no magnetically dead layers occurred and an appreciable induced magnetisation was found in the semiconductor subsystem. Investigating the hyperfine interaction and the magnetic circular dichroism (MCXD) more detailed information on the electronic structure could be obtained. Calculating in addition the magneto-crystalline anisotropy energy for thin layers of a ferromagnet on a semiconductor substrate allows comparison with recent experimental results. Similar to metallic multilayer systems it could be shown that the magneto-crystalline anisotropy correlates very well with the anisotropy of the orbital moment.

Exchange interactions

P27 Long-range interactions between magnetic 3d adatoms on Cu(111)

L. Niebergall[1], V.S. Stepanyuk[2], A.N. Baranov[1], W. Hergert[1] and P. Bruno[2]

[1] *Martin-Luther-University Halle-Wittenberg, Department of Physics, Von-Seckendorff-Platz 1, 06120 Halle, Germany*

[2] *Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany*

Ab initio Korringa-Kohn-Rostoker (KKR) Green's function method is applied to resolve long-ranged interactions between $3d$ adatoms on Cu(111) surface. Due to the quantum interference of the surface state electrons scattered by the adatoms, the energy resolved Friedel oscillations of local density of states (LDOS) around adatoms are found. The oscillations of the electron density around adatoms lead to a Friedel-type adatom-adatom interaction, which oscillates with the adsorbate separation. Surface states mediated oscillations have been found for exchange interactions between $3d$ adatoms.

P28 Indirect Exchange Interaction between two Quantum Dots in an Aharonov-Bohm Ring

Yasuhiro Utsumi[1], Jan Martinek[2,3], Patrick Bruno[1] and Hiroshi Imamura[4]

[1] *Max-Planck-Institut für Mikrostrukturphysik Weinberg 2, D-06120 Halle (Saale), Germany*

[2] *Institut für Theoretische Festköperphysik, Universität Karlsruhe, 76128 Karlsruhe, Germany*

[3] *Institute of Molecular Physics, Polish Academy of Sciences, 60-179 Poznań, Poland*

[4] *Graduate School of Information Sciences, Tohoku University, Sendai 980-8579, Japan*

The indirect exchange interaction in magnetic nanostructures is one of basic mechanisms for spintronics. For semiconductor nanostructures, a quantum dot can be considered as a local spin, because the strong Coulomb interaction forbids the double occupation of a state and thus only a single spin can be inside it. Recent improvement of the fabrication technique enables one to make rather complicated structures including quantum dots. However indirect exchange interaction between quantum dots has not yet been observed, in spite of the importance as a basic physics and the potential application for semiconductor nanospintronics.

We theoretically investigate the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction between two local spins located at two quantum dots embedded in an Aharonov-Bohm (AB) ring (Fig. 3(1)). In such a system the RKKY interaction, which oscillates as a function of $k_F l/\pi$ (l: the length of an arm, k_F: the Fermi wave number), is also affected by the flux. For the case of the ferromagnetic RKKY interaction ($2k_F l/\pi$ is an integer), we find that the amplitude of AB oscillations is enhanced by the Kondo correlations and an additional maximum appears at half flux (the solid line in Fig. 3 (2-a)), where the interaction is switched off . For the case of the antiferromagnetic RKKY interaction ($2k_F l/\pi$ is a half-integer), we find that the phase of AB oscillations is shifted by π (the solid line in Fig. 3 (2-b)), which is attributed to the formation of a singlet state between two spins close to integer value of flux. We suggest that such characteristic behavior will be an observable evidence of the RKKY interaction in semiconductor nanostructures.

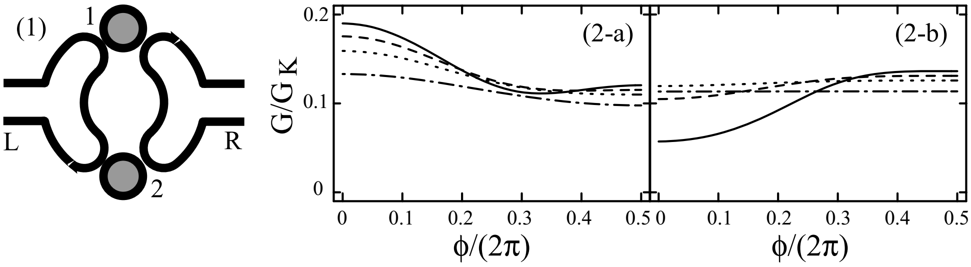

Figure 3: Aharonov-Bohm ring embedded with one quantum dot (denoted with 1 or 2) in each arm. The current flows from the left lead (L) to the right lead (R). The conductance as a function of the flux ϕ for (2-a) $k_F l/(2\pi) = 5$ and (2-b) 5.25 for various temperatures.

P29 Inter–sublattice Exchange Interactions in Full Heusler Alloys

E. Şaşıoğlu, L. M. Sandratskii and P. Bruno
Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany

We study exchange interactions and Curie temperature in full Heusler alloys Ni_2MnX (X=Ga, In, Sn, Sb). This class of systems has recently attracted attention as a possible source of spin-polarized carriers for spintronic applications. To calculate the interatomic exchange interactions we employ the frozen-magnon approach. Special attention is paid to the consequent account for the exchange interactions between the atoms of different magnetic sublattices. The Curie temperature was calculated within the mean–field approximation to the classical Heisenberg Hamiltonian by solving a matrix equation for a many-sublattice system. We obtain good agreement with experiment for all four systems. We show that despite similarity of the Curie temperatures of these systems there is strong difference in the underlying magnetic interactions. In Ni_2MnGa and Ni_2MnIn the exchange interactions between different sublattices play important role in the formation of the Curie temperature. On the other hand, in Ni_2MnSn and Ni_2MnSb the role of the Mn–Ni interaction is much less important and the account for Mn–Mn interaction along provides good estimation of the Curie temperature. The physical origin of this difference in the magnetism of the systems is discussed.

Miscellaneous

P30 Computation of the Berry phase in two-dimensional periodic magnetic structures

M. Taillefumier$^{1,2)}$, V.K. Dugaev$^{1)}$, and P. Bruno$^{1)}$

$^{1)}$*Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany*

$^{2)}$*Laboratoire Louis Néel, CNRS Boite Postale 166, 38042 Grenoble Cedex 09 France*

We compute numerically the Berry phase associated with the motion of electrons in a periodic field of magnetic nanowires on top of a two-dimensional electron gas. To compute the Berry phase, we first calculate a non-uniform magnetic field created by the magnetic nanowires in the case of square and hexagonal nanowire lattices, and then we calculate the topological field, which is related to the Berry phase. We also study the effect of an external uniform magnetic field acting on the system. In the case of hexagonal nanowire lattice, we found some critical values of the external field, for which the topological field per unit cell jumps from 0 to $+\Phi_0$, then to $-2\Phi_0$, and again to 0 with increasing the external field. This effect can be observed experimentally by measuring the Hall effect in semiconductor quantum wells packed into the structure with magnetic nanowires. We used different methods to calculate the magnetic field. First we calculated the magnetic field in real space using the image of magnetic charges. The second method use also the magnetic charges and the Poisson equation in fourier space.

P31 On the calculation of Lloyd's formula in the KKR method

Rudolf Zeller

Institut für Festkörperforschung, Forschungszentrum Jülich,
D-52425 Jülich

Lloyd's formula is an important concept in multiple-scattering theory since for a potential described by a few low angular momentum components it directly and exactly gives the integrated density of states without the need to sum over infinitely many angular-momentum components of the wave function. Its evaluation, however, is difficult because of the numerical complexity arising from the multivaluedness of the imaginary part of the logarithm of the KKR determinant. It will be shown how this problem can be avoided in numerical calculations by using a complex-energy contour integration where only the real part of the logarithm enters. For finite temperature results for metals and semiconductors will be presented which have been obtained with the correct Fermi-Dirac broadening. The problems to apply Lloyd's formula to obtain a properly normalized charge density despite the angular-momentum cutoff in the KKR Green function will be discussed and a method to solve these problems will be suggested.

P32 AB-INITIO STUDIES OF Ni-Mn-Ga SHAPE MEMORY ALLOY

J. Enkovaara$^{1,2)}$, A. Ayuela$^{2)}$, O. Heczko$^{3)}$, L. Nordström$^{4)}$ and
R. M. Nieminen$^{2)}$

$^{1)}$*Institut für Festkörperforschung, Forschungszentrum Jülich, Germany*

$^{2)}$*Laboratory of Physics, Helsinki University of Technology, Finland*

$^{3)}$*Laboratory of Biomedical Engineering, Helsinki University of Technology*

$^{4)}$*Department of Physics, Uppsala University, Sweden*

Ni_2MnGa is an example of magnetic shape memory alloy which can undergo reversible shape changes up to 10 % in an external magnetic field. As the origin of the effect is magnetic, detailed understanding of the microscopic magnetic properties is important. In continuation to the previous work with collinear ferromagnetic order [1], we study here non-collinear magnetic configurations [2] as well as novel antiferromagnetic order coexisting with the ferromagnetic one. The investigations are carried out by state-of-the-art first-principles calculations.

The calculations of spiral magnetic order in stoichiometric Ni_2MnGa confirm that the ground state is ferromagnetic. The results allow an estimation of finite temperature properties such as spin stiffness and Curie temperature which are in good agreement with the experiments. The analysis of the results shows the importance of Ni in determining the Curie point. This finding is surprising because the magnetic moment of Ni is only about 10 % of that of Mn.

Since the most of the magnetic moment originates from Mn the total magnetic moment of non-stoichiometric Ni-Mn-Ga alloys should increase with increasing Mn content. Experiments show, however, that after the amount of Mn is larger than the stoichiometric 25 %, the total magnetic moment starts to decrease. We present total energy calculations about the composition $Ni_2Mn_{1.25}Ga_{0.75}$ and show that the energy is minimized when the additional Mn couples *antiferromagnetically* to the other Mn atoms. This result explains perfectly the experimentally observed puzzle in the variation of the total magnetic moment with the composition.

[1] J. Enkovaara, A. Ayuela, L. Nordström, and R. M. Nieminen, Phys. Rev. B 65, 134422 (2002).

[2] J. Enkovaara, A. Ayuela, J. Jalkanen, L. Nordström, and R. M. Nieminen, Phys. Rev. B 67, 212405 (2003).

P33 Pressure induced superconductivity in phosphorus: implication for spintronics

S. Ostanin$^{1)}$, J.B. Staunton$^{1)}$, V. Trubitsin$^{2)}$ and S.Y. Savrasov$^{3)}$
$^{1)}$*Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom*
$^{2)}$*PTI, Ural Branch of RAS, 132 Kirov Str., 426001 Izhevsk, Russia*
$^{3)}$*Department of Physics, New Jersey Institute of Technology, Newark, NJ 07102, USA*

The high-pressure phase diagram of phosphorus is studied using density functional total energy, linear response lattice dynamics and model Debye-Grueneisen theories. The volume dependent electron-phonon coupling (0.7-0.9) is extracted for the bcc structure and found to increase with increasing volume. We propose that this phase might be realized in epitaxial thin films using templates such as V(100), Fe(100) or Cr(100) relevant to spintronics applications.

P34 Photoelectron Diffraction in Magnetic Solids: Theory and Applications

Angelika Chassé
Martin-Luther-University Halle-Wittenberg, Department of Physics,
Von-Seckendorff-Platz 1, 06120 Halle, Germany

It is well known that photoelectron diffraction (PED) is a powerful technique to investigate the atomic structure at surfaces, interfaces or in thin films. When a photoelectron is emitted from a core level of an atom, its wavefield interferes coherently with components elastically scattered by the surrounding atoms. This leads to variations in the measured photoelectron flux as a function of emission angle and energy. These diffraction effects contain information about the local crystal structure in the vicinity of the emitting atom.

Additional information is expected if the effect of the spin of the electrons on the scattering is considered. Recently a new tool, magnetism-induced symmetry breaking in photoelectron diffraction patterns, has been applied to get information about both the local crystal structure and the magnetic order.

The information about the crystal structure and the magnetic order contained in PED patterns follows from the comparison of experimental and calculated photoelectron distribution patterns. A one-electron non-relativistic multiple-scattering cluster model is applied to discuss spin-resolved PED in magnetic solids. Both spin-orbit coupling and exchange interaction with the spin-polarized valence band have been taken into account in the description of the initial core state where the exchange interaction is treated by means of a homogeneous spin field.

In particular spin polarization and magnetism-induced symmetry breaking of the circular dichroism in the angular distribution of photoelectrons from thin magnetic films are discussed. It is shown that spin-resolved PED in magnetic solids may be used to investigate the magnetic and structural geometry simultaneously.

Participants

1 **Abrikosov, Igor**
Uppsala University, Department of Physics
P.O. Box 530, 751 21 Uppsala, Sweden
phone: +46 18 471 3568, fax: +46 18 511784
mail: Igor.Abrikosov@fysik.uu.se
contribution: C13 (p.17), P9 (p.26)

2 **Ahuja, Rajeev**
Uppsala University, Physics Department
Box 530, 751 21 Uppsala, Sweden
phone: +46 18 471 3626, fax: +46 18 511784
mail: Rajeev.Ahuja@fysik.uu.se
contribution: C6 (p.14), P4 (p.24), P19 (p.30)

3 **Alouani, Mébarek**
IPCMS, Groupe d'Étude des Máteriaux Métaliques
23, rue du Loess, 670 34 Strasbourg, France
phone: +33 03.88.10.70.06
mail: Mebarek.Alouani@ipcms.u-strasbg.fr
contribution: P13 (p.27), P24 (p.32), P25 (p.33)

4 **Bagrets, Alexej**
Martin-Luther-Universität Halle-Wittenberg, Fachbereich Physik
06099 Halle, Germany
phone: +49 345 5525434, fax: +49 345 5525446
mail: bagrets@physik.uni-halle.de
contribution: C15 (p.18)

5 **Banach, Grzegorz**
Daresbury Laboratory, Computational Science& Engineering Department
Daresbury, Warrington, Cheshire WA4 4AD, UK
phone: +44 1925 603227, fax: +44 1925 603634
mail: g.banach@dl.ac.uk
contribution: P20 (p.30)

6 **Baranov, Artem**
Martin-Luther-Universität Halle-Wittenberg, Fachbereich Physik
06099 Halle, Germany
phone: +49 345 5525428, fax: +49 345 5525446
mail: baranov@hera.physik.uni-halle.de
contribution: C17 (p.19), P5 (p.24), P27 (p.35)

7 **Bauer, Gerrit**
Delft University of Technology, Department of NanoScience
Lorentzweg 1, 2628 CJ Delft, The Netherlands
phone: +31 15 278 47 19, fax: +31 15 278 12 03
mail: G.E.W.Bauer@tn.tudelft.nl
contribution: C3 (p.13), C4 (p.13), P21 (p.30)

8 **Berakdar, Jamal**
Max-Planck-Institut für Mikrostrukturphysik,
Weinberg 2, 06120 Halle, Germany
phone: +49 345 5582-666, fax: +49 345 5582-765
mail: jber@mpi-halle.de
contribution: P22 (p.31)

9 **Bergman, Anders**
Uppsala University, Department of Physics
Box 530, 751 21 Uppsala, Sweden
phone: +46 18 471 5866, fax: +46 18 511784
mail: Anders.Bergman@fysik.uu.se
contribution:

10 **Bihlmayer, Gustav**
Forschungszentrum Jülich GmbH, Institut für Festkörperforschung
52425 Jülich, Germany
phone: +49 2461 61 4677, fax: +49 2461 61 2620

mail: g.bihlmayer@fz-juelich.de
contribution: C11 (p.16), C21 (p.21)

11 **Blügel, Stefan**
Forschungszentrum Jülich GmbH, Institut für Festkörperforschung
52425 Jülich, Germany
phone: +49 2461 61 4249, fax: +49 2461 61 2620
mail: s.bluegel@fz-juelich.de
contribution: C21 (p.21)

12 **Brocks, Geert**
University of Twente, Faculty of Applied Physics
P.O. Box 217, 7500 AE Enschede, The Netherlands
phone: +31 53 489 3155, fax: +31 53 489 2910
mail: G.H.L.A.Brocks@tn.utwente.nl
contribution: C18 (p.20)

13 **Bruno, Patrick**
Max-Planck-Institut für Mikrostrukturphysik,
Weinberg 2, 06120 Halle, Germany
phone: +49 345 5582-763, fax: +49 345 5582-765
mail: bruno@mpi-halle.de
contribution: C5 (p.13), C17 (p.19), C19 (p.20), P2 (p.23), P5 (p.24), P6 (p.25), P11 (p.27), P17 (p.29), P27 (p.35), P28 (p.35), P29 (p.36), P30 (p.37)

14 **Bultmark, Fredrik**
Uppsala University, Deaprtment of Physics
Box 530, 751 21 Uppsala, Sweden
phone: +46 18 471 5866, fax: +46 18 511784
mail: Fredrik.Bultmark@fysik.uu.se
contribution: P7 (p.25)

15 **Chassé, Angelika**
Martin-Luther-Universität Halle-Wittenberg, Fachbereich Physik
06099 Halle, Germany
phone: +49 345 5525436, fax: +49 345 5525446
mail: chasse@physik.uni-halle.de
contribution: P34 (p.38)

16 **Czerner, Michael**
Martin-Luther-Universität Halle-Wittenberg, Fachbereich Physik
06099 Halle, Germany
phone: +49 345 5525460, fax: +49 345 5525446
mail: czerner@physik.uni-halle.de

17 **Däne, Markus**

Martin-Luther-Universität Halle-Wittenberg, Fachbereich Physik
06099 Halle, Germany
phone: +49 345 5525439, fax: +49 345 5525446
mail: daene@physik.uni-halle.de

18 **Dederichs, Peter H.**
Forschungszentrum Jülich GmbH, Institut für Festkörperforschung
52425 Jülich, Germany
phone: +49 2461 61 4351, fax: +49 2461 61 2620
mail: p.h.dederichs@fz-juelich.de
contribution: C12 (p.16), C22 (p.21), P1 (p.22), P23 (p.32), P26 (p.34)

19 **Drchal, Vaclav**
Academy of Sciences of the Czech Republic, Institute of Physics
Na Slovance 2, 182 21 Prague 8, Czech Republic
phone: +420 2 66052926, fax: +420 2 86890527
mail: drchal@fzu.cz
contribution: C7 (p.14), C10 (p.15), P2 (p.23)

20 **Dugaev, Vitalii**
Max-Planck-Institut für Mikrostrukturphysik,
Weinberg 2, 06120 Halle, Germany
phone: +49 345 5582-970, fax: +49 345 5582-765
mail: vdugaev@mpi-halle.de
contribution: P22 (p.31), P30 (p.37)

21 **Dziekan, Thomas**
Uppsala University, Department of Physics
Box 530, 751 21 Uppsala, Sweden
phone: +46 18 471 5860, fax: +46 18 511784
mail: ThomasDziekan@fysik.uu.se
contribution: C16 (p.19)

22 **Enkovaara, Jussi**
Forschungszentrum Jülich GmbH, Institut für Festkörperforschung
52425 Jülich, Germany
phone: +49 2461 61 4210, fax: +49 2461 61 2850
mail: j.enkovaara@fz-juelich.de
contribution: P32 (p.37)

23 **Eriksson, Olle**
Uppsala University, Department of Physics
Box 530, 751 21 Uppsala, Sweden
phone: +46 18 471 3625, fax: +46 18 511784
mail: Olle.Eriksson@fysik.uu.se
contribution: C8 (p.14), C13 (p.17), C14 (p.17), P9 (p.26)

24 **Ernst, Arthur**
Max-Planck-Institut für Mikrostrukturphysik,
Weinberg 2, 06120 Halle, Germany
phone: +49 345 5582-666, fax: +49 345 5582-765
mail: aernst@mpi-halle.de
contribution: P6 (p.25), P17 (p.29)

25 **Fert, Albert**
CNRS-THALES, Unité Mixte de Physique
Domaine de Corbeville, 91404 Orsay, France
mail: albert.fert@thalesgroup.com
contribution: I2 (p.11)

26 **Fransson, Jonas**
Uppsala University, Department of Physics
Box 530, 751 21 Uppsala, Sweden
phone: +46 18 471 5862, fax: +46 18 511784
mail: Jonas.Fransson@fysik.uu.se
contribution: C14 (p.17)

27 **Gajek, Martin**
CNRS-THALES, Unité Mixte de Physique
Domane de Corbeville, 91404 Orsay, France
mail: martin.gajek@thalesgroup.com
contribution: P14 (p.28)

28 **Graca-Araujo, Carlos Moyses**
Uppsala University, Department of Physics
Box 530, 751 21 Uppsala, Sweden
phone: +46 18 471 3532, fax: +46 18 511784
mail: Moyses.Araujo@fysik.uu.se
contribution: P4 (p.24)

29 **Heiliger, Christian**
Martin-Luther-Universität Halle-Wittenberg, Fachbereich Physik
06099 Halle, Germany
phone: +49 345 5525460, fax: +49 345 5525446
mail: c.heiliger@physik.uni-halle.de
contribution: P18 (p.29)

30 **Henk, Jürgen**
Max-Planck-Institut für Mikrostrukturphysik,
Weinberg 2, 06120 Halle, Germany
phone: +49 345 5582-970, fax: +49 345 5582-765
mail: henk@mpi-halle.de
contribution: C19 (p.20), P6 (p.25)

31 **Hergert, Wolfram**
Martin-Luther-Universität Halle-Wittenberg, Fachbereich Physik
06099 Halle, Germany
phone: +49 345 5525445, fax: +49 345 5525446
mail: hergert@physik.uni-halle.de
contribution: C17 (p.19), P8 (p.25), P11 (p.27), P15 (p.28), P18 (p.29), P27 (p.35)

32 **Jaffrés, Henri**
CNRS-THALES, Unité Mixte de Physique
Domaine de Corbeville, 91404 Orsay, France
mail: henri.jaffres@thalesgroup.com
contribution: I2 (p.11)

33 **Johansson, Börje**
Uppsala University, Department of Physics
Box 530, 751 21 Uppsala, Sweden
phone: +46 18 471 3623, fax: +46 18 511784
mail: Borje.Johansson@fysik.uu.se
contribution: P19 (p.30)

34 **Karas, Piotr**
Max-Planck-Institut für Mikrostrukturphysik,
Weinberg 2, 06120 Halle, Germany
phone: +49 345 5582-968, fax: +49 345 5582-765
mail: karas@mpi-halle.de

35 **Karpan, Volodymyr**
University of Twente, Faculty of Physics
P.O. Box 217, 7500 AE Enschede, The Netherlands
phone: +31 53 4891082, fax: +31 53 489 2910
mail: v.karpan@tnw.utwente.nl
contribution:

36 **Kelly, Paul**
University of Twente, Faculty of Physics
P.O. Box 217, 7500 AE Enschede, The Netherlands
phone: +31 53 489 3166, fax: +31 53 489 2910
mail: P.J.Kelly@tnw.utwente.nl
contribution: C18 (p.20), P21 (p.30)

37 **Kern, Klaus**
Max-Planck-Institut für Festkörperforschung,
Heisenbergstr. 1, 70569 Stuttgart, Germany
phone: +49 711 689-1660, fax: +49 711 689-1662
mail: klaus.kern@fkf.mpg.de
contribution: I3 (p.12), P5 (p.24)

38 **Khmelevski, Sergii**
TU Wien, Institut für Allgemeine Physik
Gumpendorfer Str. 1a, 1060 Wien, Austria
mail: sk@cms.tuwien.ac.at
contribution: C1 (p.12)

39 **Klavsyuk, Andrej**
Martin-Luther-Universität Halle-Wittenberg, Fachbereich Physik
06099 Halle, Germany
phone: +49-345 5525428, fax: +49 345 5525446
mail: klavsjuk@physik.uni-halle.de
contribution: C17 (p.19)

40 **Kormilets, Viatscheslav**
Universität Leipzig, Institut für Theoretische Physik
Permoserstr. 15, 04318 Leipzig, Germany
mail: korm@pcserv.exphysik.uni-leipzig.de

41 **Košuth, Michal**
Ludwig-Maximilians-Universität München, Physikalische Chemie
Butenandtstr. 11 Haus E, 81377 München, Germany
phone: +49 89 2180 77577, fax: +49 89 2180 77568
mail: Michal.Kosuth@cup.uni-muenchen.de
contribution: P26 (p.34)

42 **Kovalev, Alexey A.**
Delft University of Technology, Department of NanoScience
Lorentzweg 1, 2628 CJ Delft, The Netherlands
phone: +31 15 278 38 69, fax: +31 15 278 12 03
mail: A.A.Kovalev@tnw.tudelft.nl
contribution: C3 (p.13)

43 **Kuch, Wolfgang**
Max-Planck-Institut für Mikrostrukturphysik,
Weinberg 2, 06120 Halle, Germany
phone: +49 345 5582-615, fax: +49 345 5511223
mail: kuch@mpi-halle.de
contribution: I1 (p.10)

44 **Kudrnovský, Josef**
Academy of Sciences of the Czech Republic, Institute of Physics
Na Slovance 2, 182 21 Praha 8, Czech Republic
mail: kudrnov@fzu.cz
contribution: C7 (p.14), C10 (p.15), P2 (p.23)

45 **Longo, Roberto**

Martin-Luther-Universität Halle-Wittenberg, Fachbereich Physik
06099 Halle, Germany
phone: +49 345 5525460, fax: +49 345 5525446
mail: romade@usc.es
contribution: P8 (p.25)

46 **Maca, Frantisek**
Academy of Sciences of the Czech Republic, Institute of Physics
Na Slovance 2, 182 21 Prague, Czech Republic
phone: +420 2 6605 2914, fax:
mail: maca@fzu.cz
contribution: C9 (p.15)

47 **Mankovskyy, Sergiy**
Ludwig-Maximilians-Universität München, Physikalische Chemie
Butenandtstr. 11 Haus E, 81377 München, Germany
phone: +49 89 2180 7577, fax: 089 2108 7584
mail: Sergiy.Mankovskyy@cup.uni-muenchen.de
contribution: C20 (p.21)

48 **Manschot, Jan**
Delft University of Technology, Department of NanoScience
Lorentzweg 1, 2628 CJ Delft, The Netherlands
mail: J.Manschot@student.tnw.tudelft.nl
contribution: C4 (p.13)

49 **Marushchenko, Illya**
University of Twente, Faculty of Applied Physics
P.O. Box 217, 7500 AE Enschede, The Netherlands
phone: +31 53 489 2624, fax: +31 53 489 2910
mail: I.Marushchenko@tn.utwente.nl

50 **Mavropoulos, Phivos**
Forschungszentrum Jülich, Institut für Festkörperforschung
52425 Jülich, Germany
phone: +49 2461 61-5956, fax: +49 2461 61-2620
mail: ph.mavropoulos@fz-juelich.de
contribution: C22 (p.21)

51 **Mertig, Ingrid**
Martin-Luther-Universität Halle-Wittenberg, Fachbereich Physik
06099 Halle, Germany
phone: +49 345 5525430, fax: +49 345 5525446
mail: mertig@physik.uni-halle.de
contribution: C15 (p.18), C17 (p.19), P12 (p.27), P18 (p.29)

52 **Metalidis, Georgo**
Max-Planck-Institut für Mikrostrukturphysik,
Weinberg 2, 06120 Halle, Germany

53 **Minar, Jan**
Ludwig-Maximilians-Universität München, Physikalische Chemie
Butenandtstr. 11 Haus E, 81377 München, Germany
phone: +49 89 2180 77579
mail: Jan.Minar@cup.uni-muenchen.de
contribution: C12 (p.16)

54 **Mirbt, Susanne**
Uppsala University, Department of Physics
Box 530, 751 21 Uppsala, Sweden
phone: +46 18 471 5861, fax: +46 18 511784
mail: Susanne.Mirbt@fysik.uu.se
contribution: C16 (p.19), P3 (p.23), P7 (p.25)

55 **Nadjib, Baadji**
IPCMS, Groupe d'Étude des Máteriaux Métaliques
23, rue du Loess, 670 34 Strasbourg, France
mail: baadji@ipcms.u-strasbg.fr
contribution:

56 **Niebergall, Larissa**
Martin-Luther-Universität für Mikrostrukturphysik, Fachbereich Physik
06099 Halle, Germany
phone: +49 345 5525439, fax: +49 345 5525446
mail: niebergall@physik.uni-halle.de
contribution: P27 (p.35)

57 **Osorio-Guillén, Jorge**
Department of Physics, Condensed Matter Theory Group
BOX 530, 751 21 Uppsala, Sweden
phone: +46 18 471 5865, fax: +46 18 511784
mail: Jorge.Osorio@fysik.uu.se
contribution: P19 (p.30)

58 **Ostanin, Sergei**
University of Warwick, Department of Physics
Coventry CV4 7AL, UK
phone: +44 24 7652 3965, fax: +44 24 7669 2016
mail: phsgv@warwick.ac.uk
contribution: P33 (p.38)

59 **Perlov, Alexander**

Ludwig-Maximilains Universität München, Physikalische Chemie
Butenandtstr. 11 Haus E, 81377 München, Germany
phone: +49 89 2180-77589, fax: +49 89 2180 77568
mail: Alexander.Perlov@cup.uni-muenchen.de
contribution: C2 (p.12), C20 (p.21)

60 **Pick, Stepan**
Academy of Sciences of the Czech Republik, Institute of Physical Chemistry
Doleiskova 3, 182 23 Prague, Czech Republic
phone: +420 2 66053496, fax: +420 2 8582307
mail: pick@jh-inst.cas.cz
contribution: P10 (p.26), P11 (p.27)

61 **Popescu, Voicu**
Ludwig-Maximilians-Universität München, Physikalische Chemie
Butenandtstr. 11 Haus E, 81377 München, Germany
phone: +49 89 2180 7581, fax: +49 89 2180 7568
mail: voiu.popescu@cup.uni-muenchen.de
contribution: C22 (p.21), P23 (p.32), P26 (p.34)

62 **Rode, Karsten**
CNRS-THALES, Unité Mixte de Physique
Domaine de Corbeville, 91404 Orsay, France
mail: karsten.rode@thalesgroup.com
contribution: P16 (p.29)

63 **Sandratskii, Leonid**
Max-Planck-Institut für Mikrostrukturphysik,
Weinberg 2, 06120 Halle, Germany
phone: +49 345 5582-537, fax: +49 345 5582-765
mail: lsandr@mpi-halle.de
contribution: C5 (p.13), P17 (p.29), P29 (p.36)

64 **Sanyal, Biplab**
Uppsala University, Department of Physics
Box 530, 751 21 Uppsala, Sweden
phone: +46 18 471 3624, fax: +46 18 511784
mail: Biplab.Sanyal@fysik.uu.se
contribution: P3 (p.23), P7 (p.25)

65 **Sasioglu, Ersoy**
Max-Planck-Institut für Mikrostrukturphysik,
Weinberg 2, 06120 Halle, Germany
phone: +49 345 5582-913, fax: +49 345 5582-765
mail: ersoy@mpi-halle.de
contribution: P29 (p.36)

66 **Sato, Kazunori**
Forschungszentrum Jülich, Institut für Festkörperforschung
52425 Jülich, Germany
mail: k.sato@fz-juelich.de
contribution: C22 (p.21), P1 (p.22)

67 **Seifert, Gotthard**
Technische Universität Dresden, Institut für Physikalische Chemie u Elektrochemie
Mommsenstr. 13, 01062 Dresden, Germany
phone: +49 351 463 37637, fax: +49 351 463 35953
mail: Gotthard.Seifert@chemie.tu-dresden.de
contribution: I4 (p.12)

68 **Skubic, Björn**
Uppsala University, Department of Physics
Box 530, 751 21 Uppsala, Sweden
phone: +46 18 471 3622, fax: +46 18 511784
mail: Bjorn.Skubic@fysik.uu.se
contribution: P9 (p.26)

69 **Sommers, Charles**
Université Paris-Sud, Laboratoire de Physique des Solides
Bat. 510, 91405 Orsay Cedex, France
mail: sommers@lps.u-psud.fr

70 **Starikov, Anton**
University of Twente, Faculty of Applied Physics
P.O. Box 217, 7500 AE Enschede, The Netherlands
phone: +31 53 489 3167, fax: +31 53 489 2910
mail: A.Starikov@tn.utwente.nl

71 **Stepanyuk, Valeri**
Max-Planck-Institut für Mikrostrukturphysik,
Weinberg 2, 06120 Halle, Germany
phone: +49 345 5582-537, fax: +49 345 5582-765
mail: stepanyu@mpi-halle.de
contribution: C17 (p.19), P5 (p.24), P8 (p.25), P11 (p.27), P27 (p.35)

72 **Szunyogh, Laszlo**
Budapest University of Technology and Economics, Department of Theoretical Physics
Budafoki u't 8, 1521 Budapest, Hungary
phone: +36 1 463 4109, fax: +36 1 463 3567
mail: szunyogh@heisenberg.phy.bme.hu
contribution: C23 (p.22)

73 **Taillefumier, Mathieu**

Max-Planck-Institut für Mikrostrukturphysik,
Weinberg 2, 06120 Halle, Germany
phone: +49 345 5582-913, fax: +49 345 5582-765
mail: taillefu@mpi-halle.de
contribution: P30 (p.37)

74 **Talanana, Moland**
University of Twente, Faculty of Applied Physics
P.O. Box 217, 7500 AE Enschede, The Netherlands
phone: +31 53 4892624, fax: +31 53 4892910
mail: M.Talanana@tn.utwente.nl
contribution: P21 (p.30)

75 **Temmerman, Walter**
Daresbury Laboratory, Computational Science& Engineering Department
Daresbury, Warrington, Cheshire WA4 4AD, UK
phone: +44 1925 603227, fax: +44 1925 603634
mail: w.m.temmerman@dl.ac.uk
contribution: I5 (p.12), P15 (p.28), P17 (p.29)

76 **Turek, Ilja**
Academy of Sciences of the Czech Republic, Institute of Physics of Materials
Zizkowa 22, 61662 Brno, Czech Republic
fax: +420 5 412 12 301
mail: turek@drs.ipm.cz
contribution: C7 (p.14), C10 (p.15), P2 (p.23), P10 (p.26), P24 (p.32)

77 **Udvardi, Laszlo**
Budapest University of Technology and Economics, Institute of Physics
Bdafoki ut 8, 1521 Budapest, Hungary
fax: +36 1 4633567
mail: udvardi@bolyai.phy.bme.hu
contribution: C23 (p.22)

78 **Utsumi, Yasuhiro**
Max-Planck-Institut für Mikrostrukturphysik,
Weinberg 2, 06120 Halle, Germany
phone: +49-345 5582-968, fax: +49 345 5582-765
mail: utsumi@mpi-halle.de
contribution: P28 (p.35)

79 **Vlaic, Petru**
IPCMS, Groupe d'Étude des Máteriaux Métaliques
23, rue du Loess, 67034 Strasbourg, France
phone: +33 03.88.10.70.05
mail: Petru.Vlaic@ipcms.u-strasbg.fr

contribution: P24 (p.32), P25 (p.33)

80 **Weinberger, Peter**
TU Wien, Institut für Allgemeine Physik
Gumpendorfer Str. 1a, 1060 Wien, Austria
phone: +43 1 58801-15830, fax:
mail: pw@cms.tuwien.ac.at
contribution: C7 (p.14), C10 (p.15), C23 (p.22), P2 (p.23)

81 **Yavorsky, Bogdan**
Martin-Luther-Universität Halle-Wittenberg, Fachbereich Physik
06099 Halle, Germany
phone: +49 345 5525434, fax: +49 345 5525446
mail: yavorsky@physik.uni-halle.de
contribution: P12 (p.27)

82 **Zahn, Peter**
Martin-Luther-Universität Halle-Wittenberg, Fachbereich Physik
06099 Halle, Germany
phone: +49 345 5525434, fax: +49 345 5525446
mail: zahn@physik.uni-halle.de

83 **Zeller, Rudi**
Forschungszentrum Jülich GmbH, Institut für Festkörperforschung
52425 Jülich, Germany
phone: +49 2461 61 5192, fax: +49 2461 61 5192
mail: ru.zeller@fz-juelich.de
contribution: C12 (p.16), C22 (p.21), P23 (p.32), P26 (p.34), P31 (p.37)

84 **Zwierzycki, Maciej**
University of Twente, Faculty of Applied Physics
P.O. Box 217, 7500 AE Enschede, The Netherlands
phone: +31 53 489 1082, fax: +31 53 489 2910
mail: m.zwierzycki@tnw.utwente.nl
contribution: C18 (p.20), P21 (p.30)

4 News from the Research Network 'Psi-k f-electron' (RTN2)

4.1 First Annual Report of RTN 'Psi-k f-electron' (RTN2)

RTN Network Title	:	Ab-initio Computation of Electronic Properties of f-electron Materials.
Network Short Title	:	Psi-k f-electron
Co-ordinator	:	Axel Svane Department of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark
Network home page	:	http://www.phys.au.dk/˜svane/rtn.htm

Part A: Research Results

A.1.: Scientific Highlights

Methodological Developments

Several improvements of Dynamical Mean Field Theory methodology have been made in the first year. Within the Exact Muffin Tin Orbital method a charge and self-energy self-consistent spin-polarized T-matrix plus FLEX (SPTF) scheme has been implemented. [1] A continuous time, full-interaction vertex, multiorbital Quantum Monte Carlo scheme for fermions has been developed and first numerical tests completed. The QMC scheme has been generalized to allow for a non-diagonal and low-symmetry matrix form of the local temperature-dependent Green-function within the Nth order MTO method. [2] The extension of DMFT to clusters of correlated atoms has been implemented and tested. The ambitious GW+DMFT scheme has been formally developed and implementation is in progress. (Paris, Nijmegen, Rutgers and Uppsala teams)

A local version of the self-interaction corrected (L-SIC) local spin density approach has been developed. This is being tested for Ce and NiO. The L-SIC is implemented in the multiple scattering band theory and therefore the Green's function is easily evaluated. This allows to implement the CPA to treat not only substitutional disorder but also charge and spin disorder. While the full many-body interacting system with on-site Coulomb interactions can be described as a one-electron system in fluctuating charge and spin fields, we are presently engaged in developing the static approximation. Therefore, as a first approximation, the dynamics of the fluctuations are neglected, however still capturing an important part of the correlations which might be sufficient for many systems (Daresbury and Aarhus teams).

A new LDA+U scheme for intermediate localization has been checked with the LDA+DMFT for the transition from magnetic to non-magnetic ground state for correlated metallic systems. (Nijmegen team)

Pu and other actinides

The electronic structure of $PuO_{2\pm x}$ was studied using first-principles quantum mechanics, realized with the self-interaction corrected local spin density method. In the stoichiometric PuO_2 compound, Pu occurs in the Pu(IV) oxidation state, corresponding to a localized f^4 shell. If oxygen is introduced onto the octahedral interstitial site, the nearby Pu atoms turn into Pu(V) (f^3) by transferring electrons to the oxygen. Oxygen vacancies cause Pu(III) (f^5) to form by taking up electrons released by oxygen. At $T = 0$ the PuO_2 compound is stable with respect to free oxygen, but the delicate energy balance suggests the possible deterioration of the material during long-term storage [3] (Aarhus and Daresbury teams). The crystal fields in PuO_2 have been calculated (Uppsala team).

The electronic structure of the exotic superconducting compound $PuCoGa_5$ has been calculated and the pairing of itinerant Pu $5f$ electrons has been identified as the cause of superconductivity. (Dresden team, Uppsala team).

The spectral function of δ-Pu at high-temperature has been computed and compared with photoemission experiments. (Nijmegen, Uppsala and Rutgers teams)

The intricate U f-electron manifold in UPd_2Al_2 has been investigated within the SIC-LSD approach [4], as has magnetism of UO_2 (Århus and Daresbury teams).

Rare Earth and Actinide Surfaces

The interpretation of scanning tunneling spectroscopy (STS) data taken on U/W(110) surfaces was facilitated by ab-initio calculation. It is demonstrated by fully relativistic total energy calculations including full optimization of all lattice parameters that the prepared structure can be a hexagonal Uranium phase, stabilized by the substrate, as seen in LEED and STM. Further, local densities of states are found to compare well with scanning tunneling spectra. This gives evidence for the possibility to observe f-states with STS. (Dresden team).

The lattice parameter and valence stability of the surface of Sm was calculated and good agreement with experimental photoemission work was demonstrated. (Uppsala team).

Magnetism of Gd

The origin of the magneto crystalline anisotropy of hcp Gd has been subject to intense study. Several mechanism have been proposed, e.g. the mixing of higher multiplets into the otherwise spherically symmetric S-state, or the effect of relativity of the $5d$ valence band. The latter contribution has been shown to reproduce the experimental data with good accuracy. Based on Hartree-Fock theory the mixing in of high multiplet configurations to the $4f^7$ configuration is found to be very small.[5] (Uppsala team)

The spontaneous anisotropic magnetostriction of hcp Gd has been investigated within the LSDA and the LSDA+U approximations. As a rough model for the paramagnetic state with persisting $4f$ moments several static antiferromagnetic arrangements were considered. The calculated values of the spontaneous volume magnetostriction are in reasonable agreement with the experiment, but the sign of the anisotropic magnetostriction is wrong in the LSDA+U approach

(Dresden team).

Other rare-earth systems

Full geometry optimization of both lattice parameters and the internal atom positions in the crystal unit cell has been completed for a series of cerium compounds including CeS, Ce_2S_3 and Ce_3S_4. Comparisons with available experimental structural data show a level of agreement which is typical for DFT-GGA calculations, i.e. deviations between computed and experimental structural parameters in the range of a few percent. Initial results for optical excitations has been obtained with the LDA+U method. As expected, the energy of the f-bands is very sensitive to the U parameter. Therefore, current research efforts are addressing the issue of a physically meaningful and consistent determination of U (LeMans team).

Metallic Magnetism in $LaCrSb_3$ has been investigated. This system is a non-collinear ferromagnet with a spin reorientation at about 95 K. Coexistence of itinerant and localized spins at one and the same Cr site has been suggested to explain the experimental results. Strong arguments against this model have been presented on the basis of electronic structure calculations and re-evaluation of experimental information. (Dresden team)

The electronic structure and magnetic properties of compounds formed between f-electron materials and transition metals have revealed many intriguing properties, ranging from quenched orbital moments and electron states that are on the border between localized and delocalized. In addition these materials sometimes exhibit complex non-collinear magnetic interactions which have been studied theoretically for several of these systems. The agreement with experiment is good, and mechanisms that determine if a non-collinear or collinear magnetic coupling occurs have been identified. (Uppsala team)

A.2.: Joint Publications

1. L. Chioncel, L. Vitos, I. A. Abrikosov, J. Kollar, M. I. Katsnelson, and A. I. Lichtenstein *Ab initio electronic structure calculations of correlated systems: An EMTO-DMFT approach,* Phys. Rev. B 67, 235106 (2003) KUN and UU partners.
2. E. Pavarini, S. Biermann, A. Poteryaev, A. I. Lichtenstein, A. Georges, O.K. Andersen, *Mott transition and suppression of orbital fluctuations in orthorhombic* $3d^1$ *perovskites*, cond-mat/0309102 ENS-ULM and KUN partners.
3. L. Petit, A. Svane, W. M. Temmerman, and Z. Szotek, *First Principles Calculations of* $PuO_{2\pm x}$*,* Science, **301**, 498 (2003). UAA and CCLRC partners.
4. L. Petit, A. Svane, W. M. Temmerman, and Z. Szotek, *Ab-initio study of the localized/delocalized f-manifold in* UPd_2Al_3, Europhys. Lett. **62**, 391 (2003). UAA and CCLRC partners.
5. M.Colarieti-Tosti, S.Simak, R.Ahuja, O.Eriksson, L.Nordström and M.S.S.Brooks, *On the magnetic anisotropy of Gd metal* Phys. Rev. Lett. **91** 157201 (2003). UU with external team member ITU-Karlsruhe.
6. Z. Szotek, W. M. Temmerman, A. Svane, L. Petit, G. M. Stocks, and H. Winter, *Half-metallic transition metal oxides*, Proc. ICM 2003, Rome (submitted, 2003). UAA and CCLRC partners.

7. G. M. Stocks, W. M. Temmerman, Z. Szotek, A. Svane, D. Ködderitzsch, and H. Winter, *LSD-SIC studies of localization in the 4d-transition metal oxides* $SrRu_2O_4$ *and* $CaRu_2O_4$. (accepted, 2003). UAA and CCLRC partners.

8. Z. Szotek, W. M. Temmerman, A. Svane, L. Petit, G. M. Stocks, and H. Winter, *Ab initio Study of Charge Order in* Fe_3O_4, Phys. Rev. B. **68**, 054415 (2003). UAA and CCLRC partners.

9. Z. Szotek, W. M. Temmerman, A. Svane, L. Petit, and H. Winter, *Electronic Structure of half-metallic double perovskites*, Phys. Rev. B. **68**, 104411 (2003). UAA and CCLRC partners.

10. Z. Szotek, W. M. Temmerman, D. Ködderitzsch, W. Hergert, A. Svane, L. Petit, G. M. Stocks, and H. Winter, *SIC-LSD Description of Half-metallic transition metal oxides*, Summer School, Poznan, Proc. (submitted, 2003). UAA and CCLRC partners.

11. S. Pankov, S. Florens, A. Georges, G. Kotliar, S. Sachdev, *Non-Fermi liquid behavior from two-dimensional antiferromagnetic fluctuations: a renormalization-group and large-N analysis*, Phys. Rev. B. **xx** , yyyyyy (2003) ENS-ULM and RUTGERS partners.

12. D. W. Boukhvalov, E. Z. Kurmaev, A. Moewes, D. A. Zatsepin, V. M. Cherkashenko, S. N. Nemnonov, L. D. Finkelstein, Yu. M. Yarmoshenko, M. Neumann, V. V. Dobrovitski, M. I. Katsnelson, A. Lichtenstein, B. N. Harmon and P. Kögerler, *Electronic Structure of magnetic molecules* V_{15}*: LSDA+U calculations, x-ray emissions, and photoelectron spectra*, Phys. Rev. B **67**, 134408 (2003) KUN and UU partners.

13. T. Giamarchi, S. Biermann, A. Georges, A. Lichtenstein, *Dimensional Crossover and Deconfinement in Bechgaard Salts*, Proceedings of the International Symposium on Crystalline Organic Metals, Superconductors and Ferromagnets, Port-Bourgenay, France, 2003 – Journal de Physique IV, in press (2003). ENS-ULM and KUN partners.

Part B: Comparison with the Joint Programme of Work

B.1.+2.: Research Objectives and Method

The research objectives of the Network are theoretical investigations of the physical properties of materials containing atoms with incompletely filled f-shells.
The research methodology of the Network is that of *ab-initio* quantum mechanics based upon Density Functional Theory and enhanced with the Dynamical Mean Field Theory capability.

B.3.: Workplan

- **Schedule and Milestones**

The Work Program comprises the following sub-projects: Milestones for first results of each of the subtasks are given in bold. Comments on the last years progress are given.

1. **Dynamical Mean Field Theory in the Linear Muffin-Tin-Orbital method** (Task leader: ENS-ULM, collaborating with UAA, CCLRC, RUTGERS, KUN and UU)

1.1 Impurity solvers.

1.1.A IPT (**12 months** DONE) Implementation of self-consistent (in charge density and local self-energy (DMFT)) spin-polarized T-matrix plus FLEX (SPTF) scheme has been completed within the Exact MTO-method

1.1.B Extended NCA and other new impurity solvers. (**24 months**)

1.1.C QMC (**18 months**) Continuous time, full-interaction vertex, multiorbital QMC scheme for fermions has been developed. First applications (5-orbital model) done. This QMC-scheme will be used for calculation of Ce on Ag(111) surface (task 3.3). QMC with NMTO implementation of Hamiltonian has been tested (generalized QMC scheme for non-diagonal, low-symmetry matrix form of the local temperature-dependent Green-function within NMTO-TB) This scheme will be useful for complex d- and f-compounds. First application for transition-metal perovskite.

1.2 Green's Functions.

1.2.A $T = 0$, full self-energy (**24 months**) A significant development of the DMFT methodology is towards the integration with the GW-approximation, which combines the DMFT treatment of strongly correlated degrees of freedom with approximate (random-phase-approximation) treatment of screening of the nearly-free electron degrees of freedom. This rather ambitious development most likely will outdate the IPT and extended NCA impurity solvers in terms of accuracy. On the other hand the technical problems in connection with generating a full GW-DMFT self-energy are large, and a realistic milestone is more likely 36 months. A second new development is that of Cluster-DMFT. Within this scheme nonlocal spin and orbital fluctuations can be investigated. First applications for the metal-insulator transition in the systems with strong pair-bonding structure (Ti_2O_3, VO_2 etc.).

1.2.B Finite T (**36 months**) Awaits the completion of 1.2.A.

1.3 Combine 1.1 with 1.2 (**24 months**) In progress.

1.4 Include phonons in 1.3. (**48 months**) First effects of phonons included in discussion of δ-Pu.

2. **Actinides:** (Task leader: UU, collaborating with UAA, CCLRC, RUTGERS, IFW-DRESDEN, KUN, and ENS-ULM)

2.1 **Phase Diagram of Pu** (sub-task leader: RUTGERS)

2.1.A δ-phase ($T = 0$: **18 months**, finite T: **48 months**) Several attacks on the Pu δ-phase have been made by network partners ($T = 0$). Spectral function for high-temperature have been compared with photoemission experiments. Start of calculations of δ-Pu with QMC in LDA+DMFT scheme.

2.1.B ϵ-phase ($T = 0$: **18 months**, finite T: **48 months**)

2.1.C α-phase (**36 months**)

  - 2.1.D Pu compounds (**36 months**) The superconducting $\mathrm{PuCoGa_5}$ compound has attracted quite extensive interest in the past year, and several Network contributions have been published in the past year. Also, the Pu valency and crystal field splitting in the $\mathrm{PuO_2}$ compound has been investigated.

  - 2.2 Am and compounds. (**24 months**, finite T: **48 months**) Disordered local moments theory of actinide metals has been investigated and a paper completed.
  - 2.3 Np (**24 months**) and compounds.
  - 2.4 U (**24 months**) and compounds. The U valency in $\mathrm{UX_3}$ compounds has been investigated, revealing a shift in the series X=Rh, Pd, Pt, Au. Magnetism of $\mathrm{UO_2}$ has been the subject of a study. U adlayers on W surfaces have been studied (also part of task 4).

3. **Rare-earth systems:** (Task leader: KUN, collaborating with UAA, CCLRC, RUTGERS, IFW-DRESDEN, ENS-ULM, UU and MD)
   - 3.1 Ce (**24 months**, finite T: **48 months**) Improved and simplified SIC methodology has been developed and tested on the $T = 0$ $\alpha \rightarrow \gamma$ phase transition of Ce.
   - 3.2 Optical properties of pigments such as $\mathrm{Ce_2S_3}$ (**36 months**) (sub-task leader: MD) Geometry optimizations for CeS, $\mathrm{Ce_2S_3}$ and $\mathrm{Ce_3S_4}$ compounds have been completed. Initial results for optical excitations has been obtained with the LDA+U method.
   - 3.3 Ce on Ag(111) (**24 months**) Methodology development in progress.
   - 3.4 SmS and TmSe (**36 months**) (sub-task leader: UAA) SmX compounds and their isostructural high pressure phase transitions have been studied. A paper is in preparation.
   - 3.5 rare-earths in high-T_c superconductors (**18 months**) (sub-task leader: CCLRC) Several RE-$\mathrm{Ba_2Cu_3O_{6+x}}$ compounds have been studied, with rather inconclusive results due to high sensitivity to structural details.
   - 3.6 luminescence (**48 months**)
   - 3.7 magneto-caloric materials (**36 months**) (sub-task leader: UU)

4. **Surface magnetism:** (Task leader: IFW-DRESDEN, collaborating with CCLRC, UU and MD)
   - 4.1 Gd(0001) and related systems (**18 months**) In a study of the Sm(0001) surface the Sm atoms have been shown to exhibit divalency, as opposed to the trivalency of bulk Sm. Magnetic anisotropy has been investigated by LSD and LDA+U methods in bulk (hcp) Gd.
   - 4.2 non-collinear moments (**30 months**)

5. **Workshops:** (Task leaders: UAA and CCLRC, involves all partners)
   - 5.1 5 Annual progress workshop (**0-1, 12, 24, 36 and 48 months**) A Euresco conference was organised by CCLRS and ENS-ULM partners cosponsored by the Network in August 2003. The first annual meeting is scheduled for November 2003 in Aarhus.

5.2 DFT and DMFT tutorial workshop (**18 months**) DMFT tutorial workshop was organized in Daresbury in June 2003.

5.3 Industry workshop (**36 months**) (sub-task leader: MD)

5.4 Hands-on course (**48 months**) FPLO hands-on-course was organized in Dresden in March 2003.

6. **Newsletter and Home page:** (Task leader: CCLRC, involves all partners) 6 Newsletters have been published (October, December 2002, February, April, June, August 2003).

B.4.: Organisation and Management

B.4.1. Management.

The Network's scientific programme is broken down into sub-tasks each of which is managed by a board of two or more node leaders, coordinated through the Network Coordinator and the Network Secretary. The major part of network management happens through frequent email contact. Secondments and mini-meetings between two or more network partners, including post-docs, is used to plan the near future scientific research programme of the sub-tasks. Major organisatorial planning is usually done in connection with Network meetings. First major coordination meeting was held in conjunction with the Karlsruhe workshop, April 2003. The first meeting of the entire Network board will take place in Aarhus in November 2003 and will review the progress sofar in particular concerning recruitment of young researchers. Network announcements, including abstracts of submitted papers, vacant positions and network meetings are announced in the bimonthly Psi-k newsletter, which currently is distributed to more than 1000 email addresses worldwide. The dissemination of scientific results is taking place through publication in research journals as well as presentations at conferences.

B.4.2. Main network meetings.

FPLO hands-on-course, Dresden March 28-April 1, 2003. 38 attendees, including the following External Experts, who gave seminars on their experience with this software package in research projects:
M. Divis (Prague) on "WIEN and FPLO: a comparison",
P. Novak (Prague) on "lo-WIEN and R-FPLO: a comparison",
S. Cottenier (Leuven, Belgium) on "Miscellaneous thoughts from an occasional FPLO-user"

DMFT tutorial session, Daresbury June 5-6, 2003. 24 attendees. A. Georges and S. Biermann from partner ENS-ULM gave a series of tutorials on the basics of DMFT for newcomers in the field.

Ab initio Many-Body Theory for Correlated Electron Systems, Trieste 25-29 August, 2003. This Euresco conference was organized by the CCLRC and ENS-ULM partners and cosponsored by the Network. 117 attendees.

A bilateral mini-meeting between the ENS-ULM and KUN partners in Paris included an External Expert, E. Pavarini, Pavia, Italy, who presented her implementation and investigations with the DMFT method in a seminar.

The Karlsruhe external team member of the UU partner arranged a meeting on ’f-electron’, which had a substantial number of Network people included.

The autumn 2002 research workshop at Santa Barbara, US, *Realistic Theories of Correlated Electron Materials* was organised by the RUTGERS, KUN and ENS-ULM nodes, but did not involve Network finance.

4.2 Reports on RTN2 Workshops

4.2.1 Report on RTN2 Workshop on "The Physics of f-electron Solids"

RTN Workshop:
The Physics of f-electron Solids

November 6-7, 2003, Aarhus, Denmark

INSTITUT FOR FYSIK OG ASTRONOMI
IFA

SOLIDUM PETIT IN PROFUNDIS · UNIVERSITAS ARHUSIENSIS

This workshop was the first annual workshop of the RTN2 network 'Psi-k f-electron'. All network nodes with the exception of the US partner at Rutgers were represented. The six young researchers currently employed under the network contract all attended the workshop thus having an opportunity to present themselves to the network. Two of the young researchers gave talks on their research projects.

This workshop brought together 35 researchers in the area of f-electron materials. A lively debate evolved around central issues of high current interest, including the new Pu based superconducting compounds, $PuCoGa_5$ and $PuCoRh_5$, the dual (localized and delocalized) character of f-electrons in U compounds, the oxidation of Ce and Pu oxides, and magnetic structures of f-electron materials.

Several talks presented new theoretical developments, including the merge of GW and Dynamical Mean Field Theory, DMFT and exact diagonalizations, DMFT with Quantum Monte Carlo, the local self-interaction-correction method and improved (screened) exchange interaction. Finally, a talk reviewed the industrial aspects of f-electron materials and the use of f-electron dopants as the 'vitamins' of materials design.

Programme:

The Physics of f-electron Solids

November 6-7, 2003, Aarhus, Denmark

Thursday 6/11:

	Chairman: A. Svane.
9:00-9:35	B. Johansson, *on Theory*
9:35-10:10	F. Wastin, *Experimental progresses on* $PuCoGa_5$ *and related compounds*
10:10-10:30	Coffee
	Chairman: M. Richter.
10:30-11:05	I. Opahle, *Electronic structure of* $PuCoGa_5$ *and related compounds*
11:05-11:40	J.-C. Griveau, *Actinides Superconductors Under Pressure*
11:40-12:15	O. Eriksson, *Electronic structure of* δ*-Pu and* $PuCoGa_5$*; similarities from photoemission data*
12:30-13:30	Lunch
	Chairman: A. Lichtenstein.
13:30-14:05	M. Brooks, *Screened Exchange Interactions in Actinides*
14:05-14:40	G. Zwicknagl, *Partial localization, dual nature of 5f electrons and heavy fermions in U compounds*
14:40-15:05	M. Colarieti-Tosti, *Valence Stability in* UPd_3 *and* UPt_3
15:05-15:30	N. Skorodumova, *Catalysis with Cerium Oxides*
15:30-15:50	Coffee
	Chairman: E. Wimmer.
15:50-16:25	L. Petit, *SIC-LSD theory of Actinides*
16:25-17:00	M. Lüders, *Local Self-interaction correction in the KKR method*
18:30-	Dinner: PLAZA hotel

Friday 7/11:

9:00-10:00 RTN Board meeting

Chairman: A. Svane.
10:00-10:35 E. Wimmer, *Industrial Aspects in the Use of f-electron Solids*

10:35-10:50 Coffee

Chairman: W. Temmerman.
10:50-11:25 S. Biermann, *Electronic structure of correlated materials – ”LDA+DMFT” and beyond*
11:25-12:00 K. Held, *The Mott-Hubbard transition in* V_2O_3 *and the Ce volume collapse: LDA+DMFT and experiments*
12:00-12:35 A. Lichtenstein, *Efficient LDA+DMFT calculations for f-electron systems*

12:35-13:30 Lunch

Chairman: O. Eriksson.
13:30-14:05 M. Richter, *Surface geometry and electronic structure of U/W(110)*
14:05-14:40 L. Nordström, *Magnetic structure of the heavy rare earth metals*
14:40-15:15 R. Caciuffo, *Spherical neutron polarimetry and anisotropic magnetic excitations in* UO_2

15:15-15:45 Coffee

Chairman: A. Svane.
15:45-16:20 R. Laskowski, *Non-collinear magnetism and EFG in* UO_2
16:20-16:55 G. Santi, *Coexistence of ferromagnetism and superconductivity in* $ZrZn_2$

The Physics of f-electron Solids

November 6-7, 2003, Aarhus, Denmark

ABSTRACTS

on Theory

B. Johansson *Uppsala University, Sweden*

Experimental progresses on $\mathrm{PuCoGa_5}$ and related compounds

F. Wastin, P. Boulet, E. Colineau, J. -C. Griveau, P. Javorsky, J. Rebizant and G.H. Lander *ITU Karlsruhe, Germany*

The discovery of superconductivity in $\mathrm{PuCoGa_5}$ [1] raises large interest. This new superconductor is the first one to be reported with a transuranium element that, moreover, displays astonishingly high critical parameters ($T_c > 18$ K, $H_{c2} \sim 700$ kOe and $J_c > 10^4$ $\mathrm{Acm^{-2}}$). Theoretical calculations suggest that the electrons at EF have dominantly Pu $5f$ character, and therefore it may be concluded that the Cooper pairs are formed by the pairing of Pu $5f$-electrons [2,3]. Further investigations of Pu compounds have revealed that the isostructural $\mathrm{PuRhGa_5}$ compound is also a superconductor [4] ($T_c \sim 8.7$ K and $H_{c2} > 200$ kOe). The crucial question is, in which framework should the superconductivity of these systems be placed? Two experimental approaches have been considered at ITU. First the isostructural Np and Am compounds have been investigated. Second, $\mathrm{Pu(Co_{1-x}Rh_x)Ga_5}$ solid solutions have been synthesised and their physical properties studied. In this paper we will review the experimental results obtained and propose an empirical comparison of these systems with their Ce-analogues.

[1] J.L. Sarrao et al., Nature **420**, 297 (2002)

[2] I. Opahle and P.M. Oppeneer, Phys. Rev. Lett. **90**, 157001 (2003)

[3] T. Maehira et al., Phys. Rev. Lett. **90**, 207007 (2003)

[4] F. Wastin et al., J. Phys. Condens Matter **15**, S2279-S2285(2003)

Electronic structure of $PuCoGa_5$ and related compounds

I. Opahle and P. M. Oppeneer *IFW Dresden, Germany*

On the basis of electronic structure calculations we identify the superconductivity in the novel, high-temperature superconductor $PuCoGa_5$ (T_c=18.5 K) to be caused by the pairing of Pu $5f$ electrons. The results have been obtained with the relativistic (4-component) version of the full-potential local-orbital method (RFPLO) using the local density approximation (LDA). Assuming delocalized Pu $5f$ states we compute theoretical crystallographic constants very near to the experimental ones, and the calculated specific heat coefficient compares reasonably to the measured coefficient. The theoretical Fermi surface is quasi-two-dimensional and the material appears to be close to a magnetic phase instability.

Actinides Superconductors Under Pressure

J. -C. Griveau, P. Boulet, F. Wastin, J. Rebizant, and G. H. Lander
ITU Karlsruhe, Germany
G. Kotliar, *Rutgers, USA*

Bulk properties of Actinides and more particularly, of the Transuranium compounds (Np, Pu, Am...) are poorly known at low temperature and at high pressure. Here we report high pressure resistivity measurements on Americium metal down to 400 mK and under magnetic field and on the recently discovered superconductors $PuCoGa_5$ and $PuRhGa_5$ compounds. Americium is at the junction of heavy and light actinides. Although we should observe magnetic behaviour due to localised f electrons, americium metal presents non magnetic properties because of its $5f^6$ ground state ($J = 0$). Pressure effect leads to a transition from localised to delocalised state. This is also accompanied by several structural phase transitions in the 10-20 GPa pressure range [1]. It displays superconducting behaviour as a function of the pressure [2]. The evolution of T_c and H_c with p is complex and not yet explained. The recently discovered plutonium based superconductors $PuCoGa_5$ and $PuRhGa_5$ [3, 4] present very surprising properties. The values of T_c (18.5 K and 8.5 K, respectively) and H_{c2} (73 T and 23 T, respectively) exceed that of any known $5f$-superconductors. Pressure studies of these compounds show that the pairing mechanism is not strongly pressure dependent. The stabilisation of the superconducting state suggested by the increase of T_c opposes the sensitivity of unconventional superconducting states in f-electron heavy fermion materials. Recent electronic structure calculations [5] suggest that the pairing of plutonium $5f$ electrons can be responsible for the superconductivity. All these recent results indicate that transuranium compounds studies present a huge interest in the comprehension and models validation for the $5f$ systems and especially for superconductivity.

[1] S. Heathman et al., Phys. Rev. Lett. **85** (2000) 2961

[2] P. Link et al., J. Alloys Comp. **213** (1994) 148

[3] J.L. Sarrao et al., Nature **420** (2002) 297

[4] F. Wastin et al., J. Phys.: Condens. Matter **28** (2003) 2279

[5] I. Opahle et al., Phys. Rev. Lett. **90**, 157001 (2003)

Electronic structure of δ-Pu and $PuCoGa_5$; similarities from photoemission data

O. Eriksson *Uppsala University, Sweden*

Screened Exchange Interactions in Actinides

M. S. S. Brooks *ITU Karlsruhe, Germany*

An approximate orbital dependent treatment of exchange is used to replace the local spin density approximation. The exchange integrals are calculated for a screened Coulomb interaction. We report application of this approximation to US and UFe_2.

For US the measured magnetic amplitude and total magnetic moment are reproduced almost exactly - the calculated orbital and spin moments of 1.25 and -2.92 at the uranium site being somewhat less than in previously published results.

For UFe_2 the calculated total magnetic moment is $1.4\mu_B$/f.u. and almost entirely due to an Fe moment of $0.7\mu_B$. The small uranium moment consists of spin and orbital moments of $-0.19\mu_B$ and $0.17\mu_B$, respectively. The calculated magnetic amplitude is in excellent agreement with the results of neutron diffraction experiments. The calculated orbital contribution to the Fe moment of $0.1\mu_B$ is one order of magnitude larger than measured.

Partial localization, dual nature of 5f electrons and heavy fermions in U compounds

G. Zwicknagl *TU Braunschweig, Germany*

There is growing evidence that actinide ions may have localized as well as delocalized 5f electrons. These observations form the basis of the dual model which provides a microscopic theory for the heavy quasiparticles in U compounds. In the present talk, I shall present results for the Fermi surface and effective masses in U-based heavy fermion compounds. In addition, I shall show how the dual character of the 5f electrons may arise from the interplay between (effective) hopping and Hund's rule correlations.

Valence Stability in UPd_3 and UPt_3

M. Colarieti Tosti *Uppsala University, Sweden*

We have calculated the electronic structure of UPd_3 and UPt_3 when the occupation number for the U 5f-orbitals is constrained to $n = 1, 2, 3$. Combining these results with experimental data for the atomic $f \rightarrow d$ promotion energies of Uwe have estimated that the energetically most favourable configuration is obtained for $n = 1$ in UPt_3 and $n = 2$ in UPd_3. The transistion pressure to the f^1 configuration has been calculated for UPd_3.

Cerium oxides from first principles

N. Skorodumova *Uppsala University, Sweden*

The ability of ceria to store, transport and release oxygen is of great importance in a range of clean-energy technologies from catalytic converters to solid-state fuel cells. This property of ceria derives from its ability to undergo a reversible transition between two different oxidation states: CeO2 and Ce2O3, with very different oxygen stoichiometries. We show that it is possible to describe the ground state and magnetic properties of both oxides within LDA(GGA) approximations by treating the 4f-state of Ce as a part of the inert core in Ce2O3 and as a valence, band-like, state in CeO2. Using this approach the oxygen vacancy formation energy in ceria have been calculated for different local environments. Based on our results we show that the reversible CeO2 - Ce2O3 reduction transition associated with oxygen vacancy formation and migration is directly coupled with the quantum process of electron localization.

SIC-LSD theory of Actinides

L. Petit, A. Svane, *University of Aarhus, Denmark*
W. M. Temmerman, Z. Szotek *Daresbury, UK*

The electronic structure of actinide compounds is studied using first-principles quantum mechanics, realized with the self-interaction-corrected(SIC) local spin density (LSD) approximation. This method allows for the description of actinide ions, with some f-electrons localized in atomic-like orbitals, while other f-degrees of freedom are forming hybridized bands. Apart from UPd_2Al_3, where we find coexisting localized and delocalized f-electrons, we show results for UX_3 (X=Rh, Pd, Pt, and Au) and PuO_2, where we observe f-electron delocalization under pressure and oxidation, respectively.

Local Self-interaction correction in the KKR method

A. Ernst[1], **M. Lüders**[2], D. Ködderitzsch[1], 2, Z. Szotek[2], A. Svane[3], B. L. Györffy[4], W. Temmerman[2] [1]*Halle, Germany,* [2]*Daresbury, UK,* [3]*Aarhus, Denmark,* [4]*Bristol, UK.*

Some problems of the local spin-density (LSD) approximation when applied to *d*- or *f*-electron systems are related to the spurious self-interaction of the LSD. It has already been demonstrated that these shortcomings can be largely remedied by applying the so called self-interaction correction (SIC) to the LSD. However, traditional LSD-SIC calculations are computationally very demanding, and applications to alloys, for instance, are very difficult.

Here we will propose a simplified version of LSD-SIC, based on the multiple scattering formalism, which uses a local self-interaction correction, and show how it can be implemented in the KKR method. This new SIC method, naturally, lends itself to a combination with the coherent potential approximation (CPA), which facilitates applications of the SIC to alloys.

As a first demonstration of the method, we study the well-known α-γ transition of Ce, where we also show how the SIC operates in terms of multiple scattering theory.

Industrial Aspects in the Use of f-electron Solids

E. Wimmer *Materials Design, Le Mans, France*

Among the various industrial applications of solids with f-electrons, the optical properties of compounds containing rare earth elements are particularly intriguing and thus will be the focus of this paper. For example, rare earth elements are used to create beautifully colored glasses, Eu doped barium aluminum magnesium oxides (BAM) are widely used in lighting systems, Y_2O_2S with Eu is applied as red luminophor in cathode ray tube (CRT) displays, and Nd is used in lasers. A recent application of the optical properties of rare earth compounds has been driven by the search of environmentally (i.e. non-toxic) high performance inorganic pigments. In this context, cerium sulfide has been introduced as a red pigment under the name Neolor®, which replaces the toxic red pigments based on cadmium and lead. The fascinating optical properties of these materials have their origin in the behavior of f-electrons in the field of neighboring atoms. Thus, systematic improvements and further innovations would be greatly facilitated, if one would have accurate descriptions of the relationships between chemical composition, crystal structures, and optical properties. This paper will discuss our current theoretical and computational capabilities in this field, it will point out the current shortcomings, and it will attempt to prioritize future research needs.

Electronic structure of correlated materials – "LDA+DMFT" and beyond

S. Biermann *Ecole Normale Superieure, Paris, France*

Dynamical mean field theory (DMFT) allows for a quantitative description of electronic correlations. Originally designed for the study of lattice models of correlated fermions, such as the Hubbard or Kondo models, DMFT has recently been combined with electronic structure techniques, in particular with density functional theory within the local density approximation (DFT-LDA). This "LDA+DMFT" approach provides a realistic description of the excitation spectra of materials with arbitrary strength of electronic correlations and has led to tremendous progress in our understanding of correlated materials.

After a short introduction to "LDA+DMFT", we will discuss its strong points as well as its shortcomings, and describe a recent attempt to go beyond heuristic combinations of band structure methods and DMFT. This approach, dubbed "GW+DMFT" combines ideas from the GW approximation and from extended dynamical mean field theory, and leads to a first-principles description of the screened Coulomb interaction within a non-perturbative scheme for local correlations. Results of a preliminary approximate implementation are presented for the electronic structure of ferromagnetic nickel [1].

[1] S.Biermann, F.Aryasetiawan, A.Georges, Phys. Rev. Lett. **90** 086402 (2003).

The Mott-Hubbard transition in V_2O_3 and the Ce volume collapse: LDA+DMFT and experiments

K. Held *MPI for Solid State Research, Stuttgart, Germany*

Conventional band structure calculations in the local density approximation (LDA) are highly successful for many materials, but miss important aspects of the physics and energetics of strongly correlated electron systems, such as transition metal oxides and f-electron systems displaying, e.g., Mott insulating and heavy quasiparticle behavior. In this respect, the LDA+DMFT approach which merges LDA with a modern many-body approach, the dynamical mean-field theory (DMFT) has proved to be a breakthrough for the realistic modeling of correlated materials. Depending on the strength of the electronic correlation, a LDA+DMFT calculation yields the weakly correlated LDA results, a strongly correlated metal, or a Mott insulator.

In this talk I present LDA+DMFT results for two prime examples of strongly correlated electron systems, i.e., the Mott-Hubbard metal-insulator transition in V_2O_3 [2] and the volume collapse transition in Ce [3]. Also discussed are the most recent developments in the photoemission spectroscopy of V_2O_3 [4].

I acknowledge support by the Emmy-Noether program of the DFG and thank the coauthors below for the joint work.

[1] For a pedagogical introduction to LDA+DMFT see:
K. Held, I. A. Nekrasov, G. Keller, V. Eyert, N. Blümer, A. K. McMahan, R. T. Scalettar, T. Pruschke, V. I. Anisimov, and D. Vollhardt, "Realistic investigations of correlated electron systems with LDA+DMFT", Psi-k Newsletter #56, 65 (2003) [psi-k.dl.ac.uk/newsletters/News_56/Highlight_56.pdf].

[2] K. Held, G. Keller, V. Eyert, V. I. Anisimov, and D. Vollhardt, Phys. Rev. Lett. 86, 5345 (2001).

[3] K. Held, A. K. McMahan, and R. T. Scalettar, Phys. Rev. Lett. **87**, 276404 (2001); Phys. Rev. B **67**, 75108 (2003).

[4] S.-K. Mo, J. D. Denlinger, H.-D. Kim, J.-H. Park, J. W. Allen, A. Sekiyama, A. Yamasaki, K. Kadono, S. Suga, Y. Saitoh, T. Muro, P. Metcalf, G. Keller, K. Held, V. Eyert, V. I .Anisimov, and D. Vollhardt,

Phys. Rev. Lett. **90**, 186403 (2003); unpublished.

Efficient LDA+DMFT calculations for f-electron systems

A. Lichtenstein *University of Nijmegen, The Netherlands*

We analyzed different ways to go beyond the mean-field (LDA+U) approximation and include in the self-consistent manner effects of the spin- and charge-fluctuations in f-electron systems. Realistic dynamical mean field theory (LDA+DMFT), which takes into account a frequency dependence of the self energy, has been combined with the first-principles LMTO-TB scheme. A simplified version of the Exact-Diagonalization scheme as well as the Quantum Monte-Carlo method are generalized to the spin-polarized multi-orbital f-electron case. The accuracy and efficiency of proposed LDA+DMFT scheme will be discussed.

Surface geometry and electronic structure of U/W(110)

M. Richter *IFW Dresden, Germany*

Evidence is provided for the formation of hexagonal Uranium films on tungsten (110) by combination of experimental techniques (LEED, STM) with density functional calculations. Hexagonal patterns are observed both in real space (STM) and reciprocal space (LEED) pictures taken on in-situ prepared thin Uranium films. The possible existence of a hexagonal phase (stabilized by the substrate) is confirmed by fully relativistic (4-component) LDA calculations using the FPLO (full-potential local-orbital) method that yield a total energy of hexagonal Uranium only slightly higher than that of the high-temperature gamma-phase. Electronic structure results for this geometry are in very good agreement with angle-resolved photoemission and scanning tunneling spectroscopy data.

Magnetic structure of the heavy rare earth metals

L. Nordström *Uppsala University, Sweden*

The magnetic structure of the hcp rare earth metals are calculated within DFT and the standard model. Results will be presented for the helical ordering in the right part of the series and the non-uniaxial anisotropy for ferromagnetic Gd. The validity of the standard model will be discussed, and what requirements are put on theories which try to go beyond it.

Spherical neutron polarimetry and anisotropic magnetic excitations in UO_2

R. Caciuffo *UniversitàPolitecnica delle Marche Ancona, Italy, and ITU Karlsruhe, Germany*

Spherical neutron-polarimetry has been applied to study the nature of magnetic fluctuations in the ordered phase of uranium dioxide. The rotation of the neutron polarisation at magnetic Bragg peaks is consistent with a transverse 3-k magnetic structure with [0 0 1] propagation vector. Unexpected, anomalous behaviour is exhibited by the lowest energy spin-wave branch for which no components of the transverse fluctuations are observed along the magnetic propagation vector.

Non collinear magnetism and Electric Field Gradient in UO_2

R. Laskowski *University of Aarhus, Denmark*

The magnetic structure of uranium dioxide is annalysed by means of linear augmented plane wave ab-initio calculations taking into account spin-orbit coupling and strong Coulomb correlation (using the LDA+U approach). The 1-**k** collinear anti-ferromagnetic type-I structure and the non-collinear anti-ferromagnetic 2-**k** and 3-**k** orderings have been tested. By a comparison of the calculated and experimental uranium electric field gradients the 1-**k** and 2-**k** structures can be excluded. It is shown that the measured EFG can be achieved only for the 3-**k** by allowing a deformation of the oxygen cage.

Coexistence of ferromagnetism and superconductivity in the d-electron compound ZrZn2

G. Santi *University of Aarhus, Denmark*

The weak ferromagnetism of ZrZn2 has made it the focus of much attention in the beginning of the 80s. In some respect, this was unexpected since none of its elemental constituents are magnetic (but both are superconducting). At the time, it had been conjectured that the longitudinal spin-fluctuations could lead to spin-triplet p-wave superconductivity. In spite of that, no trace of superconductivity was found until very recently with the observation of the coexistence of ferromagnetism and superconductivity [1]. I will present here the results from our ab-initio electronic structure calculations using the LMTO method within the local spin density approximation (LSDA) [2]. The excellent agreement found between the calculated Fermi surface and recent dHvA frequencies [3], as well as momentum densities from positron annihilation indicates that LSDA is well suited for this material. From our electronic structure, we calculated the generalised susceptibilities in order to investigate the viability of longitudinal spin-fluctuation-induced spin-triplet supercon- ductivity in the ferromagnetic state. We found a critical temperature, Tc, of the order of 1 K. We also found that in spite of an expected strong calculated electron-phonon coupling (ph = 0.7), the spin fluctuations are so strong that they should prevent the onset of conventional s-wave superconductivity.

[1] C. Pfleiderer, M. Uhlarz, S. M. Hayden, R. Vollmer, H. V. Lohneysen, N. R. Bernhoeft and G. G. Lonzarich, Nature 412, 58 (2001).
[2] G. Santi, S. B. Dugdale and T. Jarlborg, Phys. Rev. Lett. 87, 247004 (2001)
[3] S. J. C. Yates, G. Santi, S. M. Hayden, P. J. Meeson and S. B. Dugdale, Phys. Rev. Lett. 90, 057003 (2003)

The Physics of f-electron Solids

November 6-7, 2003, Aarhus, Denmark

Participants:

A. Svane, Aarhus, Denmark
W. M. Temmerman, Daresbury, UK
Z. Szotek, Daresbury, UK
M. Lüders, Daresbury, UK

D. Ködderitzsch, Daresbury, UK
N. E. Christensen, Aarhus, Denmark
G. R. Santi, Aarhus, Denmark
R. Laskowski, Aarhus, Denmark
F. Tasnadi, Dresden, Germany
I. Opahle, Dresden, Germany
M. Richter, Dresden, Germany
F. Wastin, Karlsruhe, Germany
M. S. S. Brooks, Karlsruhe, Germany
J.-C. Griveau, Karlsruhe, Germany
R. Caciuffo, Ancona, Italy
B. Johansson, Uppsala, Sweden
O. Eriksson, Uppsala, Sweden
L. Nordström, Uppsala, Sweden
M. Colarieti Tosti, Uppsala, Sweden
N. Skorodumova, Uppsala, Sweden
O. Bengone, Uppsala, Sweden
A. Grechnev, Uppsala, Sweden
S. Lebegue, Uppsala, Sweden
P. Andersson, Stokholm, Sweden
T. Burkert, Uppsala, Sweden
E. Wimmer, Le Mans, France
S. Biermann, Paris, France
K. Held, Stuttgart, Germany
G. S. Vaitheeswaran, Stuttgart, Germany
V. K. Kanchana, Stuttgart, Germany
A. Lichtenstein, Nijmegen, Holland
L. Pourovskii, Nijmegen, Holland
G. Zwicknagl, Braunschweig, Germany
L. Petit, Oak Ridge, USA
I. Hughes, Coventry, UK

5 News from the ESF Programme

"Towards Atomistic Materials Design"

5.1 Reports on ESF Workshops/Meetings/Conferences

5.1.1 Report on CECAM Workshop on Extended Systems

POSITION OPERATOR $\vec{r}$ IN EXTENDED SYSTEMS WITHIN DFT AND HF

CECAM, Lyon, France, September 29th – October 1st, 2003

Sponsors:

- ESF Ψ_k Programme "Towards Atomistic Materials Design"
- Centre Européen de Calcul Atomique et Moléculaire (CECAM)

Organisers:

- Michael Springborg, Physical Chemistry, University of Saarland, Saarbrücken, Germany
- Raffaele Resta, INFM DEMOCRITOS National Simulation Center, Trieste, Italy and Dipartimento di Fisica Teorica, Universitá di Trieste, Italy

Report

The quantum-mechanical operator $\vec{r}$ (i.e., the electronic position) is the key quantity for dealing with electric polarization in atomic, molecular, and solid-state physics. Whenever the electronic system is microscopic (i.e., an atom, a molecule, a cluster, ...) the treatment of $\vec{r}$ is a relatively trivial matter: its integral over the ground-state density provides by definition the dipole of the system, possible in the presence of a given external perturbation. However, even in this case, if the external perturbation is due to an externally applied electric field problems may occur: there is no bound state but instead resonances with shorter or longer lifetimes exist.

For extended systems (e.g., polymers and solids) the treatment of $\vec{r}$ has been a challenging issue over the years that has been addressed both by physicists (with the main emphasis on the calculation of polarization of solids in the absence or presence of an external electrostatic field) and by chemists (focusing mainly on linear and non-linear responses of polymers to external AC or DC fields). Each community has developed useful concepts and methods, and in order to improve the interaction between the two communities, Michael Springborg (Physical Chemistry, University of Saarland, Germany) and Raffaele Resta (Theoretical Physics, University of Trieste, Italy) organized a three-days workshop at CECAM, Lyon, France.

The workshop was attended by 32 scientists and contained 24 oral presentations. No poster presentation was organized; instead ample time was devoted to discussions (15 min. per presentation), which turned out to be extremely useful. Although there was a slight asymmetry between the number of chemists and that of physicists and despite the slightly different notations and concepts, it was clear that both communities could and did learn from each other. In some cases very similar concepts had been developed independently by the two communities, whereas in others the concepts of one community could be taken over by the other. Thus, in total the workshop did fulfil its purpose of bridging the gap between theoretical chemistry and theoretical physics.

The workshop opened with two overview lectures by the organizers on solids (Raffele Resta) and polymers (Michael Springborg) which was aimed at giving the non-expert an introduction to the two fields. Raffaele Resta emphasized the role of currents in defining a polarization and showed how the concept of Berry phases leads to an elegant way of calculating the polarization of an extended system. Michael Springborg discussed methods and results for the calculation of polarizabilities and hyperpolarizabilities of conjugated polymers, emphasizing that extrapolation of finite-chain results to the infinite chain may be problematic.

Subsequently, in 22 contributions different aspects of treating $\vec{r}$ in current research projects were reported. In some of those (Ivo Souza, Feliciano Giustino, Paolo Umari) the properties of crystalline materials exposed to an external electrostatic field were treated. The effects of the external field were included via an extra term in the Hamiltonian $\vec{E} \cdot \vec{P}$, where the polarization $\vec{P}$ was calculated using the Berry-phase approach. Since the calculation of the polarization can be done using Wannier functions, several presentations (Roberto Dovesi, Daniel Sebastiani, Ricardo Nunes, Marek Veithen) discussed how to construct Wannier functions, in some cases also in the presence of an external field.

One of the ultimate goal of theoretical calculations is to extend and explain experimental studies and, therefore, the calculation of experimentally accessible quantities (e.g., spectra) is of great importance. Several contributions at the workshop (Mebarek Alouani, Alberto Debernardi, Alfredo Pasquarello, Michele Lazzeri) emphasized this and in particular the calculation of Raman spectra (not only position but also intensities of the peaks) was found to be a considerable challenge since the calculation of the intensities in effect involves the calculation of non-linear responses of the system to external perturbations (electric fields and vibrations).

Other presentations focused on the role of electric currents either in approximate density functionals (Paul L. de Boeij, Oleg V. Gritsenko) where in particular extended quasi-one-dimensional systems pose a problems for presently applied approximate density functionals, or in the calculation of transport through a nanojunction (Andrea Dal Corso). Two different approaches for studying polymers in external fields were presented (Bernie Kirtman, Feng Long Gu); in one truly infinite, but periodic chains were studied, whereas in the other finite, not necessarily periodic chains were treated.

Several contributions focused on fundamental aspects of treating extended systems in external fields. In one (John E. Sipe) a formalism based on polarization and magnetization in contrast to electron density and current was presented, although it still is in its infancy, so that no applications could be presented. Alternatively, Michele Lazzeri presented a a method based on the density matrix that allowed for the direct inclusion of external fields. This method, as well as the method based on the $2n + 1$ theorem, presented by Marek Veithen, allow for the calculation both of polarization and polarizabilities as well as of hyperpolarizabilities, i.e., of non-linear responses.

Michel Rérat presented results of calculations using the CRYSTAL programs where an external electrostatic field was directly included by approximating it with a saw-tooth curve. Richard F. W. Bader emphasized that systems exposed to external fields are open systems and, therefore, that surface effects are important. He showed how any system, molecule or solid, could be decomposed into atoms and how, e.g., polarization could be written as contributions from the individual atoms when taking the surface terms (i.e., currents) into account. Finally, Fred Nastos discussed how some semiconductors respond nonlinearly by inducing a polarization when been exposed to strong and short laser pulses.

The wealth of the issues that were discussed shows that the treatment of $\vec{r}$ for extended systems is of central importance for many questions. Not only for the calculation of linear and non-linear responses of polymers and solids to external static or dynamic electric fields a proper treatment of $\vec{r}$ is required, but also in developing new and more accurate density functionals within density-functional theory and in characterizing materials, to name just two examples, problems related to the treatment of $\vec{r}$ occur. It shall therefore not surprise that how to treat $\vec{r}$ for extended systems is been discussed in many areas of physics and chemistry. Therefore, the workshop, where representatives from many different communities, each with their motivation for dealing with $\vec{r}$, were brought together was highly informative and productive for all participants.

Raffaele Resta Michael Springborg

List of participants:

1. Mebarek Alouani, IPCMS, UMR 7504 du CNRS, 23 rue du Loess, 67037 Strasbourg, France, EU (mea@ipcms.u-strasbg.fr)
2. Abu Assaduzzaman, Physical Chemistry, University of Saarland, 66123 Saarbrücken, Germany (abu@springborg.pc.uni-sb.de)
3. Richard F. W. Bader, Chemistry, McMaster University, Hamilton, Ont. L8S 4M1 Canada (bader@mcmaster.ca)
4. Agnese Callegari, INFM DEMOCRITOS National Simulation Center, Trieste, Italy and Dipartimento di Fisica Teorica, Universitá di Trieste, Italy (callegar@democritos.it)
5. Stephanie Chalmet, Theory Group, European Syncroton Facility (ESRF), F – 38043 Grenoble, France (stephanie.chalmet@esrf.fr)
6. Andrea Dal Corso, SISSA, Via Beirut 2/4, 34014 Trieste, Italy (dalcorso@sissa.it)
7. Paul L. de Boeij, Theoretical Chemistry, Materials Science Centre, Rijksuniversiteit Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands (p.l.de.boeij@chem.rug.nl)
8. Alberto Debernardi, Theoretical Physics, University of Trieste, Italy (alberto.debernardi@ts.infn.it)
9. Yi Dong, Physical Chemistry, University of Saarland, 66123 Saarbrücken, Germany (y.dong@mx.uni-saarland.de)
10. Roberto Dovesi, Dipartimento di Chimica IFM, Università di Torino, Via P. Giuria 7, 10125 Torino, Italy (roberto.dovesi@unito.it)
11. Feliciano Giustino, Institut de Théorie des Phénomènes Physiques (ITP), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland, and Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), CH-1015 Lausanne, Switzerland (feliciano.giustino@epfl.ch)

12. Xavier Gonze, Unité PCPM, Université Catholique de Louvain, Place Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium (gonze@pcpm.ucl.ac.be)
13. Oleg V. Gritsenko, Department of Physical and Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands (gritsenk@chem.vu.nl)
14. Feng Long Gu, Department of Chemistry, Graduate School of Science, Hiroshima University, Kagamiyama 1-3-1, Higashi-Hiroshima 739-8526, Japan; and Group, PRESTO, Japan Science and Technology Corporation (JST), Kawaguchi Center Building, Honcho 4-1-8, Kawaguchi, Saitama 332-0012, Japan (gu@th.chem.sci.hiroshima-u.ac.jp)
15. Jean-Pierre Julien, Laboratoire d'Etudes des Propriétés Electroniques des Solides, CNRS, Boîte Postale 166, F – 38042 Grenoble Cedex 9, France (jpjulien@grenoble.cnrs.fr)
16. Bernie Kirtman, Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA. 93106, USA (kirtman@chem.ucsb.edu)
17. Michele Lazzeri, Laboratoire de Minéralogie Cristallographie de Paris, 140 rue de Lourmel, 75015 Paris, France (michele.lazzeri@lmcp.jussieu.fr)
18. Fred Nastos, Department of Physics, University of Toronto, Toronto ON, M5S 1A7, Canada (nastos@physics.utoronto.ca)
19. Richardo Wagner Nunes, Departamento de Fisica - C.P. 702, Universidade Federal de Minas Gerais - UFMG, Av. Antonio Carlos 6627 - Belo Horizonte, MG - 30161-970 - Brasil (rwnunes@cedro.fisica.ufmg.br)
20. Alfredo Pasquarello, Institut de Théorie des Phénomènes Physiques (ITP), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland, and Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), CH-1015 Lausanne, Switzerland (alfredo.pasquarello@epfl.ch)
21. Michel Rérat, Laboratoire de Chimie Structurale, Unité Mixte de Recherche 5624 du CNRS, Université de Pau, F-64000 Pau, France (michel.rerat@univ-pau.fr)
22. Raffele Resta, INFM DEMOCRITOS National Simulation Center, Trieste, Italy and Dipartimento di Fisica Teorica, Universitá di Trieste, Italy (resta@ts.infn.it)
23. Daniel Sebastiani, Max-Planck-Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany (sebastia@mpip-mainz.mpg.de)
24. John E. Sipe, Department of Physics, University of Toronto, Toronto ON, M5S 1A7, Canada (sipe@physics.utoronto.ca)
25. Chris-Kriton Skylaris, Theory of Condensed Matter Group, Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK (cks22@cus.cam.ac.uk)
26. Ivo Souza, Department of Physics and Astronomy, Rutgers University, Piscataway, NJ, USA (ivo@physics.rutgers.edu)
27. Michael Springborg, Physical Chemistry, University of Saarland, 66123 Saarbrücken, Germany (m.springborg@mx.uni-saarland.de)
28. Michael Towler,Theory of Condensed Matter Group, Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK (mdt26@cam.ac.uk)
29. Vu Ngoc Tuoc, Physics, Hanoi University of Technology, Vietnam, and Theoretical Physics, University of Paderborn, Paderborn, Germany (vungoctuoc@phys.upb.de)
30. Paolo Umari, Institut de Théorie des Phénomènes Physiques (ITP), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland, and Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), CH-1015 Lausanne, Switzerland (paolo.umari@epfl.ch)

31. Marek Veithen, Département de Physique (B5), Université de Liège, Allée du 6 août 17,B-4000 Sart Tilman, Belgium (marek.veithen@ulg.ac.be)
32. Valentina Vetere, Theory Group, European Syncroton Facility (ESRF), F – 38043 Grenoble, France (vetere@esrf.fr)

Programme

Monday, September 29

		Overview Session
9:15	9:30	Opening
9:30	10:30	**R. Resta:** Position Operator, Dipole, and Polarization, in Extended Systems
10:30	11:30	Coffee Break
		Overview Session
11:30	12:30	**M. Springborg:** Linear and non-linear optical properties of polymers
12:30	14:30	Lunch
		Polarization
14:30	15:15	**J. E. Sipe:** Beyond $\mathbf{r}$: the search for polarization and magnetization fields
15:15	16:00	**I. Souza:** Dynamics of Berry-phase polarization in time-dependent electric fields
16:00	17:00	Coffee break
		Wannier functions
17:00	17:45	**R. Dovesi:** Wannier functions and Berry phase as alternative strategies in the calculation of Born charges, ferroelectric and piezoelectric properties in a localized basis set. The implementation and performance in the CRYSTAL code
17:45	18:30	**D. Sebastiani:** The explicit saw-tooth shaped position operator under periodic boundary conditions

Tuesday, September 30

		Density-functional theory
8:30	9:15	**P. L. de Boeij:** Current-Dependent Exchange-Correlation
9:15	10:00	**O. V. Gritsenko:** Ultra-non-local orbital structures and mechanisms of the field-counteracting effect in the Kohn-Sham exchange-correlation potential and kernel
10:00	11:00	Coffee Break
		Materials
11:00	11:45	**F. Giustino:** Dielectric permittivity of atomic-layer thick SiO_2 films or interlayers on silicon substrates
11:45	12:30	**M. Alouani:** All-electron GW RPA applied to the electronic structure of materials
12:30	14:30	Lunch
		Polymers
14:30	15:15	**B. Kirtman:** Static and Dynamic Electric Field Polarization in Quasilinear Polymers
15:15	16:00	**F. L. Gu:** Application of the elongation method to nonlinear optical properties of periodic and non-periodic systems
16:00	16:30	Coffee break
		Uniform fields
16:30	17:15	**M. Lazzeri:** High-order density-matrix perturbation theory
17:15	18:00	**P. Umari:** Ab Initio Molecular Dynamics in a Finite Homogeneous Electric Field
18:00	18:45	**A. Debernardi:** Ab initio simulation of uniform electric field spectroscopy

Wednesday, October 1

Polarization

8:30	9:15	**M. Rérat:** Calculation of the optical dielectric constant and non linear electric susceptibilities of periodic systems by the finite field perturbation method
9:15	10:00	**R. F. W. Bader:** Dielectric Polarisation: A Problem In The Physics Of An Open System

10:00	10:30	Coffee Break

Materials

10:30	11:15	**M. Veithen:** First-principles study of the electrooptic effect in ferroelectric oxides
11:15	12:00	**A. Pasquarello:** Infrared and Raman spectra of disordered oxides from first

12:00	13:00	Lunch

Currents and Transport

13:00	13:45	**A. Dal Corso:** Complex band structures and ballistic conductance with ultrasoft pseudo-potentials.
13:45	14:30	**F. Nastos:** Using the position operator to describe optically generated currents in unbiased semiconductors

14:30	15:00	Coffee break

Materials

15:00	15:40	**R. W. Nunes:** Berry-phase treatment of the homogeneous electric field perturbation in insulators
15:40	16:20	**M. Lazzeri:** First principles calculation of vibrational Raman spectra in large systems: signature of small rings in crystalline SiO_2 principles
16:20	17:00	**M. Veithen:** Localization tensor and Born effective charges in complex materials: application to ferroelectric oxides and skutterudites

Abstracts

(In alphabetic order of presenting author)

All-electron GW RPA applied to the electronic structure of materials

S. Lebègue, B. Arnaud[†], M. Alouani

IPCMS, UMR 7504 du CNRS, 23 rue du Loess, 67037 Strasbourg, France, EU,
[†]GMCM, campus de Beaulieu, 35042 Rennes Cedex, France, EU

`e-mail: mea@ipcms.u-strasbg.fr`

The GW approximation (GWA) based on the all-electron Projector-Augmented-Wave method (PAW) will be presented, where the self-energy is a product of the one-particle Green's function G and the dynamically screened interaction W, computed within the random phase approximation (RPA) instead of the plasmon-pole model. Two different ways of computing the self-energy will be reported. It is surprising, however, that the quasiparticle energies are found to be neither sensitive to the scheme used for decoupling the core and valence electrons nor to the different types of screening the Coulomb interaction (different plasmon-pole models versus the full RPA dielectric function). The method is successfully used to determine the quasiparticle energies of six semiconducting or insulating materials: Si, SiC, AlAs, InAs, NaH and KH. To illustrate the novelty of the method the real and imaginary part of the frequency-dependent self-energy together with the spectral function and life-times of the quasiparticles of silicon will be presented. Finally, we will show how the GWA together with the generalized-gradient approximation (GGA) were used to predict a pressure-induced simultaneous metal-insulator transition (MIT) and structural-phase transformation (from the B1 to B2 phase) in lithium hydride with about 1.3% volume collapse. The local density approximation (LDA) predicts that the MIT occurs before the structural phase transition, and the GGA alone predicts the simultaneous transitions but with a very small band gap of the B1 phase at the transition.

Dielectric Polarisation: A Problem In The Physics Of An Open System

R. F. W. Bader

McMaster University, Hamilton, Ont. L8S 4M1 Canada

`e-mail: bader@mcmaster.ca`

Properties of extended systems that depend upon the electronic position co-ordinate - electric or magnetic polarisation, permanent or induced - require the physics of an open system for their statement and solution. The treatment of an extended system as a collection of cells defined as bounded regions of real space, necessarily leads to the inclusion of a contribution to the polarisation arising from the transfer of charge across or from the flux in current through a cell's boundary, in addition to its internal polarisation. The measurement of electric polarisation in terms of the time integral of an induced current for a set of unit cells of arbitrary size within the crystal is shown to include a contribution from the flux in the position weighted current through its boundary. A crystal whose induced current is measured in a shorted capacitor is a macroscopic open system and in this case it is the flux in the position weighted current through the surfaces that the crystal shares with the plates of the capacitor that contributes to the measured polarisation. The present approach, stated in terms of the electron density and its current, challenges the philosophy underlying the "modern theory of polarisation" which contends that the polarisation of a dielectric can only be achieved by shifting the problem from one stated in terms of the electron density to one stated in terms of the phase of the wave function.

Complex band structures and ballistic conductance with ultrasoft pseudo-potentials.

Andrea Dal Corso

SISSA, Via Beirut 2/4, 34014 Trieste, Italy

`e-mail: dalcorso@sissa.it`

The approach proposed by Choi and Ihm (Phys. Rev. B **59**, 2267 (1999)) for calculating the ballistic conductance of open quantum systems is generalized to deal with magnetic transition metals described by ultrasoft pseudo-potentials. I shall discuss the complex band structures of periodic systems which are an important ingredient of the method presenting applications to polyethylene, bulk nickel and nickel nanowires. Finally, I shall focus on the ballistic conductance of cobalt and nickel monatomic wires with a magnetization reversal.

Work done in collaboration with A. Smogunov and E. Tosatti.

Current-Dependent Exchange-Correlation

P.L. de Boeij

Theoretical Chemistry, Materials Science Centre, Rijksuniversiteit Groningen,
Nijenborgh 4, 9747 AG Groningen, The Netherlands

`e-mail: p.l.de.boeij@chem.rug.nl`

Ordinary time-dependent density-functional theory has the potential to be a very versatile method to calculate various excitation and response properties of large molecular systems, like it is in small systems. However, the static axial polarizability of (conjugated) oligomers obtained within this method is greatly overestimated when using the standard adiabatic local density approximation (ALDA). This local approximation, but also the more advanced generalized gradient approximations, is unable to describe the highly nonlocal exchange and correlation effects found in these quasi-one-dimensional systems [1]. We have found a successful approach towards the solution of this longstanding problem by using time-dependent current-density-functional theory [2], in which we describe these ultranonlocal exchange-correlation effects within a local current description. Time-dependent current-density-functional theory uses the induced current density rather than the particle density as the fundamental quantity. This method provides a natural way to calculate response properties of extended systems like polymers and solids [3]. Due to the periodic boundary conditions used in describing such systems, the time-dependent density has to be supplemented with at least the uniform component of the time-dependent current (i.e. the induced macroscopic polarization) in order to fully characterize the dielectric response of the system to an external perturbation [4]. This holds even for the longitudinal (or density) response. For the Kohn-Sham system one therefore needs, next to the usual xc scalar potential, also a (uniform) xc vector potential to obtain the - in principle exact - dielectric response. In its simplest current dependence, this xc vector potential takes the form of a polarization functional [5]. Moreover, in order to correctly reproduce, in addition to the longitudinal response, also the transverse response of the true system within the Kohn-Sham approach, one needs in addition to the fully microscopic xc-contributions to the scalar potential also a fully microscopic description of the xc-contributions to the vector potential. Vignale and Kohn have derived such an xc-functional [6], which has been very successfully applied to the calculation of the axial polarizabilities of conjugated oligomers [2]. This local current functional was able to describe the highly nonlocal exchange and correlation effects that are found in these quasi-one-dimensional systems. For the prototype polyacetylene (Fig. 1) and many other systems excellent agreement with high level ab initio quantum chemical methods was obtained. We have now implemented the full Vignale-Kohn current-functional in the periodic structure response code for polymers and solids, so we are now able to include ultranonlocal exchange and correlation effects in the response properties of infinite chains and crystals. Time-dependent current-density-functional theory can be formulated in several ways, either to treat the induced density and current density as response to an external perturbation, or to treat the excitation frequencies and excitation eigenmodes directly as the roots of a Bethe-Salpeter-like equation. In finite systems the latter formulation makes use of the fact that excitations are all isolated poles of the true response function. For the long chains and for a set of benchmark molecules we have already obtained the excitation energies and oscillator strengths and we can explain the large reduction of the static polarizability by the way in which the VK-functional modifies these excitation properties. In extended systems, however, we have to deal with both isolated and continuous ranges of excitations. We have found that inclusion of a polarization-dependent xc-functional in the response formulation for solids leads to a better description of sharp features near the absorption edge [5] that are usually attributed to excitonic effects. Here we give the excitation formulation for molecules and extended systems, in which we explicitly include the treatment of the fully microscopic current-dependent xc-functional In this way we are now able to treat in an efficient way nonlocal xc-effects in the excitation spectra of molecules and extended systems. These nonlocal xc-effects, we believe, are needed to describe e.g. the isolated excitations inside the band-gap of semiconductors (bound excitons).

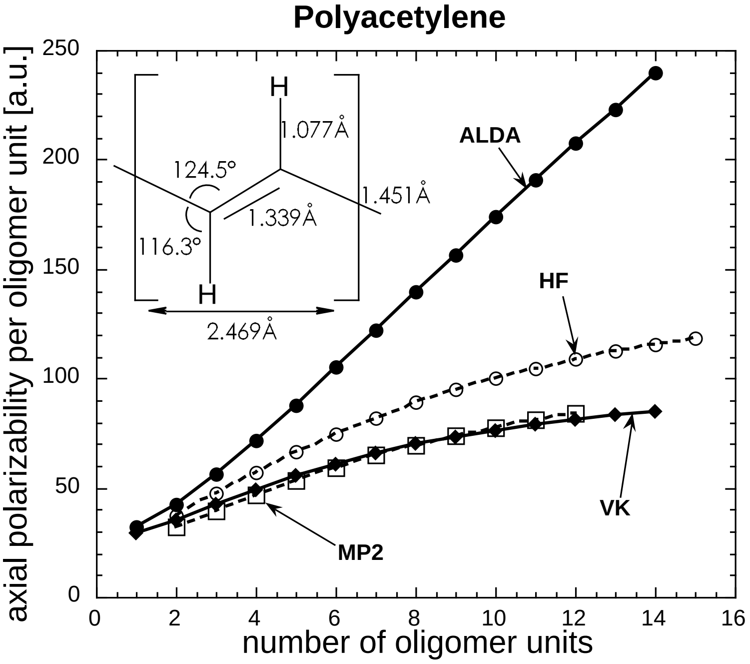

Figure 4: ALDA and VK static axial polarizability of polyacetylene compared with restricted Hartree-Fock [B. Kirtman et al, J. Chem. Phys. **102**, 5350 (1995)] and MP2 [T. T. Toto et al, Chem. Phys. Lett. **244**, 59 (1995)] results

References

1. S.J.A. van Gisbergen, P.R.T.Schipper, O.V.Gritsenko, E.J.Baerends, J.G.Snijders, B.Champagne, and B.Kirtman, Phys.Rev.Lett.83, 694 (1999).
2. M.van Faassen, P.L.de Boeij, R.van Leeuwen, J.A.Berger, J.G.Snijders, Phys.Rev.Lett. 88, 186401 (2002); J.Chem.Phys. 118, 1044 (2003).
3. F.Kootstra, P.L.de Boeij, J.G.Snijders, J.Chem.Phys.112, 6517 (2000); Phys.Rev.B 62, 7071 (2000).
4. X.Gonze, P.Ghosez, and R.W.Godby, Phys.Rev.Lett.74, 4035 (1995); 78, 294 (1997).
5. P.L.de Boeij, F.Kootstra, J.A.Berger, R.van Leeuwen, J.G.Snijders, J.Chem.Phys. 115, 1995 (2001).
6. G.Vignale, W. Kohn, Phys.Rec.Lett.77, 2037 (1996).

Ab initio simulation of uniform electric field spectroscopy

Alberto Debernardi

Theoretical Physics, University of Trieste, Italy

`e-mail: alberto.debernardi@ts.infn.it`

The response to uniform electric field in periodic solids is the main ingredient of to obtain ab initio spectra that can be directly compared with experimental data. We recall as the infra red spectra can be obtained by Car-Parrinello molecular dynamics for disordered systems or the $2n + 1$ theorem can be efficiently employed to obtain the coupling between an electric field and phonons.

Wannier functions and Berry phase as alternative strategies in the calculation of Born charges, ferroelectric and piezoelectric properties in a localized basis set. The implementation and performance in the CRYSTAL code

R. Dovesi[1] and C. M. Zicovich-Wilson[2]

[1] *Dipartimento di Chimica IFM, Università di Torino, Via P. Giuria 7, 10125 Torino, Italy*

[2] *Departamento de Física, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Col. Chamilpa, 62210 Cuernavaca (Morelos), Mexico*

`e-mail: roberto.dovesi@unito.it`

A computational scheme for the generation of well localized Wannier functions has been implemented [1] in the CRYSTAL03 code [2], that uses a local basis set and is now in distribution (www.crystal.unito.it); a generalization that ensures maximum localization has been implemented too, that marginally improves previous results [3]. Its efficiency in describing the chemical features of a family of crystalline oxides ranging from fully ionic to covalent is documented [4]. It can be used as an alternative to the Berry phase approach in the calculation of ferroelectricity [5], piezoelectricity [6,7] and the non-analytical part of the dynamical matrix [8]. Well localized Wannier functions are also used as a starting point for the evaluation of electron correlation in solids [9], according to schemes that are becoming popular for their efficiency in the molecular context [10].

References

1. C. Zicovich-Wilson, R. Dovesi, and V. Saunders, J. Chem. Phys. **115**, 9708 (2001).
2. V. R. Saunders, R. Dovesi, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, N. M. Harrison, K. Doll, B. Civalleri, I. J. Bush, P. D'Arco, and M. Llunell, *CRYSTAL03 User's Manual*, Università di Torino, Torino, 2003.
3. C. Zicovich-Wilson and R. Dovesi, In preparation (2003).
4. C. Zicovich-Wilson, A. Bert, C.Roetti, R. Dovesi, and V. Saunders, J. Chem. Phys. **116**, 1121 (2002).
5. P. Baranek, C. Zicovich-Wilson, C. Roetti, R. Orlando, and R. Dovesi, Phys. Rev. B **64**, 125102 (2001).
6. Y. Noel, C. Zicovich-Wilson, B. Civalleri, P. D'Arco, and R. Dovesi, Phys. Rev. B **65**, 014111 (2001).
7. M. Catti, Y. Noel, and R. Dovesi, J. Chem. Phys. Solids **in press**, (2003).
8. C. Z. Wilson, R. Orlando, C. Roetti, V. Saunders, and R. Dovesi, In preparation (2003).
9. C. Pisani et al., in preparation (2003).
10. M. Schutz, G. Hetzer, and H.-J. Werner, J. Chem. Phys. **111**, 5691 (1999).

Dielectric permittivity of atomic-layer thick SiO_2 films or interlayers on silicon substrates.

Feliciano Giustino, P. Umari, and Alfredo Pasquarello

Institut de Théorie des Phénomènes Physiques (ITP), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland,
and Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), CH-1015 Lausanne, Switzerland

`e-mail: feliciano.giustino@epfl.ch`

To address the dielectric effect of a thin silica interlayer between silicon and high-κ oxides, we investigated the dielectric permittivities of atomic-layer thick SiO_2 films on silicon using a density functional approach. We constructed several model structures of the Si/SiO_2 interface with oxide thickness varying between 3 and 12 Å, and for each of them we calculated both the static and high-frequency permittivities. We found that a classical three-layer model (including the silicon substrate, a 3 Å thick suboxide, and the pure SiO_2 oxide) reproduces to a high degree of accuracy the results obtained from first principles. This suggests that the evolution of the screening properties from Si to SiO_2 is rather abrupt, and essentially takes place within the suboxide region. To check the validity of this conclusion, we investigated the microscopic polarization induced at the interface by an external electric field. We found that the local polarization is approximately constant in the substrate and in the pure oxide, and that the transition essentially occurs within the suboxide. This result provides a truly microscopic justification for the classical three-layer model. Static and high-frequency permittivities of the suboxide layer were found to be significantly larger than the corresponding values of bulk SiO_2 (3.8 and 6.8 instead of 2.0 and 3.8, respectively). To interpret this enhanced screening, we analyzed the interface from a chemical point of view. Following the Berry-phase theory of polarization, we determined the maximally localized Wannier functions of the system, and assigned each of them to a specific chemical bond (Si-Si or Si-O). Then, we evaluated the effective polarizability for each Wannier function, and found that the screening provided by Si-Si and Si-O bonds

is almost independent of their location with respect to the interface. As a consequence, the enhanced screening of the suboxide layer must arise from the chemical grading. Similar conclusions hold for the ionic screening. Metal-induced gap states are shown to contribute to the polarization of the suboxide, but their role in enhancing the SiO_2 permittivity in proximity of the substrate appears less prominent than previously suggested.

Ultra-non-local orbital structures and mechanisms of the field-counteracting effect in the Kohn-Sham exchange-correlation potential and kernel

O. V. Gritsenko, M. Grüning, E.J. Baerends

Department of Physical and Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands

`e-mail: gritsenko@chem.vu.nl`

Orbital mechanisms behind the ultra-non-local field-counteracting term (FCT) of the Kohn-Sham (KS) density functional theory (DFT) exchange potential of a molecular chain in the static electric extra field is established. Theoretical analysis for a simple helium dimer and calculations of the prototype hydrogen chains performed in the common energy denominator approximation (CEDA) for the static orbital Green's function show, that FCT originates in the response part of the exchange potential. One-electron mechanism behind FCT in the response potential is polarization of the lower-lying occupied KS orbitals at the low-field end of a molecular chain, while the higher-lying orbitals polarize at the high-field end. This polarization is, mainly, due to the mixing between the ground-state occupied KS orbitals in the extra r-like potential. Two-electron mechanism behind FCT is a "self-coupling" of the orbital products of a proper symmetry, which depend on the coordinates of the first and second electrons in the response part of the CEDA exchange kernel. FCT of the KS exchange potential is required, in order that DFT calculations would correctly reproduced (hyper)polarizabilities of molecular chains, which are greatly overestimated with the standard DFT local density approximation (LDA) and generalized gradient approximations (GGAs).

Application of the elongation method to nonlinear optical properties of periodic and non-periodic systems

Feng Long Gu

Department of Chemistry, Graduate School of Science, Hiroshima University,
Kagamiyama 1-3-1, Higashi-Hiroshima 739-8526, Japan;
and Group, PRESTO, Japan Science and Technology Corporation (JST), Kawaguchi
Center Building, Honcho 4-1-8, Kawaguchi, Saitama 332-0012, Japan

`e-mail: gu@th.chem.sci.hiroshima-u.ac.jp`

The elongation method [1-3] is applied to determine nonlinear optical properties of periodic and non-periodic polymers. The finite-field elongation approach [4] is employed for calculating electric (hyper)polarizabilities for some model systems. The most important advantage of this approach is the large compute time saving in the SCF stage since the dimension of the HFR equations remains the same regardless of the number of the atoms in the system. Another advantage is that this approach can be used to treat non-periodic polymers by building up polymer chains with arbitrary sequence of monomers.

References

1. A. Imamura, Y. Aoki, and K. Maekawa, J. Chem. Phys. **95**, 5419 (1991).
2. Y. Aoki and A. Imamura, J. Chem. Phys. **97**, 8432 (1992)
3. A. Imamura, Y. Aoki, K. Nishimoto, Y. Kurihara, and A. Nagao, Int. J. Quantum Chem. **52**, 309 (1994)
4. F. L. Gu, Y. Aoki, A. Imamura, D. M. Bishop, and B. Kirtman, Mol. Phys. **101**, 1487 (2003)

Static and Dynamic Electric Field Polarization in Quasilinear Polymers

Bernard Kirtman

Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA. 93106, USA

`e-mail: kirtman@chem.ucsb.edu`

A time-dependent Hartree-Fock treatment of linear and nonlinear electric field polarization in quasilinear polymers is presented [1,2]. The electric field is derived from the vector potential, while the polarization is obtained by means of a prescription due to Blount [3-4]. A convenient method for specifying the arbitrary phase factor [5-7] that multiplies the orbital eigenvectors is given. The choice of (Berry) phase affects the dipole moment, which is determined only up to an arbitrary multiple of the unit cell length, but not the (hyper)polarizabilities. The same general formulation applies to TDDFT but conventional functionals lead to large overestimates of the polarization [8-9]. Possible cures of the latter problem include use of either polarization [10] DFT or current density DFT [11,12] or accurate self-interaction-free orbital potentials [13]. **References**

1. B. Kirtman, F.L. Gu and D.M. Bishop, J. Chem. Phys. **113**, 1294 (2000)
2. D.M. Bishop, F.L. Gu and B. Kirtman, J. Chem. Phys. **114**, 7633 (2001)
3. E.I. Blount in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic, New York, 1962). Vol.13, p.305
4. See also V.N. Genkin and P.M. Mednis, Sov. Phys. JETP **27**, 609 (1968); [Zh. Eksp. Teor. Fiz. **54**, 1137 (1968).]
5. R.D. King-Smith and D. Vanderbilt, Phys. Rev. B **47**, 1651 (1993)
6. R. Resta, Rev. Mod. Phys. **66**, 899 (1994)
7. G. Ortiz and R.M. Martin, Phys. Rev. B **49**, 14202 (1994)
8. B. Champagne, E.A. Perpete, S.J.A. van Gisbergen, E.J. Baerends, J.G. Sniders, C. Soubra-Ghaoui, K.A. Robins, and B. Kirtman, J. Chem. Phys. **109**, 10489 (1998)
9. B. Champagne, E.A. Perpete, D. Jacquemin, S.J.A. van Gisbergen, E.J. Baerends, C. Soubra-Ghaoui, K.A. Robins, and B. Kirtman, J. Phys. Chem. A **104**, 4755 (2000)
10. X. Gonze, P. Ghosez and R.W. Godby, Phys. Rev. Lett. **74**, 4035 (1995)
11. M. van Faassen, P.L. de Boeij, R. van Leeuwen, and J.G. Snijders, Phys. Rev. Lett. **88**, 186401 (2002)
12. M. van Faassen, P.L. de Boeij, R. van Leeuwen, J.A. Berger, and J.G. Snijders, J. Chem. Phys. **118**, 1044 (2003)

13. S.J.A. van Gisbergen, P.R.T. Schipper, O.V. Gritsenko, E.J. Baerends, J.G. Snijders, B. Champagne, and B. Kirtman, Phys. Rev. Lett. 83, **694** (1999)

First principles calculation of vibrational Raman spectra in large systems: signature of small rings in crystalline SiO_2

Michele Lazzeri and Francesco Mauri

Laboratoire de Minéralogie Cristallographie de Paris, 140 rue de Lourmel, 75015 PARIS, France

e-mail: `michele.lazzeri@lmcp.jussieu.fr`

We present an approach for the efficient calculation of vibrational Raman intensities in periodic systems within density functional theory. The Raman intensities are computed from the second order derivative of the electronic density matrix with respect to a uniform electric field. In contrast to previous approaches, the computational effort required by our method for the evaluation of the intensities is negligible compared to that required for the calculation of vibrational frequencies. As a first application, we study the signature of 3- and 4-membered rings in the the Raman spectra of several polymorphs of SiO_2, including a zeolite having 102 atoms per unit cell.
Phys. Rev. Lett. **90**, 036401 (2003).

High-order density-matrix perturbation theory

Michele Lazzeri and Francesco Mauri

Laboratoire de Minéralogie Cristallographie de Paris, 140 rue de Lourmel, 75015 PARIS, France

e-mail: `michele.lazzeri@lmcp.jussieu.fr`

We present a simple formalism for the calculation of the derivatives of the electronic density matrix ρ at any order, within density functional theory. Our approach, contrary to previous ones, is not based on the perturbative expansion of the Kohn-Sham wavefunctions. It has the following advantages: (i) it allows a simple derivation for the expression for the high order derivatives of ρ; (ii) in extended insulators, the treatment of uniform-electric-field perturbations and of the polarization derivatives is straightforward.
http://arXiv.org/abs/cond-mat/0307603

Using the position operator to describe optically generated currents in unbiased semiconductors

F. Nastos and J.E. Sipe

Department of Physics, University of Toronto, Toronto ON, M5S 1A7, Canada

e-mail: `nastos@physics.utoronto.ca`

Through the absorption of light, electrical currents can be created in unbiased non-centrosymmetric semiconductors. There are two sources of these currents. In one process, the electron centre-of-mass

undergoes a shift as the electron density evolves to the excited state. Such a process is well suited for a description based on the position operator. Using Blount's representation of the position matrix elements, microscopic expressions, in terms of the bandstructure, can be derived for the shift current.∗

Another process can give rise to a current in an unbiased semiconductor. The interference between absorption pathways of different components of circularly polarized light can lead to an anisotropic distribution of electrons in the conduction band. The same formalism, based on the position operator **r** that is used for the shift current, also successfully describes the injection of these currents.

We review the formalism and present full-bandstructure calculations at the LDA+Scissors level of the these effects.
∗ J.E. Sipe and A.I. Shkrebtii, Phys. Rev. B **61**, 5337 (2000).

Berry-phase treatment of the homogeneous electric field perturbation in insulators

Ricardo Wagner Nunes

Departamento de Fisica - C.P. 702, Universidade Federal de Minas Gerais - UFMG,
Av. Antonio Carlos 6627 - Belo Horizonte, MG - 30161-970 - Brasil

`e-mail: rwnunes@fisica.ufmg.br`

A perturbation theory of the static response of insulating crystals to homogeneous electric fields, that combines the modern theory of polarization with the variation-perturbation framework is developed, at unrestricted order of perturbation. Conceptual issues involved in the definition of such a perturbative approach are addressed. In particular, we argue that the position operator, $\hat{x}$, can be substituted by the derivative with respect to the wavevector, $\partial/\partial k$, in the definition of an electric-field-dependent energy functional for periodic systems. Moreover, due to the unbound nature of the perturbation, a regularization of the Berry-phase expression for the polarization is needed in order to define a numerically-stable variational procedure. Regularization is achieved by means of a discretization procedure, which can be performed either before or after the perturbation expansion. We compare the two possibilities, show that they are both valid, and analyze their behavior when applied to a model tight-binding Hamiltonian. Lowest-order as well as generic formulas are presented for the derivatives of the total energy, the normalization condition, the eigenequation, and the Lagrange parameters.

Infrared and Raman spectra of disordered oxides from first principles

Alfredo Pasquarello

Institut de Théorie des Phénomènes Physiques (ITP), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland,
Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), CH-1015 Lausanne, Switzerland

`e-mail: alfredo.pasquarello@epfl.ch`

We describe a scheme for investigating infrared and Raman spectra of disordered oxides from first principles. Using first-principles molecular dynamics, we first generate an atomistic model structure of the oxide with a quench from the melt. The validity of our structural description is then examined by comparison with neutron diffraction experiments. The vibrational frequencies and modes are obtained

via the dynamical matrix which is calculated by taking finite differences of the atomic forces for small atomic displacements. Through the dynamical structure factor, the vibrational properties allow us to directly compare the calculated and measured neutron densities of states [1]. To access infrared and Raman spectra, we need to deal with the coupling to electric fields. One way of treating such couplings is achieved through the use of *finite* electric fields [2]. For calculating the infrared spectrum, we obtain the dynamical charges from the atomic forces in the presence of a finite electric field [2]. For the Raman spectra, we obtain the Raman tensors from the second derivative of these forces with respect to the field [3]. We illustrate this scheme in an application to vitreous B_2O_3 [3]. We find that inelastic neutron and infrared spectra are well reproduced, while the comparison between theory and experiment is less impressive for the Raman spectrum. These results can be explained as follows. The inelastic neutron and infrared data are well described because they are related to the short-range order, which is well reproduced in our structural model. At variance, the Raman spectrum is shown to depend primarily on oxygen bending motions and is therefore more sensitive to the medium range structure [4]. The medium range structure is evidently less well reproduced by our atomistic model. We can nevertheless extract useful structural information from the comparison between calculated and experimental Raman spectra. ¿From the intensity of the strong line at 800 cm^{-1}, we could extract an estimate for the fraction of boron atoms occurring in boroxol rings [3].

References

1. A. Pasquarello, J. Sarnthein, and R. Car, Dynamic structure factor of vitreous silica from first principles: Comparison to neutron-inelastic-scattering experiments, Phys. Rev. B **57**, 14133 (1998)
2. P. Umari and A. Pasquarello, *Ab initio* molecular dynamics in a finite homogeneous electric field. Phys. Rev. Lett. **89**, 157602 (2002)
3. P. Umari and A. Pasquarello, unpublished.
4. P. Umari, X. Gonze, and A. Pasquarello, Concentration of small ring structures in vitreous silica from a first-principles analysis of the Raman spectrum, Phys. Rev. Lett. **90**, 027401 (2003)

Calculation of the optical dielectric constant and non linear electric susceptibilities of periodic systems by the finite field perturbation method

Michel Rérat

Laboratoire de Chimie Structurale, Unité Mixte de Recherche 5624 du CNRS, Université de Pau, F-64000 Pau, France

`e-mail: michel.rerat@univ-pau.fr`

The dielectric constant is defined as the ratio: $\epsilon = F_0/F$, where F_0 is the displacement vector or outer field, and F is the total field related to F_0 and the macroscopic polarization vector P of the medium: $F = F_0 - P/\epsilon_0$, ϵ_0 being the vacuum permittivity.

In the electric dipole approximation, the electric potential perturbation is written: rF_0, depending of the length operator r (or electron position). Added to the Hartree-Fock or Kohn-Sham hamiltonian in the SCF method, the so called finite field method (FF) leads to the electron density $\rho(F_0)$ of the studied system in presence of the outer field. Then, the macroscopic polarization vector P can be deduced from integration in the space of the mean value of ρ per unit cell (Poisson's equation), leading to the dielectric constant $\epsilon(F_0)$ (see [1,2]).

In fact, the dielectric constant is the limit of $\epsilon(F)$ when F tends to zero, and corresponds to the linear electric susceptibility or the polarizability. The higher terms in the polynomial development of $\epsilon(F)$ versus F leads to the non linear electric susceptibilities which can be also obtained by fit.

However, the difficulty of using the finite field method for calculating the dielectric constant of a crystal, is that the periodicity of this latter is destroyed by the electric field perturbation. In order to maintain the periodicity along the applied field z-direction, avoiding like this surface or edge effects (unsaturated bonds), a "sawtooth" potential can be used in conjunction with a supercell scheme. The corresponding triangular electric potential is developped in a Fourier series, and the mean value of the electron density per unit cell can be obtained from calculated structure factors $F_{0,0,l}$. This method has been implemented in the CRYSTAL code [3] (LCAO-SCF process for periodic systems at HF or KS level) by Darrigan et al. [4], and should be available soon in its new version CRYSTAL 2003 (http://www.crystal.unito.it).

Several applications will be given in this presentation, showing different effects like the number of cells in the supercell on the susceptibility values.

References

1. A. Baldereschi, S. Baroni and R. Resta, *Phys. Rev. Lett.* **61** (1988) 734
2. L. Fu, E. Yaschenko, L. Resca and R. Resta *Phys. Rev. B*, **57** (1998) 6967
3. V. R. Saunders, R. Dovesi, C. Roetti, M. Causà, N. M. Harrison, R. Orlando, C. M. Zicovich-Wilson, *CRYSTAL98 User's Manual*, University of Torino, Torino, 1998
4. C. Darrigan, M. Rérat, G. Mallia and R. Dovesi, *J. Comp. Chem.*, **24** (2003) 1305

Introductory lecture: Position Operator, Dipole, and Polarization, in Extended Systems

Raffaele Resta

INFM DEMOCRITOS National Simulation Center, Trieste, Italy
and Dipartimento di Fisica Teorica, Universitá di Trieste, Italy

`e-mail: resta@ts.infn.it`

The concept of macroscopic polarization is the basic one in the electrostatics of dielectric materials: but for many years this concept has evaded even a precise microscopic definition, and has severely challenged quantum-mechanical calculations. Similarly problematic was the longitudinal polarization of a quasi-onedimensional polymer. While the dipole moment of any finite and neutral system–having a square-integrable wavefunction–is a well defined quantity, the same moment is ill-defined for an extended system, whose wavefunction invariably obeys periodic (Born-von Karman) boundary conditions.

The field has undergone a genuine revolution in recent years (1992 onwards). It is now pretty clear that (contrary to a widespread incorrect belief) macroscopic polarization has nothing to do with the periodic charge distribution of the polarized crystal: the former is essentially a property of the phase of the electronic wavefunction, while the latter is a property of its modulus. An outline of the modern theory, based on a Berry phase, will be presented.

Experiments invariably address polarization derivatives (permittivity, piezoelectricity, pyroelectricity, infrared charges) or polarization differences (ferroelectricity), and these differences are measured as an integrated electrical current. The modern theory addresses this same transient current, which is cast in terms of the phase of the electronic wavefunction.

First-principle calculations (for ferroelectricity, piezoelectricity, and lattice dynamics) are in spectacular agreement with experiments, and have provided thorough understanding of the behavior of several materials. Implementation of the modern theory is included in the standard distribution of some popular electronic-structure codes (ABINIT, VASP, CRYSTAL).

The explicit saw-tooth shaped position operator under periodic boundary conditions

D. Sebastiani

Max-Planck-Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

e-mail: `sebastia@mpip-mainz.mpg.de`

We discuss the realization of an explicit position operator within density functional theory under periodic boundary conditions (pbc) [1]. Using maximally localized Wannier orbitals [2] instead of the canonical Kohn-Sham orbitals (the eigenfunctions of the KS-Hamiltonian), it is possible to represent the effect of a homogeneous electric or magnetic field in a DFT calculation. The straightforward idea is implemented in a scheme to compute magnetic linear response properties under pbc (NMR chemical shifts, magnetic susceptibilities), but it presents certain drawbacks in combination the density functional perturbation framework [3,4].

References

1. D. Sebastiani and M. Parrinello, J. Phys. Chem. A **105**, 1951 (2001)
2. G. Berghold, C.J. Mundy, A.H. Romero, J. Hutter and M. Parrinello, Phys. Rev. B **61**, 10040 (2000)
3. A. Putrino, D. Sebastiani and M. Parrinello, J. Chem. Phys. **113**, 7102 (2000)
4. CPMD, a Car-Parrinello Molecular Dynamics code, `www.cpmd.org`

Beyond r: the search for polarization and magnetization fields

J.E. Sipe and F. Nastos

Department of Physics, University of Toronto, Toronto ON, M5S 1A7, Canada

e-mail: `sipe@physics.utoronto.ca`

In atomic and molecular physics, the operator $\mathbf{r}$ appears most often in connection with the dipole approximation. In that approximation it is the electric dipole moment of a charge, which is proportional to its position $\mathbf{r}$, that describes the interaction of the charge with the electromagnetic field. But one can go beyond the dipole approximation, and take into account higher multipole moments of charges. Other operators besides $\mathbf{r}$ then obviously appear as well. In fact, as most clearly systematized by Healy$*$, one can introduce microscopic polarization and magnetization fields that act as potentials for the charge and current densities, reminiscent of the way the scalar and vector potentials act as potentials for the electric and magnetic fields. The usual multipole moments can be recovered, if desired, as moments of these polarization and magnetization fields. But before any multipole moments are introduced, the minimal coupling Hamiltonian can be converted, using an appropriate canonical transformation, to one in which the interaction between the material system and the electromagnetic field is described by the polarization and magnetization fields and the electric and magnetic fields, rather than by the charge and current densities and the scalar and vector potentials. With such an approach, the effect of electromagnetic fields of arbitrary spatial variation over the atomic or molecular system can be calculated in terms of the electric and magnetic fields directly.

In solids there are also phenomena in which optical properties "beyond the dipole approximation" are of interest. These include nonlinear effects such as the "forbidden" second-harmonic generation in solids with

centre-of-inversion symmetry. But there are even linear effects, including optical activity, that also fall in this category. In treatments of these optical processes one would like to avoid the difficulties of working in the minimal coupling Hamiltonian by using an interaction Hamiltonian involving the electric and magnetic fields, rather than the scalar and vector potentials. So it is natural to ask if general polarization and magnetization fields analogous to those of Healy, or of some other sort, can be introduced for extended systems as well. We outline a framework for characterizing such fields and their associated canonical transformations, and discuss difficulties and progress in constructing such fields for extended systems.
$*$ W.P. Healy, *Nonrelativistic quantum electrodynamics,* Academic Press (1982).

Dynamics of Berry-phase polarization in time-dependent electric fields

Ivo Souza, Jorge Íñiguez, and David Vanderbilt

Department of Physics and Astronomy, Rutgers University, Piscataway, NJ (USA)

`e-mail: ivo@physics.ruthers.edu`

The work of King-Smith and Vanderbilt demonstrated that the electronic polarization, defined in terms of the current flowing during *adiabatic* evolution of an insulating system in a *vanishing macroscopic electric field*, could be related to a Berry phase defined over the manifold of occupied Bloch states [1]. We have generalized this result [2] by considering the time evolution of an initially insulating electron system under a very general Hamiltonian $H(t) = H_{\rm per}(t) + e\mathcal{E}(t)\cdot\mathbf{r}$, where the lattice-periodic part $H_{\rm per}(t)$ and the homogeneous electric field $\mathcal{E}(t)$ may have an arbitrarily strong and rapid variation. In the absence of scattering, we prove that the integrated current $\Delta\mathbf{P} = \int \mathbf{J}(t)\,dt$ is still given by the King-Smith–Vanderbilt formula, but written in terms of the instantaneous Bloch-like solutions of the time-dependent Schrödinger equation. The dynamic polarization $\mathbf{P}(t)$ is interpreted as a nonadiabatic geometric phase [3]. This nonadiabatic generalization of the Berry-phase polarization theory allows us to justify recent developments in which the energy functional of Nunes and Gonze [4] has been used as the basis for direct DFT calculations of insulating crystals in a static homogeneous electric field [5,6]. It also provides a convenient framework for the computation of coherent time-dependent excitations in insulators. As an example, the dielectric function is computed for a tight-binding model by considering the response to a step-function discontinuity in $\mathcal{E}(t)$, illustrating effects such as field-assisted tunneling and Franz-Keldysh oscillations that are characteristic of optical absorption in an electric field.

I will briefly mention work in progress on extending the variation-perturbation approach of Ref. [4] to *finite* frequencies. The required generalization of the energy functional E in a static electric field [4] is a Floquet *quasienergy* functional Q in oscillatory fields [7], from which the susceptibilities are obtained by differentiation [8]. Q can be derived from E by augmenting the Brillouin zone with a time axis $[0,T]$, and introducing the operator $\mathcal{H} = H_k^0 + ie\mathcal{E}(t)\cdot\partial_{\mathbf{k}} - i\hbar\partial_t$ in an extended Hilbert space [7]. The striking similarity between time and reciprocal space in this formulation has interesting consequences.

References

1. R.D. King-Smith and D. Vanderbilt, Phys. Rev. B **47**, 1651 (1993).
2. I. Souza, J. Íñiguez, and D. Vanderbilt, cond-mat/0309259.
3. Y. Aharonov and J. Anandan, Phys. Rev. Lett. **58**, 1595 (1987).
4. R. W. Nunes and X. Gonze, Phys. Rev. B 63, 155107 (2001).
5. I. Souza, J. Íñiguez, and D. Vanderbilt, Phys. Rev. Lett. **89**, 117602 (2002).
6. P. Umari and A. Pasquarello, Phys. Rev. Lett. 89, 157602 (2002).

7. H. Sambe, Phys. Rev. A **7**, 2203 (1973).
8. O. Christiansen, P. Jørgensen, and C. Hättig, Int. J. Quant. Chem. **68**, 1 (1998).

Introductory lecture: Linear and non-linear optical properties of polymers

Michael Springborg

Physical Chemistry, University of Saarland, 66123 Saarbrücken, Germany

e-mail: `m.springborg@mx.uni-saarland.de`

In particular conjugated oligomers and polymers with π electrons that are somewhat loosely bound to the backbone possess large linear and non-linear responses to external electric fields. Accordingly, much theoretical and experimental work has been devoted exploring this. It turns out that the non-linear responses per monomer first for large oligomers approach a saturation. Thus, studies for large oligomers or infinite polymers are highly relevant.

Theoretical studies for infinite polymers suffer from the problem that one has to consider matrix elements for an unbound potential which, in addition, destroys the periodicity. Different approaches for circumventing this approach have over the years been proposed, and shall in this overview be outlined briefly. In addition, examples of applications of these methods shall be presented.

Ab Initio Molecular Dynamics in a Finite Homogeneous Electric Field*

Paolo Umari and Alfredo Pasquarello

Institut de Théorie des Phénomènes Physiques (ITP), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), CH-1015 Lausanne, Switzerland

e-mail: `paolo.umari@epfl.ch`

We treat homogeneous electric fields within density functional calculations with periodic boundary conditions. The ground state is found by minimizing a nonlocal energy functional depending on the applied field. We show analytically that, when applied to a crystalline system, this functional preserve the translational symmetry. This approach is included within an *ab initio* molecular dynamics scheme. The reliability of the method is demonstrated in the case of bulk MgO for the Born effective charges, and the high- and low-frequency dielectric constants.

We investigate the dielectric constant calculated with this approach and with a scheme based on conventional perturbational theory. We show, both analytically and numerically, that the difference between the dielectric constants in the two schemes converges as $1/L^2$, L being the supercell size. Applications to the water molecule and bulk silicon illustrate this behavior.

The method to treat finite electric fields within periodic boundary conditions is then used to define formally a density functional depending on the electric field. An exchange and correlation energy functional depending on the electric field is introduced and an explicit expression for its dependence with respect to the field at the zero-field limit is given.

First-principles study of the electrooptic effect in ferroelectric oxides

Marek Veithen[1], Xavier Gonze[2] and Philippe Ghosez[1]

[1] *Département de Physique (B5), Université de Liège, Allée du 6 août 17,B-4000 Sart Tilman, Belgium*

[2] *Unité PCPM, Université Catholique de Louvain, Place Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium*

`e-mail: Marek.Veithen@ulg.ac.be, Philippe.Ghosez@ulg.ac.be, gonze@pcpm.ucl.ac.be`

Optical non-linearities include various phenomena directly linked to important technological applications. Ferroelectric ABO_3 compounds show particularly high electrooptic (EO) coefficients and are of direct interest for light modulation[1] or holographic data storage[2].

In the Born and Oppenheimer approximation, the electrooptic coefficients can be decomposed into (i) a bare electronic part and (ii) an ionic contribution. The electronic part describes the response of the valence electrons to a (quasi-)static macroscopic electric field when the ions are considered as artificially clamped at their equilibrum positions, and can be deduced from the non-linear optical susceptibilities. The ionic contribution is produced by the relaxation of the atoms within the quasi-static electric field. It can be computed from the knowledge of the frequency, polarity and Raman susceptibility of the zone-center transverse optical phonon modes.

We implemented into the ABINIT code[3] the formalism develloped by Nunes and Gonze[4] to access the non-linear susceptibilities and the Raman susceptibilities required to determine the electrooptic coefficients. This methodology is based on the $2n + 1$ theorem and the modern theory of polarization. We discuss various details of this implementation. In particular, we describe distinct expressions to compute third-order energy derivatives and compare their relative convergence with respect to the **k**-point sampling.

We then apply this methodology to the study of the electrooptic response of various ferroelectric oxides such as $LiNbO_3$, $BaTiO_3$ and $PbTiO_3$, with the aim to identify the origin of the large electrooptic coefficients of these compounds. We observe a giant ionic contribution related to the soft mode. Based on this result, we finally develop an effective Hamiltonian approach to simulate the temperature dependence of the electrooptic coefficients in $BaTiO_3$.

References

1. L. Wooten *et al.*, IEEE J. Sel. Top. Quantum Electron. **6**, 69, (2000)
2. K. Buse, A. Adibi and D. Psaltis, Nature **393**, 665 (1998); L. Hesselink et al., Science **282**, 1089 (1998)
3. X. Gonze *et al.*, Computational Materials Science **25**, 478 (2002) [URL: www.abinit.org]
4. R. W. Nunes and X. Gonze, PRB **63**, 155107 (2001)

Localization tensor and Born effective charges in complex materials: application to ferroelectric oxides and skutterudites

Marek Veithen[1], Xavier Gonze[2] and Philippe Ghosez[1]

[1] *Département de Physique (B5), Université de Liège, Allée du 6 août 17,B-4000 Sart Tilman, Belgium*

[2] *Unité PCPM, Université Catholique de Louvain, Place Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium*

e-mail: `Marek.Veithen@ulg.ac.be`, `Philippe.Ghosez@ulg.ac.be`, `gonze@pcpm.ucl.ac.be`

The electron localization tensor[1] in extended systems is strongly related to the macroscopic polarization. The latter quantity is determined by the position of the center of the Wannier functions of the electrons while the former one is connected to the real space extension of these Wannier functions. The localization tensor defines a characteristic and direction dependent length that is finite in insulators and diverges in metals.

We implemented the calculation of the localization tensor within the ABINIT code[2] making use of the linear-response formalism. Using an appropriate decomposition of this quantity into contributions from electrons occupying individual bands or isolated groups of bands[3], we obtain a sensitive probe to investigate the electronic structure and the chemical bonding. Comparing the results for different materials to that of the related isolated atoms, we can obtain useful informations about the hybridizations taking place in a solid. We illustrate this for the case of ferroelectric oxides and skutterudites.

For the ferroelectrics, we study the evolution of electron localization at the phase transitions, and the hybridizations that are at the origin of the valence bands in these compounds. We show that the values of the localization tensors in $BaTiO_3$ are compatible with the anomalous effective charges and the model of Harrison.

Skutterudites such as $CoSb_3$ are narrow-bandgap semiconductors. Their structure is formed of large empty voids able to accomodate various kinds of impurity atoms. Filling these voids with Tl or a rare earth atom is found to reduce their lattice thermal conductivity and makes them potentially interesting for thermoelectric applications[4]. We compute the localization tensor of the electronic states of Tl in the filled skutterudite $TlFeCo_3Sb_{12}$. In addition, we study the Born effective charges in this compound. We show that the Tl 6s electrons significantly interact with the atoms of the host crystal resulting in a huge delocalization. Moreover, the Born effective charges are found to be quite large, as suggested previously for this class of narrow-bandgap semiconductors[5].

References

1. C. Sgiarovello, M. Peressi and R. Resta, Phys. Rev. B **64**, 115202 (2001)
2. X. Gonze *et al.*, Computational Materials Science **25**, 478 (2002) [URL: www.abinit.org]
3. M. Veithen, X. Gonze and Ph. Ghosez, Phys. Rev. B **66**, 235113 (2002)
4. See for example C. Uher, Semiconductors and semimetals **69**, 139 (2001)
5. S. Ögüt and K. M. Rabe, Phys. Rev. B **54**, R8297 (1996)

5.1.2 Report on Euroconference on 'AB-INITIO MANY-BODY THEORY FOR CORRELATED ELECTRON SYSTEMS'

Trieste, Italy, 25 - 29 August 2003

Sponsored by

ESF Psi-k Programme
RTN on f-electrons
CCP9, U.K.
ICTP, Trieste, Italy

This Euroconference was motivated by recent exciting developments at the interface between two fields: that of ab-initio (density-functional based) calculations of the electronic structure of solids, and that of many-body techniques designed to handle the effects of strong electronic correlations. It is hardly necessary to emphasize the broad range of physical phenomena and potential applications of strongly correlated materials (containing incomplete d- and f-shells), such as: transition metals and their oxides as well as rare earth and actinide compounds. In those systems, many physical effects compete in a quantitative manner, so that simple models provide only general guidelines, which must be supplemented by more quantitative techniques. Recently, DFT-LDA methods have been combined with many body techniques (in particular Dynamical-Mean-Field Theory-DMFT) in order to achieve these goals.

The sessions of this Euroconference covered the latest technical developments, some targeted applications and selected recent experimental results. In more detail:

The technical topics which were stressed at this conference were:

- Dynamical Mean Field Theory and electronic structure calculations
- Recent developments in the GW approximation. This includes in particular issues related to self-consistency, and recent efforts to combine GW with DMFT towards a first-principles electronic structure method for strongly correlated electron systems
- Latest developments and applications of Quantum Monte Carlo methods
- Time-dependent DFT
- Ab-initio few-orbital Hamiltonians from downfolding techniques

The applications of the methods were:

- f-electron systems
- transition metal oxides
- diluted magnetic semiconductors
- nanoelectronics

Experimental talks covered the application of spectroscopy techniques, optical and high energy photoemission, and pressure measurements to correlated systems.

More than 120 participants attended the conference, making it an extremely lively event. Several communities were represented at this meeting, such as many-body theoreticians, band-theory theoreticians and expertimentalists, making the meeting extremely useful. One particular GW person picked up a lot of new ideas by attending talks from outside the GW realm. For anyone interested, the transparancies of the talks can be found on the ICTP web page:

`http://www.ictp.trieste.it/~smr1512/contributionspage.html`.

Programme

Monday, August 25

8:30	9:30	**Registration** **Administrative Formalities**
9:30	10:00	Opening and Introduction by Organizers **J. Grassberger:** Presentation of the ICTP Computer System
10:00	11:00	**A. Rubio:** Optical response of nanostructures & bulk systems within Time-Dependent Density-Functional-Theory
11:00	11:15	Coffee Break
		+ GW Session (1st part)
11:15	12:15	**R.W. Godby:** Non-self-consistent & self-consistent GW calculations for spectral & ground-state properties
12:15	15:00	Lunch
		Nanoelectronics Session part 2
15:00	16:00	**C.J. Lambert:** Electron transport through carbon nanotubes
16:00	17:00	**T. Kotani:** Full-potential GW; semi self-consistent results
17:00	17:30	Coffee Break
17:30	18:00	**A. Schindlmayr:** The GW Approximation within a Density-Functional Context
18:00	18:30	**N. Vast:** Anisotropy of the Microscopic Fluctuations of the Polarization, Confinement effects & the Dielectric Function of Crystals

Tuesday, August 26

		DMFT Sessions
9:00	10:00	**G. Kotliar:** Dynamical Mean Field Theory for Electronic Structure Calculations: Formulations, one Electron Spectra, Transport & Optical Properties
10:00	10:30	Coffe Break
10:30	11:30	**S. Savrasov:** Spectral Density Functional Theory and Linear Response Calculations
11:30	12:00	**M. Capone:** Strongly Correlated Superconductivity in the Fullerenes from weak to strong coupling
12:00	15:30	Lunch
		QMC Sessions
15:30	16:30	**R. Needs:** Diffusion quantum Monte Carlo for condensed matter systems
16:30	17:30	**S. Zhang:** Realistic quantum Monte Carlo calculations using auxiliary fields
17:30	17:45	Coffee Break
17:45	18:15	**C. Filippi:** Surface physics with quantum Monte Carlo
		Nanoelectronics Session
18:15	18:45	**I. Mertig:** Stability and transport of nanocontacts: Ab initio description
		Actinides Session
18:45	19:15	**J.-C. Griveau:** Superconductivity in the Actinides systems the pressure effect
19:30		**Get-together**

Wednesday, August 27

cm

		Oxides Session
9:00	10:00	**M. Rozenberg:** Recent developments on the Mott-Hubbard transition
10:00	10:30	Coffee Break
		f-electrons Sessions
10:30	11:30	**K. Held:** The Cerium volume collapse: An LDA+ DMFT study
11:30	12:30	**W.E. Pickett:** LDA+U Applied to a Moderately Correlated Actinide Compound: UGe2
12:30	15:30	Lunch
		f-electrons Sessions (con't)
15:30	16:30	**G. Zwicknagl:** Dual nature of 5f electrons, partial localisation & heavy fermions in actinide sys
16:30	17:30	**W. Temmerman:** Self-Interaction Corrected Electronic Structure Calculations for Correlated Systems
17:30	17:45	Coffee Break
		Spectroscopies Sessions
17:45	18:45	**A. Sekiyama:** Bulk-sensitive high-energy photo-emission study of strongly correlated systems
18:45	19:15	**D. van der Marel:** Optical signatures of strong electron correlations in transition metal monosillicides
20:30		Evening POSTER SESSION

Thursday, August 28

9:00	10:00	**O.K. Andersen:** Direct generation of NMTO Wannier-like functions by means of downfolding. Application to V2O3 & other transition-metal compounds
10:00	10:30	Coffee Break

Oxides Session

10:30	11:00	**E. Pavarini:** Metal-insulator transition in orthorhombic $3d^1$ perovskites
11:00	12:00	**K. Syassen:** Transition metal oxides at high pressures
12:00	15:00	Lunch

Afternoon Session: **LDA + DMFT**

15:00	16:00	**A. Lichtenstein:** Magnetism and electronic structure of correlated systems: LDA+DMFT

+GW Sessions (2nd part)

16:00	17:00	**F. Aryasetiawan:** First-principles approach to strongly correlated systems
17:00	17:15	Coffee Break
17:15	18:15	**N. E. Zein:** Combination of GW and DMFT methods for calculating total energies & spectra of strongly correlated materials

Friday, August 29

Spectroscopies Session

9:00	10:00	**D. van der Marel:** Universal powerlaw of the optical conductivity & the phase angle spectra of optimally doped cuprates
10:00	10:30	Coffee Break

Magnetic Semi-conductor Sessions part 2

10:30	11:00	**T. Schultess:** Electronic structure and valency of Mn impurities in III-V semiconductors
11:00	11:30	**S. C. Erwin:** Compensation, interstitials, and ferromagnetism in magnetic semiconductors
12:00	14:00	Lunch
14:00	14:30	**G. Zarand:** Spin-orbit coupling and disorder in $Ga_{1-x}Mn_xAs$
14:30	15:00	**P. Boguslawski:** Interstitial and substitutional Mn in GaMnAs
15:00	15:30	**Concluding Remarks**

Participants

Amadon Bernard (Nationality: France), CEA, Dèpartement de Physique Thèorique et Appliquèe Service de Physique de la Matiere Condensèe, BP 12 91680 Bruyeres de Chatel, FRANCE.

Amovilli Claudio, (Nationality: Italy), Universitá degli Studi di Pisa Dip. Chimica e Chim. Industriale, Via Risorgimento 35, 56126 Pisa, ITALY.

Andersen Ole Krogh (Nationality: Denmark), Max-Planck-Institut Für Festkörperforschung, Heisenbergstrasse 1, Postfach 80 06 65, D-70506 Stuttgart, GERMANY.

Aryasetiawan Ferdi (Nationality: Indonesia), Research Institute for Computational Sciences (RICS), AIST Tsukuba Central 2, Umezono 1-1-1, Tsukuba Ibaraki 305-8568, JAPAN.

Bailey Steve (Nationality: United Kingdom), University of Lancaster, Department of Physics, LA1 4YB, Lancaster, UNITED KINGDOM.

Banach Grzegorz (Nationality: Poland), Council for the Central Laboratory of the Research Councils, Daresbury Laboratory, Computational Sci. & Eng. Department, Cheshire, Warrington, WA4 4AD, Daresbury, UNITED KINGDOM.

Barhdadi Abdelfattah (Nationality: Morocco), Ecole Normale Superieure de Rabat, Laboratoire de Physique des Semiconducteurs-Energie Solaire, Departement de Physique, B.P. 5118, Takaddoum Rabat, MOROCCO.

Blömer Nils Michael (Nationality: Germany), Universität Mainz, Institut Fuer Physik, Staudinger Weg 7, D-55099 Mainz GERMANY.

Boguslawski Piotr (Nationality: Poland), Polish Academy of Sciences, Institute For Theoretical Physics, Al. Lotnikow 32/46, O2-668 Warsaw, POLAND.

Boukabrine Fouzia (Nationality: Algeria), Cite Barouaine Said Ilot 291 Villa 37 S Ain-Temouchent, ALGERIA.

Camjayi Alberto (Nationality: Argentina), Universidad de Buenos Aires, Facultad de Sciences Exactes, Department of Physics, Pab.I 1428 Buenos Aires, ARGENTINA.

Capone Massimo (Nationality: Italy), Universitá di Roma 'La Sapienza', I.N.F.M. - Unitá di Roma, 1 Dip.To di Fisica 'E.Fermi', Piazzale Aldo Moro 2, 00185 Roma, Italy.

Cencarikova Hana (Nationality: Slovak Republic), Slovak Academy of Sciences, Institute of Experimental Physics, Watsonova 47, 04353 Kosice, SLOVAK REPUBLIC.

Cheraghchi Hossein (Nationality: Islamic Republic of Iran), Sharif University of Technology, Institute of Physics, P.O. Box 11365-9161, Tehran, ISLAMIC REPUBLIC OF IRAN.

Costa Filho Raimundo Nogueira (Nationality: Brazil), Universidade Federal Do Ceara, Departamento de Fisica, Campus Do Pici Caixa Postal 6030, Ceara CEP 60455-760, Fortaleza, BRAZIL.

Dang Dinh Toi (Nationality: Viet Nam), Faculty of Physics, University of Hanoi, 334 Nguyen Trai street, Hanoi, VIET NAM.

Dao Xuan Viet (Nationality: Viet Nam), Faculty of Physics, University of Hanoi, 334 Nguyen Trai street, Hanoi, VIET NAM.

De Medici Luca (Nationality: Italy), Universitè de Paris XI (Paris-Sud), Laboratoire de Physique Des Solides, BatÓment 510, Centre Universitaire, F-91405 CEDEX Orsay, FRANCE.

Didi Seddik Ali (Nationality: Morocco), Université Sidi Mohamed Ben Abdallah, Laboratoire de Physique Theorique, B.P. 1796, Fes, MOROCCO.

Dua Piyush (Nationality: India), Indian Institute of Technology Roorkee (Former University of Roorkee), Department of Physics, 247 667 Roorkee, INDIA.

Elloh Van Wellington (Nationality: Ghana), University of Cape Coast, Faculty of Science, Department of Physics, University P.O. Cape Coast, GHANA.

Erwin Steven C. (Nationality: United States of America), Naval Research Laboratory, Complex System Theory Branch, 6390 4555 Overlook Ave. Sw D.C., 20375-5345 Washington, UNITED STATES OF AMERICA.

Esfarjani Keivan (Nationality: Islamic Republic of Iran), Sharif University of Technology, Department of Physics, P.O. Box 11365-9161, Azadi Ave., Tehran, ISLAMIC REPUBLIC OF IRAN.

Farkasovsky Pavol (Nationality: Slovak Republic), Sofijska 22, 040 01 Kosice, SLOVAK REPUBLIC.

Feldbacher Martin (Nationality: Austria), Universität Stuttgart, Institut für Theoretische Physik III, Pfaffenwaldring 57, 70550 Stuttgart, GERMANY.

Filippi Claudia (Nationality: Italy), Iniversiteit Leiden, Instituut-Lorentz for Theoretical Physics, Department of Physics, P.O. Box 9506, 2300 RA Leiden, NETHERLANDS.

Floris Franca Maria (Nationality: Italy), Universitá degli Studi di Pisa, Dip. Chimica e Chim. Industriale, Via Risorgimento 35, 56126 Pisa, Italy.

Friak Martin (Nationality: Czech Republic), Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Zizkova 22, CZ-61662 Brno, CZECH REPUBLIC.

Gathoni Robinson Ndegwa (Nationality: Kenya), University of Nairobi, Department of Physics, P.O. Box 30197, Nairobi 00100, KENYA.

Georges Antoine (Nationality: France), Ecole Normale Superieure, Laboratoire de Physique Theorique, 24, Rue Lhomond, F-75231 Paris Cedex 05, FRANCE.

Gidopoulos Nikitas Ioannis (Nationality: Greece), ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX Oxon, UNITED KINGDOM.

Godby Rex William (Nationality: United Kingdom), University of York, Department of Physics, YO1 5DD, York, UNITED KINGDOM.

Griveau Jean-Christophe (Nationality: France), European Commission Joint Research Centre - Karlsruhe Establishment, Postfach 2340, D-76125 Karlsruhe, GERMANY.

Held Karsten (Nationality: Germany) Max-Planck-Institut für Festkorperforschung, Heisenbergstrasse 1, Postfach 80 06 65, D-70506 Stuttgart, GERMANY.

Hu Xing-Biao (Nationality: People's Republic of China), Academia Sinica, Inst. Computational Mathematics & Scientific/Engg. Computing, P.O. Box 2719, 100080 Beijing, PEOPLE'S REPUBLIC OF CHINA.

Ivanov Nedko Borissov (Nationality: Bulgaria), Bulgarian Academy of Science, Georgi Nadjakov Institute of Solid State Physics, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, BULGARIA.

Jafari Sayad Akbar (Nationality: Islamic Republic of Iran, Sharif University of Technology, Department of Physics, P.O. Box 11365-9161, Azadi Ave., Tehran, ISLAMIC REPUBLIC OF IRAN.

Kaduki Kenneth Amiga (Nationality: Kenya), University of Nairobi, Faculty of Science, Department of Physics, P.O. Box 30197, Chiromo Campus Nairobi, KENYA.

Kanchana Venkatakrishnan (Nationality: India), Max-Planck-Institut für Festkorperforschung, Heisenbergstrasse 1, Postfach 80 06 65, D-70506 Stuttgart, GERMANY.

Kofane Timoleon Crepin (Nationality: Republic of Cameroon), Universite de Yaounde, Laboratoire de Mecanique, Faculté de Sciences, Departement de Physique, B.P. 812, Yaounde, REPUBLIC OF

CAMEROON.

Kotani Takao (Nationality: Japan), Osaka University, Faculty of Science, Department of Physics, Toyonaka 560, Osaka, JAPAN.

Kotliar Gabriel (Nationality: United States of America, 423 Becker Street, NJ 08904, Highland Park, UNITED STATES OF AMERICA.

Koudela Daniela (Nationality: Germany), Leibniz Institute For Solid State and Material Research, D-01171 Dresden, GERMANY.

Kravtsov Vladimir E. (Nationality: Russian Federation), The Abdus Salam International Centre for Theoretical Physics, Condensed Matter Section, Strada Costiera 11, 34014 Trieste, Italy.

Kuku Titilayo Adelaja (Nationality: Nigeria), Obafemi Awolowo University, Faculty of Technology, Dept. Electronic & Electrical Engineering, Ile-Ife, NIGERIA.

Lakdja Abdelaziz (Nationality: Algeria), Université de Sidi Bel Abbes, Faculté Des Sciences, Departement de Physique, 22000 Sidi Bel Abbes, ALGERIA.

Lambert Colin John (Nationality: United Kingdom), University of Lancaster, Department of Physics, LA1 4YB, Lancaster, UNITED KINGDOM.

Lazic Predrag (Nationality: Croatia), Rudjer Boskovic Institute, Division of Theoretical Physics, Bijenicka Cesta 54, P.O. Box 180, 10002 Zagreb, CROATIA.

Lechermann Frank (Nationality: Germany), Max-Planck-Institut für Metallforschung, Institut für Physik, Heisenbergstrasse 1, Postfach 80 06 65, 70569 Stuttgart, GERMANY.

Lichtenstein Alexander (Nationality: Russian Federation), University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, NETHERLANDS.

Lim Jong Soo (Nationality: Republic of Korea), Seoul National University, Centre for Theoretical Physics, 151-742 Seoul, REPUBLIC OF KOREA.

Llois Ana Maria (Nationality: Argentina), Comision Nacional de Energia Atomica, Departamento de Fisica, Av. da del Libertador 8250, 1429 Buenos Aires, ARGENTINA.

Magnitskaya (Kondrat'eva) Maria Victorovna (Nationality: Russian Federation), Russian Academy of Sciences, LF Vereshchagin Institute of High Pressure Physics, Theor. Phys.&Mathematic. Methods, Moscow Region 142092, Troitsk, RUSSIAN FEDERATION.

Makhov Dmitry Viktorovich (Nationality: Russian Federation), University of Montreal, Department of Physics, CP 6128 Succursale Centre-Ville, Quebec, Montreal H3C 3J7, CANADA.

Mertig Ingrid (Nationality: Germany), Martin-Luther-Universität Halle-Wittenberg, Fachbereich Physik, 06099 Halle, GERMANY.

Meskini Noureddine (Nationality: Tunisia), Université de Tunis, Faculté Des Sciences, Departement de Physique, Campus Universitaire 1060, Tunis, TUNISIA.

Meza Aguilar Salvador (Nationality: Mexico), Av. 15 de Septiembre, #1715 Colonia 10 de Mayo Sinaloa, C.P. 80270 Culiacan, MEXICO.

Miyake Takashi (Nationality: Japan), Tokyo Institute of Technology (Tokyo Kogyo Daigaku), Department of Physics, 2-12-1 Oh-Okayama Meguro-Ku, 152-8551 Tokyo, JAPAN.

Molly de Raychaudhury Molly (Nationality: India), Max-Planck-Institut für Festkorperforschung, Heisenbergstrasse 1, Postfach 80 06 65, D-70506 Stuttgart, GERMANY.

Muslih Sami Ismail (Nationality: Gaza Strip), Al-Azhar University, Department of Physics, P.O. Box 1277 (Via Israel), Gaza, GAZA STRIP.

Needs Richard James (Nationality: United Kingdom), Cambridge University, Theory of Condensed Matter Group - Cavendish Laboratory, Department of Physics, Madingley Road, CB3 0HE, Cambridge, UNITED KINGDOM.

Nguyen Hoang Oanh (Nationality: Viet Nam), Hanoi University of Science, Department of Physics, 33 Nguyen Trai Str., Thanh Xuan, Hanoi, VIET NAM.

Okoye Chukwuemeka Madubuko Ijeoma (Nationality: Nigeria), University of Nigeria, Faculty of Physical Sciences, Dept. Physics & Astronomy, Enugu State, Nsukka, NIGERIA.

Onwuagba Beniah Ndudim (Nationality: Nigeria), Federal University of Technology, School of Sciences, Department of Physics, Private Mail Box 1526, Owerri, NIGERIA.

Patterson Charles (Nationality: Ireland), University of Dublin, Trinity College, Department of Physics, 2 Dublin, IRELAND.

Paudyal Durga (Nationality: Nepal), S.N.(Satyendra Nath) Bose National Centre for Basic Sciences, Block-JD, Sector-III, Salt Lake City, 700 098 Kolkata, INDIA.

Pavarini Eva (Nationality: Italy), Max-Planck-Institut für Festkorperforschung, Heisenbergstrasse 1, Postfach 80 06 65, D-70506 Stuttgart, GERMANY.

Peletminsky Alexander (Nationality: Ukraine), National Academy of Sciences of Ukraine, Electrophysical Scientific and Technical Centre, Chernishevsky Str. 28, P.O. Box 8812, 61002 Kharkov, UKRAINE.

Pentcheva Rossitza Vladimirova (Nationality: Bulgaria), Ludwig-Maximilians Universitaet, Munchen, Sektion Kristallographie Umweltwissenschaften, Theresienstrasse 41, 80333 Munich, GERMANY.

Perlov Oleksandr (Alexander) (Nationality: Ukraine), Stoeberlstr 52, 80686 Munich, GERMANY.

Pickett W.E. (Nationality: United States of America), University of California at Davis, Department of Physics, One Shields Avenue, CA 95616-8677, Davis, UNITED STATES OF AMERICA.

Poteryaev Alexander (Nationality: Russian Federation), University of Nijmegen, Department of Physics, Toernooiveld 1, NL-6500 GL Nijmegen, NETHERLANDS.

Ropo Matti Sakari (Nationality: Finland), University of Turku, Department of Physics, SF-20500 Turku, FINLAND.

Rozenberg Marcelo Javier (Nationality: Argentina), Universidad de Buenos Aires, Fac. Ciencias Exactas y Naturales, Departamento de Fisica, Pabellon I Ciudad Universitaria Intendente Cantilo 2620, 1428 Buenos Aires, ARGENTINA.

Rubio Angel (Nationality: Spain), Universidad del Pais Vasco (the University of the Basque Country), Facultad de Quimica Upv/Ehu, Departamento de Fisica, Apartado 1072, 20080 San Sebastian, SPAIN.

Rubtsov Alexey Nickolaevich (Nationality: Russian Federation), Moscow State University, Department of Physics, Vorobuevy Gory 119992, Moscow, RUSSIAN FEDERATION.

Saffarini Ghassan M. (Nationality: West Bank), An-Najah National University, Department of Physics, P.O. Box 7, 707 Nablus, WEST BANK.

Saffarzadeh Ali Reza (Nationality: Islamic Republic of Iran), Payame Noor University, Physics Department, Center of Tehran Nejatollahi St. Fallahpour St. Tehran, ISLAMIC REPUBLIC OF IRAN.

Sakho Oumar (Nationality: Senegal), Université Cheikh Anta Diop de Dakar, Faculté Des Sciences, Departement de Physique, Dakar, SENEGAL.

Salamin Yousef Is-Haq (Nationality: West Bank), Birzeit University, Faculty of Science, Department of Physics, P.O. Box 14, Palestine, Birzeit, WEST BANK.

Sangiovanni Giorgio (Nationality: Italy Universitá degli Studi di Roma 'La Sapienza', Dipartimento di Fisica, Piazzale Aldo Moro 2, 00185 Roma, Italy.

Sarkarati Saeed (Nationality: Islamic Republic of Iran), Shahid Beheshti University, Laser Research, Center Magnetooptic Laboratory, Evin 1983963113 Tehran, ISLAMIC REPUBLIC OF IRAN.

Savrasov Sergej (Nationality: Russian Federation), New Jersey Institute of Technology, Department of Physics, 161 Warren Street, NJ 07102-1982, Newark, UNITED STATES OF AMERICA.

Schindlmayr Arno (Nationality: Germany), Forschungzentrum Julich GmbH, Institut für Festkorperforschung, D-52425 Julich, GERMANY.

Schulthess Thomas (Nationality: United States of America), Oak Ridge National Laboratory, Computational Materials Science, Bethel Valley Road, Bldg. 6025, Oak Ridge, TN 37831-6359, UNITED STATES OF AMERICA.

Sekiyama Akira (Nationality: Japan), Osaka University. Graduate School of Engineering, Science Division of Material Sciences, D. of Physical Sciences, 1-3 Machikaneyama-Cho, Toyonaka 560, 8531 Osaka, JAPAN.

Sekkal Wassila (Nationality: Algeria), Kaindlstrasse 39, 70569 Stuttgart, GERMANY.

Sheng Zheng-Mao (Nationality: People's Republic of China), Zhejiang University, Department of Physics, 310028 Hangzhou, PEOPLE'S REPUBLIC OF CHINA.

Siljamaki Sami Pekka (Nationality: Finland), Helsinki University of Technology, Laboratory of Physics, P.O. Box 1100, 02015 Hut, FINLAND.

Syassen Karl (Nationality: Germany), Max-Planck-Institut für Festkorperforschung, Heisenbergstrasse 1, Postfach 80 06 65, D-70506 Stuttgart, GERMANY.

Szotek Zdzislawa (Nationality: Belgium), Council for the Central Laboratory of the Research Councils, Daresbury Laboratory, Computational Sci.& Eng. Department, Cheshire, Warrington, WA4 4AD, Daresbury, UNITED KINGDOM.

Taraphder Arghya (Nationality: India), Indian Institute of Technology, Dept. of Physics & Meteorology, District Midnapur, West Bengal, 721 302 Kharagpur, INDIA.

Temmerman Walter (Nationality: Belgium), Daresbury Laboratory, Keckwick Lane, WA4 4AD, Warrington, Daresbury, UNITED KINGDOM.

Toschi Alessandro (Nationality: Italy), Via C. Mirabello N. 6 00195 Roma, ITALY.

Vaitheeswaran Ganapathy Subramanian (Nationality: India), Max-Planck-Institut für Festkorperforschung, Heisenbergstrasse 1, Postfach 80 06 65, D-70506 Stuttgart, GERMANY.

Van Der Marel Dirk (Nationality: The Netherlands), University of Geneva D.P.M.C. - Departement de Physique de La Matiere Condensee, 24 Quai Ernest-Ansermet, CH-1211 (4) Geneva, SWITZERLAND.

Vast Nathalie (Nationality: France), Ecole Polytechnique Laboratoire Des Solides Irradies, Route de Saclay, F-91128 CEDEX Palaiseau, FRANCE.

Vildosola Veronica Laura (Nationality: Argentina), Comision Nacional de Energia Atomica, Unidad de Actividad Fisica, Av. Gral. Paz 1429 Pcia de Buenos Aires, 1650 San Martin, ARGENTINA.

von Boehm Juhani (Nationality: Finland) Helsinki University of Technology, Laboratory of Physics, P.O. Box 1100, Otakaari 1, HUT-02015 Espoo, FINLAND.

Vu Ngoc Tuoc (Nationality: Viet Nam), Universitat Gesamthochschule Paderborn, Theoretische Physik, Postfach 1621, Warburger Strasse 100, D-33095 Paderborn, GERMANY.

Wague Ahmadou (Nationality: Senegal), Université Cheikh Anta Diop de Dakar, Faculté Des Sciences, Departement de Physique, Dakar, SENEGAL.

WahnÛn Perla (Nationality: Spain), Universidad Politecnica de Madrid, Instituto de Energia Solar - ETSI Telecomunicaciones Ciudad Universitaria, E-28040 Madrid, SPAIN.

Wierzbowska Malgorzata (Nationality: Poland), University of Dublin, Trinity College, Department of Physics, 2 Dublin, IRELAND.

Yamasaki Atsushi (Nationality: Japan), Max-Planck-Institut fuer Festkoerperphysik, Heisenbergstrasse 1, D-70569 Stuttgart, GERMANY.

Zaoui Ali (Nationality: Algeria), Max-Planck-Institut für Metallforschung, Seestrasse 92, D-70174 Stuttgart, GERMANY.

Zarand Gergely (Nationality: Hungary), Technical University of Budapest, Institute of Physics XI. Budafoki Ut 8, 1111 Budapest, HUNGARY.

Zeyn Nikolay Evgenievich (Nationality: Russian Federation), Kurchatov Institute of Atomic Energy, Kurchatov Square 1, 123182 Moscow, RUSSIAN FEDERATION.

Zhang Shiwei (Nationality: People's Republic of China), College of William and Mary, Virginia, Department of Physics Va, 23187-8795 Williamsburg, UNITED STATES OF AMERICA.

ZHAO Junxiao (Nationality: People's Republic of China), Academy of Mathematics and System Sciences Institute of Computational Mathematics, Scientific Engineering Computing, P.O. Box 2719, Beijing 100080, PEOPLE'S REPUBLIC OF CHINA.

Zhukov Vladlen (Nationality: Russian Federation), Donostia International Physics Center Manuel de Lardizabal, 4 Donostia, E-20018 San Sebastian, SPAIN.

Zorkani Izeddine, Morocco, Universite' Sidi Mohamed Ben Abdellah, Fac. Des Sciences Dhar Elmahraz Departement de Physique, B.P. 1796 Atlas Dhar El Mahraz Fes, MOROCCO.

Zwicknagl Gertrud (Nationality: Germany), Technische Universitat Braunschweig Institut für Theoretische Physik, Mendelsohnstrasse 3, Postfach 33 28 38106 Braunschweig, GERMANY.

Abstracts

Optical response of nanostructures and bulk systems within Time-Dependent Density-Functional-Theory

Angel Rubio, Alberto Castro, Miguel Marques and Andrea Marini
Departamento Fisica de Materiales, UPC, Centro Mixto CSIC-UPV and DIPC,
San Sebastián, Spain
Valerio Olevano, Lucia Reining
Laboratoire des Solides Irradiés, UMR 7642 CNRS/CEA,
École Polytechnique, F-91128 Palaiseau, France

Abstract

In the present talk I will review the recent developments in the calculation of the optical spectra of nanostructures (clusters, biomolecules, etc) and extended systems withing time-dependent-density functional theory. We will show results obtained with the new implementation of TDDFT that allows to handle equally linear and nonlinear effects. We will present the deficiencies of the available functionals to handle excitonic effects in the spectra of semiconductors and insulators. We will provide a robust an efficient exchange-correlation

kernel derived from a Mny-Body approach that works extremely well for the description of bulk materials (in particular results will be shown for the bound excitons of LiF, and resonant ones in SiO_2). Applications to the lifetime of insulators will be done at the end of the talk.

This work was supported by the European Community Research Training Networks NANOPHASE (HPRN-CT-2000-00167) and COMELCAN (HPRN-CT-2000-00128), by Spanish MCyT(MAT2001-0946) and University of the Basque Country (9/UPV 00206.215-13639/2001). The computer time was granted by CEPBA and DIPC. The authors also gratefully acknowledge fruitful discussions with E.K.U Gross, G.F. Bertsch, K. Yabana, L. Wirtz, D. Varsano and C.A. Rozzi.

References:

- G. Onida, L. Reining and A. Rubio, *Electronic Excitations: Density-Functional versus Many-body Green's-Functions Approaches* Reviews of Modern Physics **74** 601-659 (2002)
- A. Castro, M.A.L. Marques, J.A Alonso, G.F. Bertsch, K. Yabana and A. Rubio *Can optical spectroscopy directly elucidate the ground state of C20 ?* Journal of Chemical Physics **118**, 1930-1934 (2002)
- L. Reining, V. Olevano, A. Rubio and G. Onida, *Excitonic effects in solids described by time-dependent density functional theory*, Physical Review Letters **88** 066404-1,4 (2002)
- G.F. Bertsch, J.-I. Iwata, A. Rubio and K. Yabana, *A Real-Space, Real-Time Method for the Dielectric Function*, Physical Review B **62**, 7998-8002 (2000)
- M.A.L. Marques, A. Castro, G.F. Bertsch and A. Rubio, *Octopus: a first-principles tool for excited electron-ion dynamics*, Computer Physics Communications **151/1** 60-78 (2003)
- M.A.L Marques, X. Lopez, D. Varsano, A. Castro, and A. Rubio, *Time-Dependent Density-functional approach for biological photoreceptors: the case of the Green Fluorescent Protein*, Physical Review Letters **90**, 158101-1,4 (2003)
- A. Castro, M.A.L. Marques, J.A Alonso, G.F. Bertsch, and A. Rubio, *Excited states dynamics in time-dependent density functional theory: high-field molecular dissociation and harmonic generation*, submitted for publication
- A. Marini, R. Del Sole and A. Rubio, *Bound excitons in time–dependent density–functional–theory: optical and energy–loss spectra*, submitted for publication.

Non-self-consistent and self-consistent GW calculations for spectral and ground-state properties

K. T. Delaney, T. Gould
Department of Physics, University of York, Heslington, York YO10 5DD, United Kingdom

P. García-González
Departamento de Fisíca de la Materia Condensada, Universidad Autonoma de Madrid, Madrid, Spain

P. Rinke, R. W. Godby
Department of Physics, University of York, Heslington, York YO10 5DD, United Kingdom

Abstract

The GW approximation is the first-order term in an expansion of the self-energy operator Σ in powers of the dynamically screened electron-electron interaction, W. The choice of whether G and/or W are made to be consistent with the Green's function that arises *from* Σ leads to three principal variants: the non-self-consistent G_0W_0, the partially self-consistent GW_0 and the fully self-consistent GW, where G_0 generally indicates the LDA Green's function. There is now considerable experience regarding the quality of *ab initio* G_0W_0 calculations of quasiparticle and spectral properties. However, GW_0 and GW are known to have important conservation properties [1] which G_0W_0 lacks, which may be of particular importance for the calculation of integrated quantities such as the ground-state total energy.

I shall present results for atoms, jellium spheres, and bulk solids at all three levels of self-consistency, covering both spectral properties and the ground-state total energy. These include converged first results resulting from the incorporation of self-consistency and GW total-energy techniques into our general-purpose "space-time" supercell code suite [2,3], which interfaces with pseudopotential plane-wave DFT calculations as its input. This allows the extension of the GW total-energy approach from high-symmetry test systems [e.g. 4,5] to general systems, and opens the possibility of applications to systems whose energetics is not described sufficiently reliably within the usual DFT-based approaches.

[1] "Diagrammatic self-energy approximations and the total particle number", Arno Schindlmayr, P. García-González and R. W. Godby, Phys. Rev. B **64** 235106 (2001).

[2] "Space-time method for *ab initio* calculations of self-energies and dielectric response functions of solids", H. N. Rojas, R. W. Godby and R. J. Needs, Phys. Rev. Lett. **74** 1827 (1995).

[3] "The GW space-time method for the self-energy of large systems", Martin M. Rieger, L. Steinbeck, I. D. White, H. N. Rojas and R. W. Godby, Computer Physics Communications **117** 211-228 (1999).

[4] "Self-consistent calculation of total energies of the electron gas using many-body perturbation theory", P. García-González and R. W. Godby, Phys. Rev. B **63** 075112 (2001).

[5] "Many-body GW calculations of ground-state properties: quasi-2D electron systems and van der Waals forces", P. García-González and R. W. Godby, Phys. Rev. Lett. **88** 056406 (2002).

Further details at http://www-users.york.ac.uk/∼rwg3/.

Electron transport through carbon nanotubes

Colin J. Lambert, S. Bailey, S. Athanasopoulos and I. Grace

Dept. of Physics, Lancaster University, Lancaster LA1 4YB, United Kingdom.

Abstract

Transport properties through three structures involving carbon nanotubes are examined. First, when a carbon nanotube undergoes a geometric distortion over part of its length, electrical conductance can be strongly modified, producing a non-linear I-V characteristic and a novel interplay between geometric twist and the chirality of an axial magnetic field. Secondly, when a carbon nanotube makes contact with ferromagnetic electrodes, the resulting

structure exhibits giant magnetoresistance associated with conductance step edges, which can be estimated using a simple single-band model. Material-specific results for a carbon nanotube coated with nickel are also presented. Thirdly, when a nanotube is inserted into another nanotube of larger diameter, the electrical conductance is an oscillatory function of the length of the insertion.

Results for the size of this effect are presented.

Full-potential GW method: semi self-consistent results

Sergey Faleev
Sandia National Laboratories

Mark van Schilfgaarde
Depr. of Chem. and Mater. Engineering, Arizona State University

Takao Kotani
Dept. of Physics, Osaka University

Abstract

We present a newly-developed all-electron full-potential *GW* approximation (GWA) based on the full-potential LMTO scheme. (The GWA code is also connected to a FP-LAPW code.) The dynamically-screened Coloumb interaction *W* is expanded into a mixed basis set, which is suitable for the expansion. Core and valence states can be treated on an equal footing. To our knowledge, all other implementations of the full-potential GWA calculate the self-energy from the valence electrons only and subtract $V_{\rm xc}$ from the corresponding valence density.

In addition to the usual "non self-consistent(SC)" $\Sigma^0 = G^0W^0$ results, we show results of a semi SC GWA. We construct a static, hermitian $\tilde{\Sigma}$, which is the "best possible" approximation to the full self-energy Σ, and iterate $\tilde{\Sigma}$ to self-consistency. A couple of variants to $\tilde{\Sigma}$ have been implemented, which will be described.

Our calculation is now in principle not dependent on LDA any more, though we still use it as a technique to prepare good basis sets. The purpose of our semi SC method is rather to get the "best one-particle picture" as in the Landau theory; so our method may be advantageous to the full SC *GW* method in this sense. In our opinion, we might not stick to the full self-consistent *GW*; further correlation effects not in *GW* might be rather easily included in our semi SC *GW* than the full scheme. The CPU time of otherwise numerically prohibited semi SC *GW* simulations has been reduced by an order of magnitude utilizing the method of Hilbert-transformation along real-axis for the polarization operator.

The results obtained for band gaps, semicore levels, and effective masses of many semiconductors and insulators are in excellent agreement with the experimental values, noticeably better then results obtained in the G^0W^0 approximation. In some cases, such as InN, CdO, and ZnO, self-consistency is essential. Small, but systematic errors remain, the most prominent being a slight tendency to overestimate the $\Gamma_{15v} \rightarrow \Gamma_{1c}$ transition. For NiO and MnO, our results are somewhat similar to LDA+U results. In each case the calculated bandgap is in good agreement with experiment. Further we will show some preliminary results for metals like Cu and Ni.

The *GW* Approximation within a Density-Functional Context

Arno Schindlmayr

Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany

Abstract

In practical applications, the perturbative implementation of the *GW* approximation, in which the self-energy is evaluated non-self-consistently with Kohn-Sham orbitals, is known to yield accurate quasiparticle band structures, especially for semiconductors and simple metals. The apparent shortcomings of this approach, such as the violation of certain sum rules, have also been highlighted. In order to remedy these problems, I derive a perturbation series for the exact quasiparticle energies within density-functional theory, designed such that the first-order term includes dynamic screening and closely resembles the non-self-consistent *GW* approximation. The scheme is internally consistent, fulfills all sum rules and provides a systematic procedure for generating higher-order corrections beyond the *GW* approximation. The performance of the *GW* method for dimensionally reduced systems is then tested in calculations for surface states and point defects on semiconductor surfaces. For the defect states and the charge-transition levels of anion vacancies on GaAs(110) and InP(110), the results indeed show a clear improvement over values obtained with the local-density approximation and are in close agreement with experimental measurements.

Spectral Density Functional Theory and Linear Response Calculations

S. Y. Savrasov

New Jersey Institute of Technology, Newark, NJ 0702, USA

Abstract

Density functional theory (DFT) known to work well for weakly correlated materials fails to attack real strongly correlated phenomena, and recent progress in understanding those using many-body model-hamiltonian-based dynamical mean-field theory (DMFT) has triggered developments of new approaches for computational material science in searching for alternatives to DFT. In this talk, one of such new techniques, a spectral density functional theory [1], which considers total free energy as a functional of a local electronic Green function, will be discussed. Local dynamical mean-field theory is seen as an approximation within this functional approach, which can be used for practical calculations of total energies, spectra, linear response functions and other properties. Illustrations of the method for systems such as Plutonium [1,2] and Mott Insulators [3] will be given.

[1] S. Savrasov, G. Kotliar, and E. Abrahams, Nature 410, 793 (2001).

[2] X. Dai, S. Y. Savrasov, G. Kotliar, A. Migliori, H. Ledbetter, E. Abrahams, Science 300, 953 (2003).

[3] S. Savrasov and G. Kotliar, Phys. Rev. Lett. 90, 056401 (2003).

M. Capone
Enrico Fermi Center, Rome, Italy.

M. Fabrizio, E. Tosatti
International School for Advanced Studies (SISSA-ISAS)
and
Istituto Nazionale per la Fisica della Materia (INFM), Via Beirut 2, 34014 Trieste, Italy
and
International Center for Theoretical Physics (ICTP), Strada Costiera 11, 34014 Trieste, Italy.

C. Castellani
Physics Department and INFM, Unitá Roma 1, University of Rome ”La Sapienza”, Piazzale A, Moro, 2, 00185 Rome, Italy.

Abstract

High-temperature superconductivity in doped Mott insulators like the cuprates denies the conventional belief that electron repulsion is detrimental to superconductivity.

We discuss a parallel situation in the alkali fullerides which, even if lacking the cuprate's spectacular T_c's, are no lesser puzzle. The repulsive electron correlations in fullerides are of comparable strength to the cuprates: yet trivalent fullerides are superconductors with an isotropic *s*-wave order parameter. We present theoretical studies of a model for alkali fullerides which reveals, in presence of a weak pairing attraction (here of Jahn-Teller origin), an unsuspected superconducting pocket near the Mott transition. We show that superconducting pairing does not only avoid frustration by strong electron-electron repulsion, but actually takes vast advantage from it (M. Capone, M. Fabrizio, C. Castellani, and E. Tosatti, Science 296, 2364 (2002)).

The above result may be understood in terms of a strong screening of the repulsive interaction, while the electron-phonon attraction, though smaller, stays unrenormalized even close to the Mott transition. This scenario is really similar in spirit to the original RVB proposal by P.W. Anderson.

We suggest that this mechanism is common to a wider class of strongly correlated models, including other models where the pairing has a Jahn-Teller origin, like a lattice of E × e Jahn-Teller centers in the presence of a strong repulsion, as well as models proposed for the cuprates.

Diffusion quantum Monte Carlo for condensed matter systems

R.J. Needs, M.D. Towler, N.D. Drummond, J.R Trail, Z. Radnai
TCM Group, Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK

R.Q. Hood
Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

P.R.C. Kent
University of Cincinnati, Cincinnati, Ohio 45221, USA

P.R. Briddon

Department of Physics, The University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK

Abstract

Fixed-node diffusion quantum Monte Carlo (DMC) is one of the most accurate methods known for calculating the energies of correlated many-electron systems. The computational cost scales as the cube of the system size, which is very favourable when compared with other correlated wave function methods. The key ingredient in a DMC calculation is an approximate wave function which guides the sampling of configuration space and fixes the nodal surface of the DMC wave function. We normally use Slater-Jastrow wave functions which consist of a determinant, or sum of determinants, multiplied by a Jastrow correlation function. The various sources of error in DMC calculations for condensed matter systems will be discussed.

DMC calculations of the ground and excited state energetics of the neutral vacancy defect in diamond will be reported. The multiplet structure of the defect is modeled using guiding wave functions with symmetrised multi-determinant Slater parts. For the ground state we obtain the ^1E state in agreement with experiment. The calculated energy of the lowest dipole allowed transition is consistent with the experimentally observed GR1 band. The calculated multiplet splitting of over 2 eV indicates the importance of a proper treatment of electron exchange and correlation in this system.

DMC calculations for three-dimensional Wigner crystals will also be reported. Very accurate calculations are required to obtain reliable values of the fluid/crystal transition densities and the guiding wave functions are optimized within DMC. We compare our crystal data with the recent fluid DMC data of Zong, Lin, and Ceperley, and find a transition density of $r_s = 106 \pm 1$. We also compare our DMC data with Hartree-Fock results, which allows us to understand the effects of correlation on Wigner crystals.

Realistic quantum Monte Carlo calculations using auxiliary fields

Shiwei Zhang and Henry Krakauer

College of William and Mary, Williamsburg, VA 23187, USA

Abstract

Quantum Monte Carlo (QMC) methods based on Hubbard-Stratonovich auxiliary fields have been used in many-body theory primarily in two forms: direct simulation for “simple” models such as the Hubbard model *and* as the impurity solver in DMFT. We have developed a quantum Monte Carlo method [1] with complex auxiliary fields for treating more realistic interactions. This is a many-body method that shares much of the machinery of more traditional electronic structure methods. As such, it provides a natural and systematic framework to go beyond standard mean-field approaches. The method projects out the many-body ground state by random walks in the space of Slater determinants. An approximate approach is formulated to control the phase problem with a trial wave function. The

method allows the use of any one-particle basis. Using a plane-wave basis and non-local pseudopotentials, we apply the method to Be, Si, P atoms and dimers, and to bulk Si with 2, 16, 54 atom (216 electrons) supercells. Single Slater determinant wave functions from density functional theory calculations were used as the trial wave function with no additional optimization. The calculated dissociation energy of the dimer molecules and the cohesive energy of bulk Si are in excellent agreement with experiment and are comparable to or better than the best existing theoretical results.

[1] Shiwei Zhang and Henry Krakauer, Phys. Rev. Lett. **90** 136401 (2003).

Surface physics with quantum Monte Carlo

Claudia Filippi
Universiteit Leiden, Instituut Lorentz, Leiden, The Netherlands

Sorcha B. Healy
NMRC Research Institute, National University of Ireland, Cork, Ireland

P. Kratzer, M. Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin-Dahlem, Germany

E. Pehlke
Institut für Laser und Plasmaphysik, Universität Essen, Essen, Germany

Abstract

The dissociative adsorption of molecular hydrogen on the Si(001) surface has become a paradigm in the study of adsorption systems. Despite its apparent simplicity and extensive experimental and theoretical investigations, fundamental aspects of the chemical reaction of H_2 with this surface have not been clarified. Theoretically, density functional theory (DFT) calculations on extended slab geometries lead to limited agreement with experiments, and, for small model clusters of the surface, are at variance with highly correlated quantum chemistry calculations.

We revisit the topic using large model clusters of the surface and pseudopotential quantum Monte Carlo (QMC) methods to accurately account for electronic correlations. Our many-body calculations predict reaction energies and barriers noticeably higher than those obtained in DFT, pointing to the inadequacy of the local density or commonly used generalized gradient approximations to describe the Si–H bond. QMC improves upon DFT by yielding adsorption barriers that account theoretically for the tiny sticking coefficient of H_2 on the clean surface. Finally, our calculations corroborate the existence of a barrier-less high-coverage mechanism recently proposed experimentally, and represent an important input for the interpretation of desorption experiments.

Recent developments in the Hubbard model metal-insulator transition

Marcelo J. Rozenberg
Departamento de Física, Ciudad Universitaria Pab.I, FCEN, Universidad de Buenos Aires, Buenos Aires 1428, Argentina

Abstract

In this talk we shall present recent advances in the investigation of the metal-insulator transition in the Hubbard model within the framework of Dynamical Mean Field Theory. Several topics shall be consider such as: the Guinzburg-Landau scenario and its relation with recent experiments in V_2O_3 and layered organics, photoemission spectroscopy and the doping driven antiferromagnetic-paramagnetic metal insulator transition.

The Cerium volume collapse:
An LDA+ DMFT study

K. Held
Max-Planck-Institut für Festkörperforschung, D-70569 Stuttgart, Germany

A. K. McMahan
Lawrence Livermore National Laboratory, University of California, Livermore, CA 94550, USA

R. T. Scalettar
Department, University of California, Davis, CA 95616, USA

Abstract

We have calculated thermodynamic and spectral properties of Ce metal over a wide range of volume and temperature, including the effects of $4f$ electron correlations, by the merger of the local density approximation and dynamical mean field theory (DMFT). The DMFT equations are solved using the quantum Monte Carlo technique supplemented by the more approximate Hubbard I and Hartree Fock methods. At large volume we find Hubbard split spectra, the associated local moment, and an entropy consistent with degeneracy in the moment direction. On compression through the volume range of the observed γ-α transition, an Abrikosov-Suhl resonance begins to grow rapidly in the $4f$ spectra at the Fermi level, a corresponding peak develops in the specific heat, and the entropy drops rapidly in the presence of a persistent, although somewhat reduced local moment. Our parameter-free spectra agree well with experiment at the α- and γ-Ce volumes, and a region of negative curvature in the correlation energy leads to a shallowness in the low-temperature total energy over this volume range which is consistent with the γ-α transition. As measured by the double occupancy, we find a noticeable decrease in correlation on compression across the transition; however, even at the smallest volumes considered, Ce remains strongly correlated with residual Hubbard bands to either side of a dominant Fermi-level structure. These characteristics are discussed in light of current theories for the volume collapse transition in Ce.

[1] K. Held, A. K. McMahan, and R. T. Scalettar, Phys. Rev. Lett. 87, 276404 (2001); A. K. McMahan, K. Held, and R. T. Scalettar, Phys. Rev. B 67, 075108 (2003).

Self Interaction Corrected Electronic Structure Calculations for Correlated Systems

W. Temmerman, Z. Szotek and M. Lueders
Daresbury Laboratory

A. Svane
Institute of Physics and Astronomy, University of Aarhus

L. Petit
Center for Computational Sciences, Oak Ridge National Laboratory

P. Strange
Department of Physics, University of Keele

A. Ernst
MPI Halle

D. Koedderitzsch
University of Halle

H. Winter
INFP, Forschungszentrum Karlsruhe

Abstract

An overview is given of applications of SIC-LSD calculations for correlated d and f electron systems. In particular it is shown that SIC-LSD splits d and f bands into a manifold of localized states, occuring well below the bottom of the valence band, and a band-like manifold represented essentially by the LSD potential. This split of the states allows for the introduction of the concept of nominal valence, which is the number of electrons left on the site to participate in band formation. Examples, such as the progression of trivalent to divalent to trivalent to divalent through the rare earth series will demonstrate these concepts. In another example, using Yb compounds, a comparison will be made with a semi-phenomelogical method of calculating valences. Applications to actinides and actinide compounds such as PuO_2 will be presented as well as some selected applications to d electron systems, namely Fe_3O_4 and $La_{0.7}Sr_{0.3}MnO_3$. Finally we remark that SIC-LSD is a scheme well suited to describe static correlations when the electrons are well localized. A road map will be presented how to incorporate dynamic correlations.

Bulk-sensitive high-energy photoemission study of strongly correlated systems

Akira Sekiyama
Graduate School of Engineering Science, Osaka University, Japan

Abstract

High-resolution photoemission spectroscopy (PES) is a powerful tool to investigate detailed occupied electronic states near the Fermi level (E_F) of strongly correlated systems. Low-energy excitation lights have so far been employed for high-resolution measurements. However, there is a drawback in the low-energy PES caused by short photoelectron mean free path (<5 Å), namely, the low-energy PES spectra of the strongly correlated systems mainly reflect the surface electronic states deviated from the bulk states. The high-energy ($h\nu$ ~1000 eV) and high-resolution valence-band PES, which has recently become a reality [1], is a more direct and promising technique to reveal the bulk electronic states owing to its longer mean free path of photoelectrons. We demonstrate some results of the high-energy PES applied for strongly correlated d and f electron systems including CeB_6, $CeRu_2Si_2$, CeNi, $CeRu_2$, $Sr_{1-x}Ca_xVO_3$ $Sr_{2-x}Ca_xRuO_4$ and so on $[2-4]$.

[1]A. Sekiyama *et al.*, Narure **403**, 396 (2000).

[2]A. Sekiyama *et al.*, J. Phys. Soc. Jpn. **69**, 2771 (2000).

[3]A. Sekiyama and S. Suga, Physica B **312-313**, 634 (2002).

[5]A. Sekiyama *et al.*, cond-mat/0206473.

Optical signatures of strong electron correlations in transition metal mono-sillicides

F. P. Mena, D. van der Marel
Materials Science Centre, University of Groningen, 9747 AG Groningen, The Netherlands

A. Damascelli
Department of Physics and Astronomy, University of British Columbia, Vancouver, British Columbia, V6T 1Z1 Canada

M. Fäth, A. A. Menovsky and J. A. Mydosh
Kamerlingh Onnes Laboratory, Leiden University, 2500 RA Leiden, The Netherlands

G. Aeppli
London Centre for Nanotechnology, Gower Street, London WC1E 6BT, UK

J. F. DiTusa
Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803

Abstract

The optical spectra of a number of solids are known to exhibit a shift of spectral weight over a large energy scale when a phase transition occurs. The magnetism of MnSi and Co-doped FeSi is commonly attributed to itinirant charge carriers[1, 2]. For MnSi this is confirmed by the observation of a narrow Drude-like peak in the optical spectra at low temperatures[3]. Yet the spectral weight in this peak is small, indicating that the charge carriers are rather heavy. When MnSi is cooled below 100 K the effective mass develops a strong frequency dependence at low frequencies, while the scattering rate develops a sub linear frequency dependence.[3] The complex optical conductivity can be described by

the phenomenological relation $\sigma(\omega, T) \propto (\Gamma(T) + i\omega)^{-0.5}$, significantly different from conventional Drude behaviour, indicating a strong coupling of the itinirant charge carriers to spin-fluctuations or other collective modes. FeSi has a gradual transition from a metal at room temperature to a semiconductor with a gap of 60 meV at 4 Kelvin. Whether or not the spectral weight which is removed due to the opening of the gap in FeSi is recovered in the frequency range just above the 60 meV gap, has been the subject of a controversy since 1993[4, 5, 6]. Here we present experimental data, showing that the spectral weight which is removed due to the opening of the gap in FeSi is not recovered up to 5 eV, which is the upper frequency limit of our experimental window. This indicates the role of strong electron correlations in the physical properties of the mono-sillicides[7, 8]. Partial or total substitution of Fe with Co and or Mn results in a suppression of the semi-conductor gap, again without recovery of the spectral weight on a low energy scale.

References

[1] C. Pfleiderer, S.R. Julian and G.G. Lonzarich, Nature **414**, 427-430 (2001).

[2] N. Manyala, Y. Sidis, J. F. DiTusa, G. Aeppli, D. P. Young and Z. Fisk, Nature **404**, 581 (2000).

[3] F. P. Mena, D. van der Marel, A. Damascelli, M. Fäth, A. A. Menovsky, and J. A. Mydosh Phys. Rev. B **67**, 241101 (2003).

[4] Z. Schlesinger,Z. Fisk, Hai-Tao Zhang, M. B. Maple, J. F. DiTusa, G. Aeppli, Phys. Rev. Lett. **71**, 1748 (1993).

[5] L. Degiorgi, M. B. Hunt, H. R. Ott, M. Dressel, B. J. Feenstra, G. Grüner, Z. Fisk, P. Canfield, Europhys. Lett. **28**, 341 (1994).

[6] A. Damascelli, K. Schulte, D. van der Marel, A. A. Menovsky,hys. Rev. B **55**, R4863 (1997).

[7] M. J. Rozenberg, G. Kotliar and H. Kajueter, Phys. Rev. B **54**, 8452 (1996).

[8] C. Fu and S. Doniach, Phys. Rev. B **51**, 17439 (1995); cond-mat/0002160.

Metal-insulator transition in orthorhombic 3d^{1}1 perovskites

E. Pavarini
INFM and Dipartimento di Fisica "A. Volta", Università di Pavia, Via Bassi 6, I-27100 Pavia, Italy

S. Biermann, A. Georges
LPT-ENS CNRS-UMR 8549, 24 Rue Lhomond, 75231 Paris Cedex 05, France

A. Poteryaev, A.I. Lichtenstein
NSRIM,University of Nijmegen, NL-6525 ED Nijmegen, The Netherlands

O.K. Andersen
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

Abstract

Using the first-principles downfolding technique, a low-energy Hamiltonian is derived for several $3d^1$ transition metal oxides. Electronic correlations are included by combining this approach with an implementation of dynamical mean-field theory appropriate for non-cubic systems. Good agreement with photoemission data is obtained. The interplay of correlation effects and structural distortions is found to strongly suppress orbital fluctuations in both $YTiO_3$ and $LaTiO_3$ (in the latter less strongly), and to favor the transition to the insulating state.

Transition metal oxides at high pressures

K. Syassen
MPI fuer Festkoerperforschung, Stuttgart

Abstract

Recent EXPERIMENTAL high-pressure investigations of materials with correlated *d* electrons will be reviewed, covering results from combined structural, spectroscopic, and transport studies. The effect of pressure on charge transfer gaps and intra-ionic (d-d) excitations in insulating monoxides will be addressed briefly. The main focus will be on perovskite-related oxides, specifically insulating manganites and ferrates. When compressed, these materials are driven across the insulator-metal (IM) borderline. The interplay between structural, vibrational, and electronic properties near the pressure-driven IM transition is of particular interest, involving the suppression of Jahn-Teller distortions or the collapse of charge disproportion phenomena.

First-principles approach to strongly correlated systems: GW+DMFT

Silke Biermann*, Ferdi Aryasetiawan** and Antoine Georges*
**LPT, l'Ecole Normale Superieure, Paris and Laboratoire de Physique des Solides, Orsay*
***Research Institute for Computational Sciences, Tsukuba, Ibaraki 305-8568 Japan*

Abstract

We propose a dynamical mean-field approach for calculating the electronic structure of strongly correlated materials from first principles. The scheme combines the GW method with dynamical mean-field theory, which enables one to treat strong interaction effects. It avoids the conceptual problems inherent to conventional "LDA+DMFT" method, such as Hubbard interaction parameters and double counting terms. The basic idea is to employ the impurity self-energy calculated from the dynamical mean-field theory for the onsite term and to approximate the off-site self-energy by the GW approximation. The idea can be formulated in a precise and self-consistent way by using a free-energy functional approach. We apply a simplified version of the GW+DMFT approach to the electronic structure of nickel and find encouraging results.

Universal powerlaw of the optical conductivity & the phase angle spectra of Optical optimally doped cuprates

D. van der Marel, H. J. A. Molegraaf, F. Carbone
Materials Science Centre, University of Groningen, 9747 AG Groningen, The Netherlands

J. Zaanen, Z. Nussinov, P. H. Kes, & M. Li
Leiden Institute of Physics, Leiden University, 2300 RA Leiden, The Netherlands

A. Damascelli, H. Eisaki, M. Greven
Department of Applied Physics and Stanford Synchrotron Radiation Laboratory, Stanford University, California 94305, USA

Abstract

In certain materials with strong electron correlations a quantum phase transition (QPT) at zero temperature can occur, in the proximity of which a quantum critical state of matter has been anticipated[1, 2]. This possibility has recently attracted much attention because the response of such a state of matter is expected to follow universal patterns defined by the quantum mechanical nature of the fluctuations. Forementioned universality manifests itself through power-law behaviours of the response functions. Candidates are found both in heavy fermion systems[3] and in the cuprate high T_c superconductors4. Although there are indications for quantum criticality in the cuprate superconductors[4], the reality and the physical nature of such a QPT are still under debate[5, 6, 7]. Here we identify a universal behaviour of the phase angle of the frequency dependent conductivity that is characteristic of the quantum critical region. We demonstrate that the experimentally measured phase angle agrees precisely with the exponent of the optical conductivity. This points towards a QPT in the cuprates close to optimal doping, although of an unconventional kind.

References

[1] C. M. Varma, Y. Nussinov, and W. van Saarloos, Physics Reports **361**, 267-417 (2002).

[2] S. Sachdev, Quantum Phase Transitions (Cambridge University Press, 1999).

[3] S.S. Saxena *et al.*, Nature **406**, 587-592 (2000).

[4] J. L. Tallon, and J. W. Loram, Physica C **349**, 53-68 (2001).

[5] J. Orenstein, and A. J. Millis, Science **288**, 468-474 (2000).

[6] A. Kaminski *et al.*, Nature **416**, 610-613 (2002).

[7] H.A. Mook *et al.*, Phys. Rev. B **66**, 144513(1-10) (2002).

Electronic Structure and Valency of Mn Impurities in III-V Semiconductors

T. C. Schulthess and G. M. Stocks
Center for Computational Sciences, Oak Ridge National Laboratory

W. Temmerman and Z. Szotek
Daresbury Laboratory

W. H. Butler
MINT Center, University of Alabama

Abstract

Mn impurities in Ga based III-V semiconductors acquire either a divalent or trivalent configuration. Simple models that are based on experimental observations assume that Mn in GaAs is in a d^5 configuration with a delocalized hole in the As p-band. Mn in GaN is found to be in a d^4 configuration but the situation in GaP is still under debate. In the present work we have performed ab-initio calculations of the valency of a substitutional Mn impurity in GaN, GaP, and GaAs. We use the self-interaction corrected local spin density (SIC-LSD) method which is able to treat localized impurity orbitals properly. For Mn in GaAs we find that all five majority d-orbitals are filled with one hole in the majority valence band. The magnetization profile shows substantial polarization on the As sites that is anti aligned with the Mn moment and extends over several shell. Magnetic coupling is thus possible between distant Mn neighbors. These results are consistent with the $(d^5 + h)$ model that is stipulated by experiment. When Mn is introduced in GaN, only four d-orbitals are filled. In this case the induced polarization is short ranged and aligned with the Mn moment. The valency of Mn in GaP is similar to that of Mn in GaN. However, the induced magnetization in the hosts shows a mixture of the two respective scenarios found in GaAs and GaN. We have also studied the effect of co-doping with donors and find that this can lead to changes in the valency depending on the relative concentrations. Work supported by the Defense Advanced Research Agency and by DEO Office of Science through ASCR/MICS and BES/DMSE under Contract No. DE-AC05-00OR22725 with UT-Battelle LLC.

Compensation, interstitials, and ferromagnetism in magnetic semiconductors

Steven C. Erwin
Center for Computational Materials Science, Naval Research Laboratory, Washington DC 20375

Abstract

Ferromagnetism in Mn-doped GaAs is generally believed to be mediated by holes created by the substitution of Mn for Ga. Over a wide range of Mn concentrations, measured hole concentrations are much smaller than expected from simple electron counting, suggesting a robust compensation mechanism. A similar effect is observed in Mn-doped Ge, where antisites cannot account for the compensation. We present a theory of self-compensation by interstitial Mn in Mn-doped ferromagnetic semiconductors. Using density-functional theory, we show that under the non-equilibrium conditions of growth, interstitial Mn is easily formed near the surface by a simple low-energy adsorption pathway. In GaAs, isolated interstitial Mn is an electron donor, each compensating two substitutional Mn acceptors. Within an impurity-band model, partial compensation actually promotes ferromagnetic order below the metal-insulator transition, with the highest Curie temperature occurring for 0.5 holes per substitutional Mn. Finally, we show that the observed properties of another dilute ferromagnetic semiconductor, Co-doped TiO2 are, in a similar way, most naturally explained as arising from self-compensation of Co substitutionals by Co interstitials.

Spin-orbit coupling and disorder in $\mathrm{Ga}_{1-x}\mathrm{Mn}_x\mathrm{As}$

Gergely Zaránd
Research Institute of Physics, Technical University Budapest, H-1521 Hungary

Greg Fiete
Department of Physics, Harvard University, Cambridge MA 02138

Boldizsár Jankó
Department of Physics, University of Notre Dame, Notre Dame IN 4661D7

Kedar Damle
Department of Physics and Astronomy, Rice University, Houston, TX 77005

Abstract

Starting from a microscopic description of the exchange interaction in $Ga_{1-x}Mn_xAs$, we first derive an effective Mn-Mn interaction in the metallic limit. Due to the strong spin-orbit coupling in the valence band, this effective interaction is anisotropic and has a spatial structure somewhat similar to dipolar interactions. The corresponding ground state has a finite magnetization but is intrinsically spin-disordered even at zero temperature, possibly explaining many features of the experimental data.

We also study the very dilute limit where $\mathrm{Ga}_{1-x}\mathrm{Mn}_x\mathrm{As}$ can be described in terms of spin $F = 3/2$ polarons hopping between the Mn sites and thus forming an impurity band. These polarons couple to the local Mn spins antiferromagnetically. We estimate the parameters of our model from microscopic calculations. Our approach treats the extremely large Coulomb interaction in a non-perturbative way, captures the effects of strong spin-orbit coupling and disorder, and is appropriate for other p-doped magnetic semiconductors. We estimate that the latter model applies to uncompensated Mn concentrations up to $x \sim 0.03$.

Strong Correlation Methods for Diluted Magnetic Semiconductors

Małgorzata Wierzbowska and Stefano Sanvito
Department of Physics, Trinity College, Dublin 2, Ireland.

The discovery of diluted magnetic semiconductors rose a broad interest as future materials for spintronics devices, opening the possibility for the integration of information processing and data storage. Here we focus our attention on Mn-doped III-V compounds, spanning over a broad range of compositions and band gaps. We consider group III elements from B to Ga and group V from N to As. In these compounds the Mn dopant states change from a shallow impurity to a deep center, with important consequences on the long range ferromagnetic order. In the case of shallow impurities, the Mn center acts also as a donor and the ferromagnetism can be understood in term of a Zener-like model [1]. In contrast, when Mn forms a deep level no holes are left in the valence band of the host semiconductor and we have to consider some other mechanisms for the ferromagnetic order.

It is therefore very important to have quantitative predictions of the actual Mn impurity states in various semiconductors. In order to achieve an accurate description we have implemented both the LDA+U [2] and LDA+SIC [3] approaches, using the localised atomic basis set DFT program SIESTA [4]. The code employs order-N methods and enables us to calculate supercells with a few thousands of atoms. With the addition of LDA+U and LDA+SIC, SIESTA can now calculate the electronic structure of strongly correlated systems in low dilutions. From our analysis we can interpret some of the recent controversial experimental results on (Ga,Mn)N [5] and make predictions on the best avenue to obtain high T_C diluted magnetic semiconductors.

We would like to thank Daniel Sánchez-Portal and Alessio Filippetti for their help in the implementation of LDA+U and LDA+SIC into SIESTA. This work is supported by Enterprise Ireland under the grant EI-SC/2002-10.

[1] T. Dietl, Semicond. Sci. Technol. 17, 377 (2002); Stefano Sanvito, Gerhard Theurich and Nicola A. Hill., J. of Supercond: Incorporating novel Magnetism, **15** 85 (2002).
[2] Vladimir I. Anisimov, Jan Zaanen, and Ole Andersen., Phys. Rev. B, **44** 943 (1991).
[3] Alessio Filippetti and Nicola A. Spaldin Phys. Rev. B **67**, 125109 (2003)
[4] José M Soler, Emilio Artacho, Julian D Gale, Alberto García, Javier Junquera, Pablo Ordejón and Daniel Sánchez-Portal. J. Phys.: Condens. Matter, **14** 2745 (2002).
[5] Alessio Filippetti, Nicola A. Spaldin and Stefano Sanvito, cond-mat/0302178

5.1.3 Report on the SPR-KKR Workshop in Poznan

Workshop on Band Structure and Spectra Calculations by SPR-KKR Method

22-24 September, 2003 Poznań, Poland

Sponsored by
- the Centre of Exellence *MMMFE*$^{(*)}$
- Ψ_k Network of the European Science Foundation (ESF):
Working Group *Complex Magnetism and Nanostructures*
- Institute of Molecular Physics of the Polish Academy of Sciences
- Committee for Scientific Research

Organized by
A. Jezierski, A. Szajek, W.L. Malinowski, P. Leśniak
Institute of Molecular Physics, Polish Academy of Sciences, Poznań, Poland

The workshop took place at the Institute of Molecular Physics of the Polish Academy of Sciences in Poznań, Poland.

The main idea of the workshop was training of young physicists in the application of ab-initio methods for calculations of physical properties of new magnetic materials.

Drs M. Košuth and J. Minar from Universitaet Physikalishe Chemie Muenchen, Germany were invited as speakers.
The workshop consisted of two lectures given by Jan Minar:
1. *A spin polarized relativistic Korringa-Kohn-Rostoker (SPR-KKR) code for calculating solid state properties*
2. *One electron theory of spectroscopies*
and the tutorial part including the practical exercises using the PC computers lead by Michal Košuth.

During the workshop participants were introduced into the Muenich SPR-KKR-CPA program package with special emphasis on spectra calculations such as XANES, EXAFS, magnetooptics, Angle Integrated Photoemission, Auger Electron Spectroscopy and Compton scattering.

The participants performed set of exercises. They calculated the electronic and magnetic properties of simple metals and more complicated systems. The participants had also an opportunity to investigate systems of their own interest. 12 young physicists from Polish universities: Białystok (1), Katowice (2), Poznań (9), took part in the Workshop.

Andrzej Jezierski

(*)the Centre of Excellence for Magnetic and Molecular Materials for Future Electronics at the Institute of Molecular Physics of the Polish Academy of Sciences in Poznań (Poland) within the European Commission Contract No. G5MA-CT-2002-04049

LIST OF PARTICIPANTS

The full addresses are available on the Workshop WWW page:
http://www.ifmpan.poznan.pl/zp2/nm03/spr-kkr.htm

E. Długaszewska, Poznań, Poland, ewa@ifmpan.poznan.pl
A. Go, Białystok, Poland, annago@alpha.uwb.edu.pl
J. Goraus, Katowice, Poland, jgoraus@o2.pl
M. Haglauer, Poznań, Poland, monika@amu.edu.pl
K. Jaśniewicz, Poznań, Poland, kja6@wp.pl
A. Jezierski, Poznań, Poland, Andrzej.Jezierski@ifmpan.poznan.pl
G. Kamieniarz, Poznań, Poland, gjk@amu.edu.pl
A. Kapitańczyk, Poznań, Poland, infernal@icpnet.pl
D. Kasperski, Poznań, Poland, caz3pr@icpnet.pl
M. Košuth, Muenchen, Germany, Michal.Kosuth@cup.uni-muenchen.de
M. Kowalewski, Poznań, Poland, adler5@wp.pl
P. Leśniak, Poznań, Poland, warlord@ifmpan.poznan.pl
W.L. Malinowski, Poznań, Poland, wlm@ifmpan.poznan.pl
G. Michałek, Poznań, Poland, Grzegorz.Michalek@ifmpan.poznan.pl
J. Minar, Muenchen, Germany, jm@hebe.cup.uni-muenchen.de
J.A. Morkowski, Poznań, Poland, Janusz.Morkowski@ifmpan.poznan.pl
P. Napierała, Poznań, Poland, Piotr.Napierala@ifmpan.poznan.pl
M. Pugaczowa-Michalska, Poznań, Poland, maria@ifmpan.poznan.pl
D. Stysiak, Katowice, Poland, sdawid@interia.pl
A. Szajek, Poznań, Poland, szajek@ifmpan.poznan.pl

5.2 ESF Workshop/Conference Announcements

5.2.1 KKR-workshop: new developments, applications and collaborations

Organized by
H. Ebert (University Munich, Germany) and
D. D. Johnson (University of Illinois, Urbana-Champaign, USA)
Sponsored by
Psi-k Programme of the European Science Foundation (ESF)
and
Materials Computation Center at the Frederick Seitz Material Research Laboratory
(University of Illinois, Urbana-Champaign, USA)
in collaboration with
RT Network "Computational Magnetoelectronics"
UK CCP9 - Collaborative Computational Project for the Study of the Electronic Structure of Condensed Matter

The topics of the workshop will emphasize the presentation of recent developments and their applications in the fields of:

- treatment of many-body effects: combination of KKR with SIC, GW, LDA+U, DMFT
- electronic transport
- electron spectroscopy
- treatment of low-dimensional systems free and deposited clusters, wires
- treatment of disorder effects: KKR with DMFT and its derivatives, e.g. non-local-CPA
- phase stability and transitions

The workshop will be held from Friday 13th February through Sunday 15th February 2004 at the University of Munich.

Workshop fee: 60 EURO

Limited support for travelling is available: European citizens should contact Hubert Ebert, US-American citizens should contact MCC Travel Program.

For more information see:

http://olymp.cup.uni-muenchen.de/ak/ebert/KKR-workshop04/

5.2.2 DEMOCRITOS-ICTP School on Continuum Quantum Monte Carlo Methods

12 - 23 January 2004

Abdus Salam ICTP, Miramare, Trieste, Italy

Directors: D. M. Ceperley, S. Moroni, S. Baroni

Partially sponsored by Psi-k ESF Programme

A tutorial course on quantum Monte Carlo methods for continuum systems will be held at the Abdus Salam International Centre for Theoretical Physics from 12 to 23 January 2004.

Topics to be covered:

Variational Monte Carlo, Projector Monte Carlo (Diffusion, Auxiliary-Field, Reptation), and Path Integral Monte Carlo.

Instuctors:

D. M. Ceperley, C. Filippi, S. Moroni, C. Pierleoni, M. Towler, S. Zhang.

The workshop will consist of lectures and computer labs. The first week will cover basic topics in quantum Monte Carlo. In the second week, more advanced topics will be discussed, with applications of complete codes to physically relevant problems. Examples include optimization of trial functions for atomic and molecular systems, pseudopotential electronic structure calculations for molecules and solids, electron gas, response functions, excited states, superfluidity and Bose condensation and exchange in quantum solids.

The school aims at graduate students and young post-doctoral scientists. Interested scientists should consult the website `http://agenda.ictp.trieste.it/agenda/current/fullAgenda.php?ida=a0332` for application details. The deadline was October 31, 2003.

The school is funded by DEMOCRITOS and ICTP. Additional funding for partial support of participants is made available from Psi-k and the MCC program. EU participants contact S. Moroni (moroni@caspur.it). US participants consult : http://www.mcc.uiuc.edu/travel.

5.2.3 International Workshop on "Progress in Ab Initio Computational Methods for Condensed Matter"

Gif/Yvette (Paris), France, 8-10 January, 2004

You might be interested to participate in the International Workshop "Progress in Ab Initio Computational Methods for Condensed Matter" that will take place on 08 (Thursday) - 10 (Saturday) January 2004 in Gif/Yvette (Paris), France.

This workshop is part of a series called "International Workshop on Computational Physics and Materials Science: Total Energy and Force Methods", held once every two years in Trieste (see

http://www.democritos.it/events/totalenergy.php

for details on the 2003 workshop). The 2004 is one of the smaller events, taking place in the intermediate years.

The registration is now open ; there is a registration fee of 156 Euros including 3 lunches (Thursday to Saturday). A number of grants is available, thanks to the financial support of the ESF Psi-k programme and of the french GDR 'DFT'.

If you wish to submit a title and an abstract for a poster contribution, please send it to

gif2004@mirto.polytechnique.fr.

Please, use only simple text or LaTeX format. Some few posters may be promoted to oral contributions.

Please, find more details about the workshop below, and/or look at its web site

http://theory.lsi.polytechnique.fr/workshops/

Please note : In order to keep this event as informal as possible, the number of participants is limited. Therefore, the registration will be closed when the limit is reached.

Purpose of the workshop

The aim of this three-day workshop is to give a snapshot of the state of the art concerning computational material science, through the presentation of some recent works. The sessions have been chosen in order to illustrate the vast applicability and the increasing complexity of atomic and electronic structure computational methods, and explore their capability to deal with systems of technological and biological interest, up to industrial applications. This workshop is also intended as a way to promote links among scientists coming from different communities and favour the exchange of ideas between distant fields, ranging from catalysis to strongly correlated materials.

Details

The workshop will be held in the Paris area, at Gif sur Yvette, and the CNRS conference room "Salle de la Terrasse" in Gif sur Yvette will host both the main conference and the poster session in a relaxed atmosphere with the surrounding park and castle; address: Salle de la Terrasse, avenue de la Terrasse - 91198 Gif-sur-Yvette Cedex. The dates of this three-day workshop are: 08 (Thursday) - 10 (Saturday) January 2004.

Local Organizers

Lucia Reining
LSI, Ecole Polytechnique, 91128 Palaiseau, France
Email: Lucia.Reining@polytechnique.fr

Phone: +33 1 6933-3690, Fax: +33 1 6933-3022
Nathalie Vast
LSI, Ecole Polytechnique, 91128 Palaiseau, France
Email: Nathalie.Vast@polytechnique.fr
Phone: +33 1 6933-3825, Fax: +33 1 6933-3022
Valerio Olevano
LSI, Ecole Polytechnique, 91128 Palaiseau, France
Email: Valerio.Olevano@polytechnique.fr
Phone: +33 1 6933-3691, Fax: +33 1 6933-3022

Scientific Commitee

Alfonso Baldereschi
Stefano Baroni
Giulia Galli
Mike Gillan
Xavier Gonze
Jisoon Ihm
Erik Koch
Karel Kunc
Steven Louie
Richard J. Needs
Pablo Ordejon
Michele Parrinello
David Vanderbilt

Scientific content

This Mini-Workshop will follow the series of Workshops started in Oxford (1983) and Braunschweig (1984) and continued in Trieste with a two-years frequency (1987, ... 2001, 2003). Non-systematical single events in the form of Mini-Workshops have usually been held in the intermediate years (e.g. Miraflores de la Sierra 2000 and Tenerife 2002). The present Gif sur Yvette 2004 event is in the line of the Mini Workshops series, both for the size and for its single edition.

Following the tradition of the previous meetings, the workshop will be devoted to recent advances in computational condensed matter physics, based on realistic calculations of the electronic structure of polyatomic systems, a topic that is today of increasing interest in physics and chemistry.

As in previous events of this series, the workshop will consist of invited talks with ample space devoted to discussion. There will also be one poster session.

Invited speakers (preliminary titles)

(*) confirmed

Magnetism and Spin Dependent Properties.

(*) V. Antropov (USA)
(*) Hadi Akbarzadeh, Isfahan University (Iran)

Core Levels.

(*) John Rehr, Washington (USA)
(*) Delphine Cabaret, Univ. Paris 6 (France)

Strongly Correlated Systems.

(*) Klaus Capelle, Sao Paulo (Brazil)
(*) Silke Biermann, Ecole Polytechnique (France)

Multiple Time and Length Scales Methods.

(*) Christoph Dellago (Austria)
(-) Jorge Kurchan, Paris (France)
(*) S.Goedecker, Basel University (Switzerland)

Surfaces.

(*) Rodolfo Del Sole, Rome II (Italy)
(*) Wolf-Gero Schmidt, Jena (Germany)
(*) Herve Toulhoat, Institut francais du petrole (France)

Clusters and Nanostructures.

(*) S.G. Louie (Berkeley, USA)
(*) Xavier Blase, Lyon (France)

Biological Systems.

(*) Elisa Molinari (Modena, Italy)
(*) Matteo Ceccarelli (Lugano, Switzerland)
(*) Miguel Marques, Berlin (Germany)

In addition, the attendance of graduate students and postdocs will be strongly encouraged through the inclusion of short contributed talks and a poster session with brief oral introductions. Furthermore, we will suggest to Ph.D. students who had presented an outstanding poster contribution to convert it into a short oral presentation.

Please, see the web site

http://theory.lsi.polytechnique.fr/workshops/

for further details.

5.2.4 ESSN-2004 Workshop, Jyväskylä, Finland

ELECTRONIC STRUCTURE SIMULATIONS OF NANOSTRUCTURES (ESSN-2004):

TOWARDS AN UNDERSTANDING OF PHYSICAL, CHEMICAL AND BIOLOGICAL PROCESSES

UNIVERSITY OF JYVÄSKYLÄ, FINLAND

JUNE 18-21, 2004

Supported by ESF Psi-k Programme

SCOPE OF THE WORKSHOP

The scope of this workshop is to explore the current status of the research in the broad area of electronic structure simulations of nanoclusters, nanoparticles and nanostructures in various fields of physics, chemistry and biology. A number of experimental talks are added in the program to promote exchange of ideas and interdisciplinary collaborative efforts between simulations and experiments. The program will consists of invited lectures, short "hot topic" presentations, poster sessions, and tutorial sessions on modern electronic structure theory, which are included for the benefit of the attending students and young researchers. This workshop will be one of the first activities organized by the new University Nanoscience Center in Jyväskylä, Finland, and it will also be part of a series of international meetings in connection with a yearlong celebration of the University's 70 years of operation.
Speakers include: W. Andreoni, T. Bernhardt, J. Eloranta, T. Frauenheim, G. Galli, R. Gebauer, B. Hammer, U. Heiz, O. Ikkala, R. Jones, U. Landman, M. Moseler, A. Nakajima, G. Pacchioni, M. Parrinello, K. Reuter, A. Rubio, G. Scoles, A. Selloni, M. Di Ventra, R. Wolkow, L. Wöste.
Organizing committee: H. Häkkinen, U. Heiz, M. Manninen, G. Pacchioni, A. Selloni.

Deadlines: Registration, accommodation and abstracts by March 31, 2004

http://www.phys.jyu.fi/essn04

essn2004@phys.jyu.fi

6 General Workshop/Conference Announcements

6.1 16th Annual Workshop on Recent Developments in Electronic Structure Methods

Preliminary Announcement

Rutgers, the State University of New Jersey

New Brunswick, NJ, USA

27-30 May, 2004

The 16th Annual Workshop on Recent Developments in Electronic Structure Methods will be held on the New Brunswick campus of Rutgers, the State University of New Jersey, May 27-30 2004.
Information about the workshop is posted at the web site:

http://es04.rutgers.edu
This workshop will bring together active participants in electronic structure theory from universities, colleges, and government and industrial labs around the world. The invited oral presentations and contributed posters will describe new methods for computing previously inaccessible properties, breakthroughs in computational efficiency and accuracy, and novel applications of these approaches to the study of molecules, liquids, and solids.

The program will begin with a welcoming reception on the evening of Thursday May 27. The scientific program will run from Friday morning until lunchtime Sunday, May 28-30. New Brunswick is conveniently served by Newark Airport, and the conference location will be within walking distance of the New Brunswick Train Station on the Amtrak and NJ Transit lines. As in the past, the cost of this workshop will be kept low so as to encourage participation by junior scientists.

Kieron Burke
Karin Rabe
David Vanderbilt
(Local Organizing Committee)

6.2 Donostia International Physics Center Workshop

Preliminary Announcement

MOLECULE-SURFACE INTERACTIONS: ELEMENTARY REACTIVE PROCESSES

Donostia / San Sebastián, September 8 - 11, 2004

Web site: http://dipc.sw.ehu.es/dipc/molecule-surface-interactions.htm

Co-chairmen:

Pedro Miguel ECHENIQUE (Donostia/San Sebastián)
Antoine SALIN (Bordeaux)

Conference Secretary:

Heriberto Fabio BUSNENGO (Rosario)

Scientific committee:

Daniel FARIAS (Madrid)
Axel GROSS (München)
Geert Jan KROES (Leiden)
Mario ROCCA (Genova)

Reactivity at gas-solid interfaces plays a fundamental role in a large number of natural processes: heterogenous catalysis, atmospheric reactions, interstellar matter, biological or geological media. Recently, reactivity studies have greatly benefited from the development of individual atom, molecule or radical manipulation and reaction control on surfaces. The latter technique allows to pilot step by step chemical reactions, to observe elementary reactions in real time, to construct nanostructured catalysts, etc... Molecular beams allow to simulate elementary steps in catalytic processes like the formation and stabilization of reactive radicals or direct reactions between adsorbates and atoms/molecules of the gas phase. On the other hand, theoretical methods for the determination of the electronic structure of adsorbates on surfaces have reached the point where they are able to deal with complex situations, like the determination of reactive paths, even when the latter involve defects or local modifications of the surface. The concerted theoretical and experimental approach has proved to be very successful for the elucidation of elementary microscopic reaction steps of molecules at surfaces. In this workshop, the current state of the art in both theory and experiment will be reviewed and promising new developments discussed.

Topics:

- Dynamics of molecular adsorption and desorption processes
- Elementary reactions involved in fundamental and catalytic processes
- Molecular vibration on surfaces
- Dissipation processes

- Electronic excitations and relaxations, photochemistry
- Scattering of molecules from surfaces. Phonon excitations
- Surface diffusion

7 General Job Announcements

One PhD Studentship and one Postdoctoral Position

Instituut-Lorentz for Theoretical Physics
Universiteit Leiden, The Netherlands

A PhD studentship and one postdoctoral postion are available at the Instituut-Lorentz for Theoretical Physics of Leiden University in the Netherlands, in the group of Dr. Claudia Filippi.

The PhD position is for 4 years and is expected to lead to a PhD thesis. The postdoctoral position is for 2 years.

The focus of the project is the application and further development of the quantum Monte Carlo method (one of the most accurate electronic structure approaches available) for the study of the complex problem of the excited states of photoactive biomolecules. The project will involve methodological and code developments to achieve an accurate description of the excited state of a realistically large model system, and the subsequent theoretical investigation of the physical behavior of photoactive molecules, in particular the interplay between their microscopic structure and spectral functions.

Applications (containing contact details, CV and names of two referees) and requests for further information should be sent to filippi@lorentz.leidenuniv.nl.

Contact: Dr. Claudia Filippi
E-mail: filippi@lorentz.leidenuniv.nl
Mail: Universiteit Leiden
Instituut-Lorentz for Theoretical Physics
P.O. Box 9506
NL-2300 RA Leiden
The Netherlands

A POSTDOCTORAL POSITION IN COMPUTATIONAL NANOSCIENCE

Department of Physics, University of Jyväskylä, Finland

This position is available in the group of Dr. Hannu Häkkinen in the Department of Physics, University of Jyväskylä, Finland. The position is for two years and available in January 2004. The current activities of the group consist of investigations of the electronic, magnetic, optical and nanocatalytic properties of metal clusters and nanoparticles, both as free gas-phase objects and as supported my metaloxides. The group is part of the new NanoScience Center in the University and has close international collaboration with several theoretical and experimental groups. The preference will be given to candidates with a strong background in density functional or quantum chemistry methods. The applicants are asked to send a CV, publication list and a brief description of their previous work to Dr. Hannu Häkkinen (hannu.hakkinen@phys.jyu.fi) and arrange for two letters of reference to be sent by email, fax or postal mail to the address given below. The evaluation of the candidates begins immediately and will continue until the position is filled.
Contact address:

Dr. Hannu Häkkinen
Department of Physics
FIN-40014 University of Jyväskylä
FINLAND

Email: hannu.hakkinen@phys.jyu.fi
Fax: +358 14 260 2351
Department web site: http://www.phys.jyu.fi
Personal home page: http://www.phys.jyu.fi/homepages/hakkinen

PhD/Postdoc positions at NMRC, Ireland

NMRC, Ireland has several postdoctoral research and PhD positions available in the areas of computational modelling, photonics theory, and condensed matter theory. We seek candidates with a background in theoretical physics or chemistry, and an interest in scientific computing, electronic structure theory, semiconductor physics, optoelectronics, atomic scale simulation, and/or technology computer aided design. Successful candidates will pursue research projects on the following topics:

endohedral doping of buckminsterfullerene (jgreer@nmrc.ie)
molecular electronic transport (jgreer@nmrc.ie)
semiconductor/oxide interfaces (jgreer@nmrc.ie)
multi-scale simulation/kinetic Monte Carlo (jgreer@nmrc.ie)
molecular modelling of self-assembled monolayers (jgreer@nmrc.ie)
defect scattering, transport and localization in semiconductor alloys (sfahy@nmrc.ie)
theory and analysis of nonlinear photonic band gap and nanophotonic structures (eoreilly@nmrc.ie).
NMRC is Ireland's largest research centre with a staff of over 240 and has extensive fabrication, characterisation and computational facilities. The NMRC hosts over 40 postgraduate students pursuing postgraduate education in science and engineering on a variety of topics. The NMRC is active in research in Information & Communication Technologies, Nanotechnologies and Biotechnologies. (http://www.nmrc.ie)
There is a large theory and modelling effort ongoing in Cork offering many opportunities for collaboration and a stimulating research environment. These acivities include the Computational Modelling Group, the Photonics Theory Group and University College Cork's Condensed Matter Theory Group.

NMRC is located in Cork (http://www.cork-guide.ie/corkcity.htm) and is a city of with a population of 170,000 (of which about 30,000 are students), with a compact city centre. The city offers a variety of entertainment options with lively traditional pubs, cafes and restaurants. Cork is situated amidst some of Ireland's most scenic regions.
Interested applicants should contact

Dr. Jim Greer - Computational Modelling Group (jim.greer@nmrc.ie)
Prof. E. O'Reilly - Photonics Theory Group (eoin.oreilly@nmrc.ie)
Prof. S. Fahy - Photonics Theory Group (sfahy@nmrc.ie)

NMRC, University College, Lee Maltings, Prospect Row,
Cork, Ireland

Telephone: +353 21 4904177
FAX: +353 21 4270271

http://www.nmrc.ie/

Postdoctoral Position in Computational Materials Science
Duke University, Durham, NC

The postdoctoral position is in the area of phase stability prediction. Candidates must have significant experience in electronic structure calculation, ab-initio techniques, statistical mechanics and thermodynamics. Research will be performed at Duke University, Durham, NC. Candidates with relevant experience should email CV, names of 2 references, and a brief description of accomplishments to auro@nietzsche.mems.duke.edu Candidates with exceptional capabilities are welcome to apply and might be considered for other research area.
Prof. Stefano Curtarolo
Duke University,
Dept. Mechanical Engineering and Materials Science,
144 Hudson Hall, Box 90300,
Durham, NC 27708-0300
Phone: 919-660-5506
E-mail: stefano@duke.edu
http://nietzsche.mems.duke.edu

Two PhD Positions in Theoretical Physics/Chemistry at Dresden

We would like to announce two open PhD positions.

(1) at the Institute of Physical Chemistry and Electrochemistry, Dresden University of Technology (http://www.chm.tu-dresden.de/pc/): This position is devoted to the computation of nuclear magnetic shielding in diamagnetic molecules.

(2) at the Leibniz-Institute for Solid State and Materials Research (IFW) Dresden (http://www.ifw-dresden.de), Group for Theoretical Solid State Physics: This position is devoted to the computation of physical and chemical properties of surfaces in strong external fields.

In both cases, the task will include the extension and application of an existing density functional computer code. Applicants with a background in either Physics or Theoretical Chemistry are welcome.

Salaries will be based on 50% BAT-O IIa, annual net income about 10 kEUR, depending on age and social status.

The city of Dresden is situated mid-way between Berlin and Prague, in the valley of river Elbe. With a population of about 500,000, it is known for a rich cultural live and for its baroque silhouette.

Interested candidates should address their questions or send their application including curriculum vitae, related documents, a brief statement about previous research activities, and 1-2 references to
position (1):

Prof. Dr. Gotthard Seifert
gotthard.seifert@chemie.tu-dresden.de

position (2):

Dr. Manuel Richter
m.richter@ifw-dresden.de

Postdoctoral Position

Surface Science at Extreme Conditions
Theoretical Chemistry, Ruhr-Universitaet Bochum, Germany

Applications are invited for a research associate position. The preferred starting date would be spring 2004.

The ideal candidate would have significant experience in electronic structure theory, DFT/MD calculations, surface science, and heterogeneous catalysis. She or he would work primarily on using dynamical (Car-Parrinello) electronic structure methods in order to understand the complex processes involved in chemical reactions occurring at surfaces in contact with dense/hot water. In addition, he/she can also be involved in other challenging research projects including both method development and large-scale applications.

Information on the techniques used and developed are accessible via http://www.theochem.ruhr-uni-bochum.de/go/cprev.html.

The Theoretical Chemistry Group at RUB offers an exciting interdisciplinary environment with excellent working conditions (including several parallel platforms and a 500 GFlop/s SCI machine in house).

Candidates should send a detailed resume including an outline of their research achievements and interests as well as contact information for academic references as one pdf/ps file to office@theochem.ruhr-uni-bochum.de.

Consideration of candidates will begin immediately and continue until the position is filled. The University particularly welcomes applications from women.

Professor Dominik Marx
Lehrstuhl fuer Theoretische Chemie
Ruhr-Universitaet Bochum
D-44780 Bochum
Germany

Phone : ++49 234 322 6485
Fax : ++49 234 321 4045
office@theochem.ruhr-uni-bochum.de
http://www.theochem.ruhr-uni-bochum.de/

Postdoctoral Position: Single-Atom/Single-Molecule Electronic Transport

MIC, Technical University of Denmark, Lyngby

We are looking to fill a postdoctoral position in theory/simulation in an exciting international project on atomic and molecular scale electronic components (Single-Atom And Single-Molecule Electronic Components). The position is with Mads Brandbyge at MIC, DTU, in close collaboration with Karsten Jacobsen, CAMP, DTU. The successful applicant will work on modelling experiments performed by the experimental partners of the project (Leiden, Madrid). The work involves using and extending existing methods for investigation of the electrical transport and atomic structure of atomic/molecular scale components. The duration of the position is at least 2.5 years. Applicants are expected to have a strong background in solid-state theory and preferably transport and density functional methods. The start date is early 2004 (preferably January 1st).

The interested candidates should send their (1) curriculum vitae, (2) publication list, (3) one or two reprints representative of previous research, and (4) confidential letters of recommendation to Mads Brandbyge.

Contact information:

Assoc. Prof. Mads Brandbyge
MIC, Oersteds plads
Tech. Univ. of Denmark (DTU)
Build. 345 east
DK-2800 Kgs. Lyngby
Denmark

Phone: +45 4525 5788
Email: mbr@mic.dtu.dk
http://www.mic.dtu.dk
http://www.fysik.dtu.dk

Marie Curie Training Site:

Materials Modelling, Characterisation and Visualisation

Institute for Materials Research
University of Salford, UK

Applications are invited for funded collaborative visits to the above site. To be elligible applicants must be registered for a PhD degree at an EU (or associated state - see below for list) university not in the UK. Visits are possible for periods between 3 and 12 months and carry a stipend of 900 euro per month with additional funds for travel.

The site is led by the Neutron Scattering and Materials Modelling group of the IMR whose interests the characterisation of complex systems using a combination of neutron scattering and DFT electronic structure methods. Current systems of interest include materials for hydrogen storage (metal hydrides, nanotobes ..) and hydrogen bonded biomolecular solids. The group employs a variety of computational methods including planewave-pseudopotential, LCAO and FLAPW and uses an in house 70GFlop computational facility.

A full list of the research interests and facilities of the IMR can be found at www.imr.salford.ac.uk.

Interested parties should contact Dr. Ian Morrison email: i.morrison@salford.ac.uk

Associated states include - Bulgaria, Cyprus, Czech Republic, Estonia, Hungary, Latvia, Lithuania, Malta, Poland, Romania, Slovakia, Slovenia, Turkey, Iceland, Liechtenstein, Norway and Israel.

Dr Ian Morrison
Joule Physics Laboratory and Institute for Materials Research
University of Salford
Tel: +44 161 2955303
Email: i.morrison@salford.ac.uk

Postdoctoral Positions at the International Centre for Theoretical Physics (ICTP), Trieste, Italy

Post-doctoral positions in ab-initio molecular dynamics and electronic structure will be available in the Condensed Matter Group of the International Centre for Theoretical Physics (ICTP), Trieste, Italy, starting Fall 2004. The deadline for applications is 31 December 2003. The appointments will be for one year, renewable for a second year. Areas of interest include high-pressure phenomena, transport, and surface physics/chemistry. More details are available by contacting Sandro Scandolo at ICTP or on the web at:
`http://www.ictp.trieste.it/~scandolo/post-doc.html` .

Sandro Scandolo
The Abdus Salam International Centre for Theoretical Physics (ICTP)
Strada Costiera 11, I-34014 Trieste, Italy
phone: +39 040 2240 209
fax: +39 040 224163
e-mail: `scandolo@ictp.trieste.it`
`http://www.ictp.trieste.it/~scandolo`

8 Abstracts

Spin-polarized magnetic circular dichroism in Ni $2p$ core-level photoemission

C. De Nadaï
European Synchrotron Radiation Facility, Grenoble, France
G. van der Laan
Magnetic Spectroscopy, Daresbury Laboratory, Warrington WA4 4AD, UK
S. S. Dhesi, N. B. Brookes
European Synchrotron Radiation Facility, Grenoble, France

Abstract

Spin-resolved photoemission from ferromagnetic Ni has been measured using circularly polarized x-rays, which allowed us to obtain the difference spectra, i.e. the magnetic circular dichroism (MCD), the spin spectrum and the spin-orbit spectrum from the same data set. The results are compared with calculations for the final-state impurity model in which the core-ionised atom is described as an impurity within a many-body formalism. A good agreement between experiment and theory is obtained for all difference spectra, although the spin-orbit spectrum shows an increased spin-polarized background. We also quantified the relation between the $2p$ spin-orbit spectrum and the $L_{2,3}$ x-ray magnetic circular dichroism.

(accepted for Phys. Rev. B)
Manuscript available from g.vanderlaan@dl.ac.uk

Induced V and reduced Co magnetic moments at the V/Co interface

Y. Huttel
Instituto de Microelectrónica de Madrid, Tres Cantos, Madrid, Spain
G. van der Laan, T. K. Johal, N. D. Telling
Magnetic Spectroscopy, Daresbury Laboratory, Warrington WA4 4AD, UK
P. Bencok
European Synchrotron Radiation Facility, Grenoble, France

Abstract

Using x-ray magnetic circular dichroism (XMCD) the vanadium and cobalt magnetic moments at the V/Co interface have been extracted for different V and Co thicknesses. We find a large magnetic moment induced on the V that is coupled antiferromagnetic to the Co. For Co both the spin and orbital moments are reduced at the interface. The evolution of the magnetic moment together with the spectral changes in the V $L_{2,3}$ XMCD upon V deposition demonstrate the complexity of the V/Co interface as manifested in its physical properties. We show how the hybridization at the interface between the Co and V can lead to a transfer of the exchange interaction, resulting in the modified magnetic moments. The change in the number of Co 3*d* holes, extracted from XAS, shows that the charge transfer over the interface is small, indicating that it can not be responsible for the change in the magnetic moments.

(submitted to: Phys. Rev B)
Preprints available from g.vanderlaan@dl.ac.uk

Magnetic circular dichroism in $L_3M_{2,3}M_{2,3}$ Auger emission from Fe and Co metal due to symmetry-breaking interactions

A. Chassé
Physics Department, Martin-Luther-University Halle-Wittenberg, D-06099 Halle, Germany
H. A. Dürr
BESSY G.m.b.H., D-12489 Berlin, Germany
G. van der Laan
Magnetic Spectroscopy, Daresbury Laboratory, Warrington WA4 4AD, UK
Yu. Kucherenko and A. N. Yaresko
Institute of Metal Physics, National Academy of Sciences of Ukraine, UA-03142 Kiev, Ukraine

Abstract

A strong magnetic circular dichroism (MCD) in the $L_3M_{2,3}M_{2,3}$ Auger-electron emission spectra was measured on Fe and Co metal in the off-resonance energy region with the light helicity vector perpendicular to the magnetization direction, despite the fact that this emission is expected to be symmetry forbidden in this geometry. The experimental results are explained quantitatively by taking into account the exchange interaction of the spin-orbit split core states with the spin-polarized valence band. It is shown that the local valence-band magnetic moment is strongly suppressed in the presence of a $2p$ hole in the intermediate state. As a result the MCD signal decreases going from Fe to Co metal, while for Ni the MCD is no longer observable. This behavior is completely different for the measurements at resonance, i.e. at the L_3 absorption edge, where the MCD signal is strong (∼9%) for Fe, Co and Ni due to the large spin polarization of the $2p$ core hole which is caused by unoccupied $3d$ states with predominantly minority spin in the vicinity of the Fermi level.

(accepted for publication in Phys. Rev. B)
Manuscript available from g.vanderlaan@dl.ac.uk

A gas microstrip detector for XAS studies in the photon energy region 300 to 1500 eV

J. D. Lipp, J. E. Bateman, G. E. Derbyshire
CCLRC Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, UK
I. W. Kirkman, G. van der Laan
CCLRC Daresbury Laboratory, Daresbury Warrington WA4 4AD, UK
R. Stephenson
CCLRC Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, UK
C. M. Teodorescu
CCLRC Daresbury Laboratory, Daresbury Warrington WA4 4AD, UK

Abstract

The ability to perform X-ray absorption spectroscopy (XAS) in the 300 to 1500 eV energy range allows measurements to be made on transition metal compounds. This paper describes a detector and the technique used to perform fluorescent measurements on such materials. A variety of test sample results are shown to illustrate the low energy and energy-resolving capabilities of the detector (based on gas microstrip technology). Two possible applications are also demonstrated. The first shows how the detector can be used to gather X-ray absorption spectra for the *L* edges of transition metals and *K* edges of light elements (C, O and N). The other shows how the magnetic immunity of the detector can be exploited to study the magnetic properties of materials.

Published in J. Synchrotron Rad. **10**, 455–460 (2003).
Reprints available from g.vanderlaan@dl.ac.uk

Theoretical studies of iridium under pressure

Sharon Grussendorff, N. Chetty
School of Chemical and Physical Sciences, University of Natal,
Private Bag X01, Scottsville 3209, South Africa
Hugues Dreyssé
IPCMS-GEMME, 23 rue du Loess, 67034 Strasbourg, France

Abstract

Recent experiments on Ir under pressure show a transition to a superlattice structure comprising 14 atomic layers. This observation has implications for high-pressure applications since Ir, with its high bulk modulus and high-thermal stability, is ideally suited for use as a gasket for high-temperature, high-pressure diamond anvil cell experiments. We perform first-principles total energy calculations to study the crystal phases and defect structures of Ir under pressure. We have extended the bond-orientation model (Chetty and Weinert 1997, Phys. Rev. B 56, 10844) to compute all of the defect structure as a function of atomic volume. We finf Ir in FCC structure to be extremely stable for pressure up to about 60 Gpa. We also calculate the stacking fault energies of Ir.

Published in : J. Phys. : Condens. Matter **15** (2003) 4127

Distortion and Magnetic Ground State of $YTiO_3$ and $LaTiO_3$

I. V. Solovyev
PRESTO-JST, Institute for Solid State Physics, University of Tokyo,
Kashiwanoha 5-1-5, Kashiwa, Chiba 277-8531, Japan

Abstract

Effects of lattice distortion on the magnetic ground state of $YTiO_3$ and $LaiO_3$ are investigated on the basis accurate tight-binding parametrization of the t_{2g} electronic structure extracted from the local-density approximation. The complexity of these compounds is related with the fact that the t_{2g}-level splitting, caused by lattice distortions, is comparable with the energies of superexchange and spin-orbit interactions. Therefore, all these interactions are equally important and should be treated on an equal footing. The Hartree-Fock approximation fails to provide a coherent description simultaneously for $YTiO_3$ and $LaTiO_3$, and it is essential to go beyond.

(Submitted to Phys. Rev. B; cond-mat/0310581)
Contact person: igor@issp.u-tokyo.ac.jp

Magnetic anisotropy of transition-metal interfaces from a local perspective: Reorientation transitions and spin-canted phases in Pd capped Co films on Pd(111)

J. Dorantes-Davila
Instituto de Fisica, Universidad Autonoma de San Luis Potosi,
Alvaro Obregon 64, San Luis Potosi, Mexico
H. Dreyssé
Institut de Physique et Chimie des Matériaux de Strasbourg,
23 rue du Loess, 67034, Strasbourg, France
G.M. Pastor
Laboratoire de Physique Quantique, CNRS, Univeristé Paul Sabatier,
34000 Toulouse, France

Abstract

Layer-resolved self-consistent electronic calculations of magnetic anisotropy energy (MAE) provide new insight on the off-plane magnetization observed in Pd capped Co films on Pd(111). We demonstrate that the transition from perpendicular to in-plane phases with increasing film thickness involves an intermediate spin-canted phase. The interfaces responsible for the stability of the off-plane easy axes are characterized microscopically. A local analysis of the MAEs reveals an unexpected internal magnetic structure of the Co-Pd interfaces in which the magnetic moments and spin-orbit interactions at the Pd atoms play a crucial role.

(published in :) Phys. Rev. Lett. **91** (2003) 197206

Adsorption Modes of Cysteine on Au(111): Thiolate, Amino-Thiolate, Disulfide

Rosa Di Felice
INFM Center on nanoStructures and bioSystems at Surfaces (S^3), 41100 Modena, Italy
Annabella Selloni
Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA

Abstract

The adsorption of cysteine on the (111) surface of gold has been studied by means of periodic supercell Density Functional Theory calculations. A number of different adsorption modes are examined, including adsorption through the thiol group in either thiolate or disulfide form, and adsorption through both the thiol and amino functional groups. We find that at intermediate coverage densities the latter mode of adsorption is favored, followed by thiolate adsorption at the bridge (slightly displace toward fcc) site. The N-Au and S-Au bond strengths in the amino-thiolate adsorption are estimated to be of the order of 6 and 47 kcal/mol, respectively. The electronic structure of the different systems is analyzed, with focus on the total and projected density of states, as well as on the detailed character of the electronic states at the interface. States near the Fermi energy are found to have a metal-molecule antibonding character, whereas metal-molecule bonding states mostly occur near the lower edge of the Au-*d* band.

(Submitted to Journal of Chemical Physics)
Contact person: Rosa Di Felice, rosa@unimore.it

Electron channels in biomolecular nanowires

Arrigo Calzolari, Rosa Di Felice, Elisa Molinari
INFM Center on nanoStructures and bioSystems at Surfaces (S^3), 41100 Modena, Italy
Anna Garbesi
CNR ISOF, Area della Ricerca, Bologna, Italy

Abstract

We report a first-principle study of the electronic and conduction properties of a quadruple-helix guanine wire (G4-wire), a DNA-derivative, with inner potassium ions. The analysis of the electronic structure highlights the presence of energy manifolds that are equivalent to the bands of (semi)conducting materials, and reveals the formation of extended electron channels available for charge transport along the wire. The specific metal-nucleobase interactions affect the electronic properties at the Fermi level, leading the wire to behave as an intrinsically p-doped system.

(Submitted to Journal of Physical Chemistry B)
Contact person: Arrigo Calzolari, calzolari.arrigo@unimore.it

---

Structure and energetics of nitride surfaces under MOCVD growth conditions

Chris G. Van de Walle[1,2,3] and J. Neugebauer[2]
[1] *Palo Alto Research Center, 3333 Coyote Hill Road,*
Palo Alto, CA 94304, USA
[2] *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,*
D-14195 Berlin, Germany
[3] *Paul-Drude-Institut, Hausvogteiplatz 5–7, D-10117, Berlin, Germany*

Abstract

We present a generalized phase diagram for GaN(0001) surfaces in the presence of hydrogen, based on first-principles calculations. The results elucidate the energetic and structural properties of GaN surfaces under realistic growth conditions. The role of NH_3 in stable growth of GaN and InGaN is discussed.

(appeared in: J. Cryst. Growth **248**, 8-13 (2003))
Contact person: Jörg Neugebauer (neugebauer@fhi-berlin.mpg.de)

Ordered (3×4) High Density Phase of Methylthiolate on Au(111)

Valentina De Renzi, Rosa Di Felice, Diego Marchetto,
Roberto Biagi, Umberto del Pennino
INFM Center on nanoStructures and bioSystems at Surfaces (S^3) and
Dipartimento di Fisica, Universitá di Modena e Reggio Emilia, 41100 Modena, Italy
Annabella Selloni
Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA

Abstract

The formation of ordered phases of dimethyl-disulfide on the Au(111) surface has been investigated by means of Low-Energy Electron Diffraction (LEED), X-ray Photoemission Spectroscopy (XPS), and state-of-the-art Density Functional Theory (DFT) periodic supercell calculations. The LEED diffraction pattern, obtained after a production method that includes a two-step dosing and prolonged post-deposition annealing, unambiguously corresponds to a novel phase that consists of (3×4) domains coexisting with the as-deposited $(\sqrt{3}\times\sqrt{3})$R30° structure. XPS measurements indicate that the coverage of the new (3×4) superstructure is the same as that of the $(\sqrt{3}\times\sqrt{3})$R30° phase. both phases, the binding energy of the S $2p_{3/2}$ core-level peak is found to be 162.2 eV, corresponding to the formation of a thiolate layer. The DFT calculations allow us to identify a viable metastable (3×4) structure where the S headgroups of the CH_3S radicals select distinct adsorption sites: three quarters of them adsorb at bridge sites and one quarter at top sites. The relative energetics of the (3×4) and $(\sqrt{3}\times\sqrt{3})$R30° configurations suggest that the two structures may coexist on the surface, in agreement with experimental data.

(Accepted for publication in the Journal of Physical Chemistry B as a Letter)
Contact person: Rosa Di Felice, rosa@unimore.it

Surface effects in GaN growth

Carlo Antonio Pignedoli, Rosa Di Felice, Carlo Maria Bertoni
INFM Center on nanoStructures and bioSystems at Surfaces (S^3) and
Dipartimento di Fisica, Universitá di Modena e Reggio Emilia, 41100 Modena, Italy

Abstract

By means of plane-wave pseudopotential periodic supercell Density Functional Theory calculations, we investigated the energetics of several GaN(0001) surfaces containing atomic and molecular adsorbates. The surface structures were selected in order to get insight into GaN epitaxial growth, in situations where NH_3 molecules are employed as the nitrogen precursor and H_2 molecules as the carrier gas, typical of standard vapor phase growth techniques adopted for the highest quality GaN films. Therefore, we considered NH_2 complexes and H atoms as molecular and atomic adsorbates, respectively, assuming they derive from molecular dissociation from the gas flows in the growth chambers. We took into account different adsorption stoichiometries, varying the relative proportion of NH_2 and H adsorbates, and different degrees of clusterization of the ad-atoms and ad-complexes. For each structure, we obtained the relaxed atomic configuration and the corresponding total energy. Hence, we describe here the relative structural stability in terms of a phase diagram that identifies the optimal growth conditions to attain at intermediate stages the most favorable equilibrium surfaces.

(Accepted for publication in Surface Science)
Contact person: Rosa Di Felice, rosa@unimore.it

Surface-Science Approach to the Study of Mercaptobenzoxazole on Cu(100)

R. Di Felice, A. Ferretti
INFM Center on nanoStructures and bioSystems at Surfaces (S^3) and
Dipartimento di Fisica, Universitá di Modena e Reggio Emilia, 41100 Modena, Italy
C. Mariani, M.G. Betti, C. Baldacchini
Dipartimento di Fisica, Universitá di Roma "La Sapienza", Roma, Italy
V. Di Castro
Dipartimento di Chimica, Universitá di Roma "La Sapienza", Roma, Italy

Abstract

We present a combined approach, based on photoemission experiments and DFT calculations, to the study of the adsorption of aromatic organic molecules on metal substrates. Our main purpose was to characterize the interface electronic properties and to search for electron states delocalized between the substrate and the molecular overlayer. We demonstrate how the interplay between theory and experiment, within a surface-science framework, is a powerful tool to gain insight into these issues. In particular, the computational results allow us to give a microscopic characterization, in terms of relative molecule-substrate coupling, of the photoemission peaks.

(Accepted for publication in Surface Science)
Contact person: Rosa Di Felice, rosa@unimore.it

Effect of spin orbit on the electronic properties of zincblende compounds

Y. Al-Douri
Department of Physics, Faculty of Science, National University of Singapore,
Singapore 119260, Singapore
R. Khenata
Laboratoire de Physique Quantique de la Matiere
et de Modelisation Mathematique (LPQ3M), Universite de Mascara,
29000 Algerie
Z. Chelahi-Chikr and M. Driz
Computational Materials Science Laboratory, Physics Department,
University of Sidi-Bel-Abbes, 22000 Algeria
H. Aourag
LERMPS, Université de Technologie de Belfort-Montbéliard,
Site de Sévenant, 90010 Belfort Cedex, France

Abstract

The empirical pseudopotential method with spin-orbit splitting is used to calculate the band structure of AlSb, GaSb, ZnTe, and CdTe. The electronic band structures appear direct gap. We have tested recent empirical model of ionicity factor under effect of spin-orbit interaction. A sensitive effect of spin orbit is shown on the band structures of these compounds but does not display structural phase transition. Reasonable agreement is obtained between our calculated and other experimental results.

(JOURNAL OF APPLIED PHYSICS **94** (2003) 4502)
Contact person:

A huge pressure-induced volume collapse in $LiAlH_4$ and its implications to hydrogen storage

P. Vajeeston, P. Ravindran, R. Vidya, H.Fjellvåg, and A.Kjekshus
Department of Chemistry, University of Oslo,
Box 1033, Blindern, N-0315, Oslo, Norway

Abstract

A detailed high-pressure study on $LiAlH_4$ was carried out using *ab initio* projected-augmented plane-wave method. Application of pressure transforms α-$LiAlH_4$ to α-$NaAlH_4$-type structure at 2.6 GPa with a huge volume collapse of 17 % ever observed in hydride family. This abnormal behavior is associated with electronic transition from Al-*s* to -*p* states. At 33.8 GPa, a β-to-γ transition is predicted from α-$NaAlH_4$-type to $KGaH_4$-type structure. Up to 40 GPa $LiAlH_4$ remains non-metallic. The high wt.% of hydrogen, around 22 % smaller equilibrium volume, and drastically different bonding behavior than α-phase indicate that β-$LiAlH_4$ is expected to be a potential hydrogen storage material.

(Phys. Rev. B (Brief report, in press, 2003).)
Contact person: ravindran.ponniah@kjemi.uio.no

Structural phase stability of BeH_2 at high pressures

P. Vajeeston, P. Ravindran, A. Kjekshus, and H. Fjellvåg
Department of Chemistry, University of Oslo,
Box 1033, Blindern, N-0315, Oslo, Norway

Abstract

The electronic structure and structural stability of BeH_2 are studied using first-principle density-functional calculation. The calculated structural parameters for α-BeH_2 at equilibrium volume is in very good agreement with experimental findings. At higher pressure α-BeH_2 successively undergoes four structural transitions: i) α- to β-BeH_2 at 7.07 GPa, ii) β- to γ-BeH_2 at 51.41 GPa, iii) γ- to δ-BeH_2 at 86.56 GPa, and iv) δ- to ϵ-BeH_2 at 97.52 GPa [an effective two-phase (γ and δ) regions is found at 73.71 GPa]. Density of state studies reveal that BeH_2 remains insulator up to 100 GPa whereupon anomalous changes are seen in the band gap region on increasing pressure.

(Appl. Phys. Lett. (in press, 2003).
Contact person: ravindran.ponniah@kjemi.uio.no

Tailor-made electronic and magnetic properties in one-dimensional perovskite-like oxides

R. Vidya,[1] P.Ravindran,[1] H. Fjellvåg,[1] A. Kjekshus,[1] and O. Eriksson[2]
[1] *Department of Chemistry, University of Oslo,*
Box 1033, Blindern, N-0315, Oslo, Norway
[2] *Department of Physics, Uppsala University,*
Box 530, 75121 Uppsala, Sweden

Abstract

Using generalized-gradient-corrected, relativistic full-potential density-functional calculations we have shown that one can vary the electronic and magnetic properties of one-dimensional oxides by magnetic field or doping. The electronic structure of one-dimensional ferrimagnetic $Ca_3Co_2O_6$, varies from metal to half-metal to insulator as its magnetic ordering changes from ferrimagnetic through ferromagnetic to paramagnetic state. The present report is the first to establish the occurrence of half metallicity in one dimensional perovskite-like oxides. Moreover the electronic and magnetic properties of these materials can be tuned by substitution of Y for Ca, as shown by our detailed study on $Ca_{3-x}Y_xCo_2O_6$ (x = 0, 0.3, 0.75, and 1). The Co ions are in two different valence states [Co^{4+} (low spin) and Co^{2+} (high spin)] and hence the occurrence of charge ordering in addition to spin ordering is established. Finally, we predict that for specific Y concentrations a rarely seen combination in condensed matter should be observed; viz. a ferromagnetic insulator.

(Phys. Rev. Lett. 91, 186404 (2003)).

Contact person: ravindran.ponniah@kjemi.uio.no

Adatom Density kinetic Monte Carlo: A hybrid approach to perform epitaxial growth simulations

L. Mandreoli and J. Neugebauer
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,
D-14195 Berlin (Dahlem), Germany
R. Kunert and E. Schöll
Institut für Theoretische Physik, Technische Universität Berlin,
Hardenbergstr. 36, D-10623 Berlin, Germany

Abstract

We describe an alternative approach to perform growth simulations which combines kinetic Monte Carlo (KMC) with elements from continuum and rate equations. Similar to KMC it takes the atomistic structure of the growing surface fully into account but is based on the adatom density rather than on explicit trajectories of the adatoms. As will be demonstrated, this approach decouples the fast time scale of adatom motion from the much slower time scale of changes in the growth morphology. This decoupling allows a reduction of the number of simulation time steps by several orders of magnitude. Based on a comparison with KMC calculations performance, reliability and limits of this approach are discussed.

(submitted to: Phys. Rev. B)
Contact person: Lorenzo Mandreoli (mandreoli@fhi-berlin.mpg.de)

Hydrogen adsorption at $RuO_2(110)$

Q. Sun, K. Reuter, and M. Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,
D-14195 Berlin-Dahlem, Germany

Abstract

The structural, vibrational, energetic and electronic properties of hydrogen at the stoichiometric $RuO_2(110)$ termination are studied using density functional theory. The oxide surface is found to stabilize both molecular and dissociated H_2. The most stable configuration in form of hydroxyl groups (monohydrides) at the undercoordinated O^{br} surface anions is at low temperatures accessed via a molecular state at the undercoordinated Ru^{cus} atoms (dihydrogen) and a second precursor in form of a water-like species (dihydride) at the O^{br} sites. This complex picture of the low-temperature dissociation kinetics of H_2 at $RuO_2(110)$ is in agreement with existing data from high-resolution energy-loss spectroscopy and temperature programmed desorption. Hydrogen adsorption at O^{br} sites increases the reactivity of the neighboring Ru^{cus} sites, which are believed to be the active sites in catalytic oxidation reactions.

(submitted to: Phys. Rev. B)
Contact person: Karsten Reuter (reuter@fhi-berlin.mpg.de)

Anisotropic diffusion of In adatoms on pseudomorphic $In_xGa_{1-x}As(001)$ films: First-principles total energy calculations

E. Penev, S. Stojković,[†] P. Kratzer, and M. Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,
D-14195 Berlin-Dahlem, Germany
[†] Present address: *CEMES/CNRS, 29, rue Jeanne Marvig, B.P. 4347,*
31055 Toulouse Cedex, France

Abstract

In the Stranski-Krastanow growth of strained pseudomorphic films, material transport by surface diffusion plays a crucial role for the development of the three-dimensional island morphology. In an attempt to elucidate the atomistic aspects of this growth mode, we study diffusion of a single indium adatom on (1×3)- and (2×3)-reconstructed subcritical $In_{2/3}Ga_{1/3}As(001)$ films using first-principles total energy calculations of the corresponding adiabatic potential-energy surfaces (PES). We find that In diffusion is anisotropic, and substantially enhanced compared to the GaAs(001)-$c(4 \times 4)$ substrate. Special attention is also paid to the methodology of deriving the tracer diffusion coefficients of indium from knowledge of the PES, using the continuous-time random walk formalism.

(submitted to: Phys. Rev. B)
Contact person: Peter Kratzer (kratzer@fhi-berlin.mpg.de)

On the thermodynamic stability of PdO surfaces

Jutta Rogal, Karsten Reuter and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,
D-14195 Berlin, Germany

Abstract

As a first step towards understanding the morphology of PdO crystals we performed a systematic full-potential density-functional theory study of all possible (1×1) terminations of the low-index surfaces of tetragonal PdO. Applying the concept of *first-principles atomistic thermodynamics* we analyze the composition, structure and stability of these PdO orientations in equilibrium with an arbitrary oxygen environment. Within the studied subset of (1×1) geometries the polar PdO-terminated PdO(100) orientation turns out to be surprisingly stable over the whole range of experimentally accessible gas phase conditions. Setting up a constrained *Wulff construction* within the compiled data set, this PdO(100)-PdO facet correspondingly dominates the obtained polyhedron by far. The real PdO crystallite shape will however likely be affected by surface reconstructions, which are not covered by the present study.

(submitted to: Phys. Rev. B)
Contact person: Karsten Reuter (reuter@fhi-berlin.mpg.de)

Ab initio DFT Cluster Studies of Angle-Resolved NEXAFS Spectra for Differently Coordinated Oxygen at the V_2O_5(010) Surface

C. Kolczewski and K. Hermann
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,
D-14195 Berlin, Germany

Abstract

At the (010) surface of vanadium pentoxide, V_2O_5, there are differently coordinated oxygen centers (1-, 2-, 3-fold), which can participate as active sites in specific oxidation reactions. In the present work we use *ab initio* density functional theory (DFT) together with cluster models to calculate 1s core excitation spectra of the differently coordinated oxygen centers at V_2O_5(010). Corresponding excitation energies and dipole transition moments are determined by details of local V-O-binding where the results vary strongly with oxygen coordination. As a result, a strong dependence of the (angle-resolved) excitation spectra on oxygen coordination is found. The differences can also be seen in the superimposed spectrum combining excitations from all oxygen centers. A comparison of our theoretical spectra with experimental NEXAFS data yields good agreement and allows an assignment of the experimental peaks to the different surface oxygen centers.

(submitted to: Surface Science)
Contact person: Kolczewski Christine (kolczew@fhi-berlin.mpg.de)

Oxygen adsorption at the V_2O_3(0001) surface: DFT cluster model studies.

I. Czekaj, M. Witko
Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences,
ul. Niezapominajek, PL-30239 Krakow (Poland)
K. Hermann
Fritz-Haber-Institut der MPG, Faradayweg 4–6, D-14195 Berlin

Abstract

Geometric and electronic details of the $V_2O_3(0001)$ surface after oxygen chemisorption are studied theoretically by density-functional theory using large cluster models. Two ideal bulk-terminated surfaces, $V'OV$ and $VV'O$, enriched by adsorbed O species i.e. $O_tV'O$ termination (formation of vanadyl $V = O_t$ groups) and O_b^2VV' and O_bVV' terminations (formation of surface $V - O_b - V$ groups with coverage $\theta\,(O_b) = 1/3$ and $2/3$) are considered. It is found that very strongly bound vanadyl groups remove part of the relaxation of the initial adsorbate-free surface. Bridging oxygen species leads for both coverages to relaxation of the topmost V surface layers, decreases the lateral distances between V/V' centers leading to honeycomb patterns as observed in STM experiments.

(submitted to: Annals of the Polish Chemical Society, in print)
Contact person: Klaus Hermann (hermann@fhi-berlin.mpg.de)

Oxygen sites at molybdena and vanadia surfaces: thermodynamics of the reoxidation process.

R. Tokarz-Sobieraj, R. Grybos, M. Witko
Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences,
ul. Niezapominajek, PL-30239 Krakow (Poland)
K. Hermann
Fritz-Haber-Institut der MPG, Faradayweg 4–6, D-14195 Berlin

Abstract

In oxidation reactions proceeding in accordance with the Mars - van Krevelen mechanism lattice oxygen plays the role of an oxidizing agent. Surface vacancies created by incorporation of lattice oxygen into reacting molecules are filled in a subsequent step by gaseous oxygen or, if not enough oxygen is present in the reaction environment, by oxygen diffusion from the bulk. During this process, a very active, electrophilic surface oxygen species may be formed. In effect, total combustion takes place decreasing the selectivity for partial oxidation products. The thermodynamic aspect of this effect (neglecting reaction barriers) is demonstrated for molybdenum trioxide and vanadium pentoxide. On the catalytically most interesting surfaces, MoO_3(010) and V_2O_5(010), three structurally different types of oxygen sites are present which exhibit different properties with respect to vacancy creation and annihilation. Re-oxidation of the catalyst by gaseous oxygen leads to oxygen molecules adsorbed in vacancies, preferably in an orientation parallel to the surface. Adsorption of the oxygen molecule in the vacancy leads to its activation followed by easy release of a neutral oxygen atom, which can be identified as the electrophilic species responsible for total combustion.

(submitted to: Collected Czech. Chemical Communications, in print)
Contact person: Klaus Hermann (hermann@fhi-berlin.mpg.de)

First-principles study of the electronic structure and exchange interactions in bcc europium

I. Turek[1,2], J. Kudrnovský[3], M. Diviš[2], P. Franek[2], G. Bihlmayer[4], and S. Blügel[4,5]
[1] *Institute of Physics of Materials, ASCR, Brno, Czech Republic*
[2] *Department of Electronic Structures, Charles University Prague, Czech Republic*
[3] *Institute of Physics, ASCR, Prague, Czech Republic*
[4] *Institut für Festkörperforschung, Forschungszentrum Jülich, Germany*
[5] *Fachbereich Physik, Universität Osnabrück, Germany*

Abstract

Magnetic properties of the europium metal in a bcc structure are studied from first principles using a two-step approach. First, the electronic structure of a ferromagnetic state is calculated in the local spin-density approximation (LSDA) to the density-functional theory whereby the highly localized $4f$ orbitals are treated as part of the atomic core. This description leads to an equilibrium lattice constant that compares well with experiment, in contrast to the standard LSDA which yields a significantly smaller atomic volume. In the second step, parameters of an effective Heisenberg Hamiltonian are derived from the selfconsistent electronic structure and they are used to determine the magnetic ground state and to estimate the magnetic transition temperature. The calculated pairwise exchange interactions tend to couple the local magnetic moments of the nearest neighbors ferromagnetically. However, the interaction parameters exhibit a slow oscillatory decay as a function of the interatomic distance which makes them fully compatible with an observed spin-spiral ground state. The resulting wave vector of the spiral as well as the Néel temperature are in fair agreement with measured values.

To be published in: Phys. Rev. B
Contact person: Ilja Turek (turek@ipm.cz).

Self-interaction Corrected Calculations of Correlated f-electron Systems

L. Petit[1,2], A. Svane[2], Z. Szotek[3], and W.M. Temmerman[3]
[1] *Computer Science and Mathematics Division*
and Center for Computational Sciences,
Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[2] *Department of Physics and Astronomy, University of Aarhus,*
DK-8000 Aarhus C, Denmark
[3] *Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK*

Abstract

The electronic structures of several actinide solid systems are calculated using the self-interaction corrected local spin density approximation. Within this scheme the $5f$ electron manifold is considered to consist of both localized and delocalized states, and by varying their relative proportions the energetically most favourable (groundstate) configuration can be established. Specifically, we discuss elemental Pu in its δ-phase, PuO_2 and the effects of addition of oxygen, the series of actinide monopnictides and monochalcogenides, and the UX_3, X= Rh, Pd, Pt, Au, intermetallic series.

(Submitted to Molecular Physics Reports (2003), cond-mat/0310729)
Contact person: W.M.Temmerman@dl.ac.uk

9 Book Announcements

Interatomic Forces in Condensed Matter

Mike Finnis

Department of Pure and Applied Physics

Queen's University, Belfast

http://www.oup.co.uk/isbn/0-19-850977-4

This book

- provides a clear, unified and self-contained account,
- combines essential theory in part one with its application to deriving models in part two,
- is a stimulating source of ideas for researchers developing new models,
- gives very thorough and pedagogic analysis of the nature of current models,
- gives derivations of equations in full.

10 SCIENTIFIC HIGHLIGHT OF THE MONTH

Quantum Monte Carlo and the CASINO program : highly accurate total energy calculations for finite and periodic systems

M. D. Towler

TCM Group, Cavendish Laboratory, University of Cambridge,
Madingley Road, Cambridge CB3 0HE, UK

Abstract

For practical computational electronic structure calculations an important and complementary alternative to density functional theory in situations where high accuracy is required is the *quantum Monte Carlo* method. This has many attractive features for probing the electronic structure of real systems. In particular, it is an explicitly many-particle technique which takes electron correlation into account from the outset, and gives consistent, highly accurate results while at the same time exhibiting favourable (cubic or better) scaling of computational cost with system size. In this article I briefly review the present state of the art, and outline the implementation of the method in the Cambridge quantum Monte Carlo code 'CASINO' [1, 2].

1 Introduction

The continuum Quantum Monte Carlo (QMC) method has been developed to calculate the properties of assemblies of interacting quantum particles. It is generally capable of doing so with great accuracy. The various different techniques which lie within its scope have in common the use of *random sampling*, and this is used because it represents by far the most efficient way to integrate numerically (wave) functions in many dimensions. In this article I shall give a brief introduction to the two most common types of QMC, namely variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC) [3, 4]. As we shall see, the first of these techniques is simple in concept and is designed just to sample a given trial wave function and calculate the expectation value of the Hamiltonian using Monte Carlo numerical integration. DMC is one of a class of so-called 'projector' methods which attempt the much more difficult job of simultaneously creating and sampling the unknown exact ground state wave function. Other variants, including those aimed at expanding the scope of the method to finite temperature such as path integral Monte Carlo (PIMC) [5, 6], or those designed to find the exact non-relativistic energy overcoming the small fixed-node approximation made in DMC (such as fermion Monte Carlo (FMC) [7, 8, 9]) will not be discussed in any detail here. The interested reader is invited to consult the literature for more detailed discussions (the extensive bibliography in Ref. [4] is a good place to start).

QMC is perhaps best known for its early application to the homogeneous electron gas by Ceperley and Alder [10], the results of which were used to develop accurate parametrizations of the local density approximation to density functional theory (DFT) in the early 1980s. However, it is of course perfectly possible to apply the method to real systems with atoms, and for small molecules containing helium and hydrogen QMC gives total energies with an extraordinary accuracy greater than 0.01 kcal/mole ($\approx 1.5 \times 10^{-5}$ Ha or 4×10^{-4} eV). In one well-known QMC study of the $H + H_2 \longrightarrow H_2 + H$ potential energy surface tens of thousands of points with accuracies close to this value were computed [11]. Despite such capabilities the technology of QMC is neither mature nor particularly widely used; its routine application to arbitrary finite and periodic systems, particularly those containing heavier atoms, has long been just out of reach and there are still many open methodological and algorithmic problems to interest the computational electronic structure theorist. The situation is clearly changing however, and it ought now to be a matter of routine for people to perform accurate *a posteriori* QMC evaluations of the correlation energy starting from the results of molecular orbital or band theory calculations. Systems and problems for which accurate calculations of the total energy actually matter, and for which DFT (for example) is not sufficiently accurate, are likely more numerous than is generally believed. To this end, our group in the Cavendish Laboratory of Cambridge University has over many years developed a general-purpose QMC computer program - CASINO [1, 2]. This is capable of performing both variational and diffusion Monte Carlo calculations on a wide variety of systems, which may be finite (atoms or molecules) or have periodic boundary conditions in one, two or three dimensions, i.e., polymers, slabs (surfaces) or crystalline solids. The code may also be used to study situations without an external potential such as the homogeneous electron gas, Wigner crystals, and various electron-hole phases. We will describe CASINO in more detail presently.

One of the main reasons that QMC is currently attracting so much interest is the scaling behaviour of the necessary computational effort with system size. This is favourable enough that we can continue to apply the method to systems as large as are treated in conventional DFT (albeit with a considerably bigger pre-factor, and thus probably not on the same computers). In fact, QMC represents the most accurate method available for medium-sized and large systems. Other quantum chemistry correlated wave function methods based on the 'standard model' of multideterminant expansions - such as configuration interaction or high-order coupled cluster theory - are capable of similar accuracy for systems containing a few electrons, but as the size of the molecule is increased they quickly become too expensive. Standard Quantum Monte Carlo calculations scale as the third power of the system size (the same as DFT), and are capable of treating solid crystalline phases as well as molecules. The largest calculations done to date on the more expensive periodic systems using the regular algorithm include almost 2000 electrons per cell in the three-dimensional electron gas [12], 1732 electrons (432 atoms) per cell in crystalline silicon [13], and 1024 electrons (128 atoms) per cell in antiferromagnetic nickel oxide [14]. Furthermore the natural observation has been made that provided localized molecular or crystalline orbitals are used in constructing the QMC trial wave function, and provided these orbitals are expanded in a localized basis set, then the scaling of the basic algorithm can be substantially improved, even as far as linear scaling in some cases [15, 16]. This capability, to be discussed in Section 4.2, has recently been introduced into CASINO and this should considerably extend the range of problems that may be studied.

Before we go further, it will be useful to list some other favourable properties of the method :

- For most practical purposes the 'basis set problem' is essentially absent in DMC; errors due to the use of a finite basis set are very small since the many-electron wave function is not represented directly in terms of a basis set, but rather by the distribution of an ensemble of particles evolving in (imaginary) time. The basis set that is employed in DMC is just used to expand a guiding function required for importance sampling. The final DMC energy depends only weakly on the nodal surface of this function (i.e., the set of points in configuration space on which the function is zero).

- The QMC algorithm is intrinsically parallel and Monte Carlo codes are thus easily adapted to parallel computers and scale linearly with the number of processors. There are no memory or disk bottlenecks even for relatively large systems.

- We can use many-electron wave functions with explicit dependence on interparticle distances and no need for analytic integrability.

- We can calculate ground states, some excited states, chemical reaction barriers and other properties within a single unified framework. The method is size-consistent and variational.

One may ask why one should formulate a method based on the many-electron wave function when so much stress is normally placed on reducing the number of variables in the quantum problem (by using, e.g., density, Green's functions, density matrices or other quantities which depend on fewer independent variables). The main point is that the many-electron wave function satisfies a rather well-known fundamental equation [17]:

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \tag{1}$$

The price we pay for reformulating the problem in terms of the density is that we no longer know the exact equation satisfied by the density. In DFT, the complicated many-body problem is effectively relocated into the definition of the exchange-correlation functional, whose mathematical expression is not currently known and unlikely ever to be known exactly. The inevitable approximations to this quantity substantially reduce the attainable accuracy.

Widely-used standard solid state texts often refute the possibility of solving the many-electron Schrödinger equation directly in any meaningful way for large crystalline systems. To take a particular example, Ashcroft and Mermin [18] state that, 'one has no hope of solving an equation such as Eq. 1' and one must reformulate the problem in such a way as 'to make the one-electron equations least unreasonable'. The key simplifying physical idea to allow one to treat crystalline solids however, is not the use of one-electron orbitals but simply the imposition of periodic boundary conditions. One can then have an explicitly correlated many-body wave function (i.e., with explicit dependence on the interparticle separations), in a box, embedded in an infinite number of copies of itself. The 'particles' in the many-body wave function are no longer individual electrons, but electrons in the cell we are focussing on moving in tandem with all of their periodic images. Clearly in order for this to have any chance of being an accurate approximation, the range of the electron-electron pair correlation function must be substantially shorter than the repeat distance and the box must be large enough so that the forces on the particles within it are very close to those in the bulk. If not, then we may get substantial 'finite-size errors'.

This problem is analagous to, but not quite the same as, the problem of representing an infinite system in DFT calculations. In that case Bloch's theorem is used in the extrapolation to infinite system size so that the problem of calculating an infinite number of one-electron states reduces to the calculation of a finite number (equal to the number of electrons in the primitive cell) of states at an infinite number of $\mathbf{k}$ points. Because the energy of states at $\mathbf{k}$ points which are close together are very similar, the $\mathbf{k}$ space may be 'sampled' and if this is done efficiently the calculated energy per cell approaches that in the infinite system. The situation in QMC is a little different since the explicit correlation between electrons means that the problem cannot be reduced to the primitive cell; a one-electron wave function on a $2 \times 2 \times 2$ $\mathbf{k}$ point grid corresponds to a many-electron wave function for a $2 \times 2 \times 2$ supercell in real space. There is a 'many-body Bloch theorem' expressing the invariance of the Hamiltonian under translations of all electrons by a primitive lattice vector or of a single electron by a supercell lattice vector [19], and thus there are two $\mathbf{k}$ vectors associated with the periodic many-body wave function. The error analagous to inadequate Brillouin zone sampling can be made smaller either by increasing the size of the simulation cell or by choosing the **k** values using 'special **k** point' techniques [20]. An additional type of finite-size error arises in periodic QMC calculations (though not in DFT) when calculating interactions between particles with long-range Coulomb sums. The difference is that in QMC we deal with instantaneous positions of electron configurations, rather than with the interaction of averaged densities. When using the standard Ewald formulation [21, 22], the choice of boundary conditions leads to an effective depolarization field which is supposed to cancel the field due to notional surface charges. As all periodic copies of the simulation cell contain, for example, the same net dipole due to the random arrangement of electrons with respect to nuclei the interaction of the dipoles and the field gives rise to 'Coulomb finite size errors'. These can be substantially reduced by using special techniques [23].

A few years ago in his Nobel prize-winning address Walter Kohn suggested that the many-electron wave function is not a legitimate scientific concept for more than about a thousand particles [24]. Does this mean we're in trouble if we use them in QMC? The main idea behind this statement is that the overlap of an approximate wave function with the exact one will tend exponentially to zero as the number of particles increases, unless one uses a wave function in which the number of parameters increases exponentially. Such an object would not be computable for large systems. This is indeed true, as is easy to verify by calculating the overlap integral directly using VMC [25]. Note that one does not need the exact wave function itself to perform this calculation. Rather one can evaluate the overlap between a single-determinant wave function on its own and multiplied by a Jastrow correlation function. The fact that these share the same nodal surface does not matter since Kohn's argument is based solely on the high-dimensionality of the overlap integrals rather than, say, the explicit cancellation of positive and negative regions. However, his objection is almost certainly not relevant to the sort of QMC calculations discussed here. Clearly the successful DMC calculations of systems containing up to 2000 electrons mentioned earlier provide some evidence in this direction. Kohn's arguments were used to motivate density functional theory (DFT), but it is possible to argue that, within the standard Kohn-Sham formulation, DFT suffers from exactly the same overlap 'catastrophe'. For a large system the overlap of the determinant of Kohn-Sham orbitals with the exact one will go to zero because of the inevitable numerical inaccuracies and the approximations to the exchange-energy functional. Fortunately the overlap 'catastrophe' is irrelevant to calculating the quantities of interest. As Kohn himself points out, we are interested in quantities such as the total energy, which can be accurate even when the overlap with the exact wave function goes to zero. To get the energy right it is required only that relatively low-order correlation functions (such as the pair-correlation function) are well-described and QMC seems to manage this very well.

To understand how accurate the total energies must be we note that the main goal is to calculate the energy difference between two arrangements of a set of atoms. The desired result might be the energy required to form a defect, or the energy barrier to some process, or whatever. All electronic structure methods for large systems rely on a cancellation of errors in energy differences. For such error cancellations to occur we require that the error in the energy per atom is proportional to the number of atoms. If this condition was not satisfied then, for example, the cohesive energy would not have a well defined limit for large systems. Many VMC (and DMC) calculations have demonstrated that the commonly-used Slater-Jastrow form of many-body wave function leads to errors which are proportional to the number of atoms, and typically gives between 70 and 80% of the correlation energy independent of system size. Additional requirements on QMC algorithms are that the number of parameters in the trial wave function must not increase too rapidly with system size and that the wave function be easily computable. Fortunately the number of parameters in a Slater-Jastrow wave function increases only linearly with system size or at worst as the square of the system size, and it can be evaluated in a time which rises as a low power of the system size.

2 QMC algorithms

In this section, we will look at the basic ideas and algorithms underlying VMC and DMC.

2.1 Variational Monte Carlo

2.1.1 Basics

With variational methods we must ‘guess’ an appropriate many-electron wave function which is then used to calculate the expectation value of the Hamiltonian operator. In general this wave function will depend on a set of parameters $\{\alpha\}$ which can be varied to optimize the function and minimize either the energy or the statistical variance. The energy thus obtained is an upper bound to the true ground state energy,

$$\frac{\langle \Psi_T(\{\alpha\})|\hat{H}|\Psi_T(\{\alpha\})\rangle}{\langle \Psi_T(\{\alpha\})|\Psi_T(\{\alpha\})\rangle} = E(\{\alpha\}) \geq E_0 \; . \tag{2}$$

The expectation value of the Hamiltonian $\hat{H}$ with respect to the trial wave function Ψ_T can be written as

$$\langle \hat{H} \rangle = \frac{\int E_L(\mathbf{R})\Psi_T^2(\mathbf{R})\, d\mathbf{R}}{\int \Psi_T^2(\mathbf{R})\, d\mathbf{R}}, \tag{3}$$

where $\mathbf{R}$ is a $3N$ dimensional vector giving the coordinates $(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ of the N particles in the system, and $E_L(\mathbf{R}) = \frac{\hat{H}(\mathbf{R})\Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})}$ is known as the *local energy.*

We can evaluate this expectation value by using the Metropolis algorithm [26] to generate a sequence of configurations $\mathbf{R}$ distributed according to $\Psi_T^2(\mathbf{R})$ and averaging the corresponding local energies,

$$\langle \hat{H} \rangle = \frac{1}{M}\sum_{i=1}^{M} E_L(\mathbf{R}_i) = \frac{1}{M}\sum_{i=1}^{M} \frac{\hat{H}\Psi_T(\mathbf{R}_i)}{\Psi_T(\mathbf{R}_i)} \; . \tag{4}$$

The question of whether or not we get the right answer with this approach is just one of *complexity* ; can we create a wave function with enough variational freedom so that the energy approaches the exact (non-relativistic) ground state energy? The answer in general is no. There is no systematic way in which one can improve the wave function until the correct answer is reached, and in general, we shouldn’t normally expect to recover much more than 80% of the correlation energy in this way. As we shall see, the the final 20% or so can be calculated by feeding the VMC wave function into a projector method such as DMC. This, to my mind, is the main use of VMC and in our laboratory we rarely use it as a method in its own right when performing calculations. With this attitude, it is not generally necessary to kill oneself optimizing wave functions in order to recover an extra 1% of the correlation energy with VMC - it is better to use DMC and let the computer do the work for you. Although the efficiency of the DMC calculations is increased with more accurate trial functions, the final DMC energy does not in principle depend on that part of the wave function that we generally optimize.

2.1.2 The form of the trial wave function

Clearly, however, for VMC the choice of the trial function is particularly important as it directly determines the accuracy of the calculation ; the answer will approach the true energy from above as we use better and better wave functions. An additional consideration is the ‘zero variance principle’. As the trial function approaches an exact eigenstate the local energy $\frac{\hat{H}\Psi}{\Psi}$ approaches a constant, E, everywhere in configuration space (check the Schrödinger equation again!) and hence the variance approaches zero.

Through its direct influence on the variance of the energy the accuracy of the trial wave function thus determines the amount of computation required to achieve a specified accuracy. When optimizing wave functions, one can therefore choose to use energy or variance as the objective function to be minimized.

The fact that arbitrary wave function forms can be used is one of the defining characteristics of QMC. We do not need to be able to integrate the wave function analytically, as is done for example in quantum chemistry methods with Gaussian basis functions. We just need to be able to *evaluate* it at a point in the configuration space. If the electrons and nuclei have certain fixed positions in space, what is the value of the wave function? This being the case, we can use correlated wave functions which depend explicitly on the distances between particles. The most commonly-used functional form is known as the Slater-Jastrow wave function [27]. This consists of a single Slater determinant (or sometimes a linear combination of a small number of them) multiplied by a positive-definite Jastrow correlation function which is symmetric in the electron coordinates and depends on the inter-particle distances. The Jastrow function allows efficient inclusion of both long and short range correlation effects. As we shall see however, the final DMC answer depends only on the nodal surface of the wave function and this cannot be affected by the nodeless Jastrow. In DMC it serves mainly to decrease the amount of computer time required to achieve a given statistical error bar and improve the stability of the algorithm.

The basic functional form of the Slater-Jastrow function is

$$\Psi(\mathbf{X}) = e^{J(\mathbf{X})} \sum_n c_n D_n(\mathbf{X}) \ , \tag{5}$$

where $\mathbf{X} = (\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$ and $\mathbf{x}_i = \{\mathbf{r}_i, \sigma_i\}$ denotes the space-spin coordinates of electron i, $e^{J(\mathbf{X})}$ is the Jastrow factor, the c_n are coefficients, and the $D_n(\mathbf{X})$ are Slater determinants of single-particle orbitals,

$$D(\mathbf{X}) = \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_1(\mathbf{x}_2) & \ldots & \psi_1(\mathbf{x}_N) \\ \psi_2(\mathbf{x}_1) & \psi_2(\mathbf{x}_2) & \ldots & \psi_2(\mathbf{x}_N) \\ \vdots & \vdots & \vdots & \vdots \\ \psi_N(\mathbf{x}_1) & \psi_N(\mathbf{x}_2) & \ldots & \psi_N(\mathbf{x}_N) \end{vmatrix} \ . \tag{6}$$

The orbitals in the determinants are often obtained from self-consistent DFT or Hartree-Fock calculations and are assumed to be products of spatial and spin factors,

$$\psi_\alpha(\mathbf{x}) = \psi_\alpha(\mathbf{r})\delta_{\sigma,\sigma_\alpha} \ , \tag{7}$$

Here $\delta_{\sigma,\sigma_\alpha} = 1$ if $\sigma = \sigma_\alpha$ and zero otherwise. If the determinant contains $N_\uparrow$ orbitals with $\sigma_\alpha = \uparrow$ and $N_\downarrow = N - N_\uparrow$ with $\sigma_\alpha = \downarrow$, it is an eigenfunction of $\hat{S}_z$ with eigenvalue $(N_\uparrow - N_\downarrow)/2$. To avoid having to sum over spin variables in QMC calculations, one generally replaces the determinants D_n by products of separate up- and down-spin determinants,

$$\Psi(\mathbf{R}) = e^{J(\mathbf{R})} \sum_n c_n D_n^\uparrow(\mathbf{r}_1, \ldots, \mathbf{r}_{N_\uparrow}) D_n^\downarrow(\mathbf{r}_{N_\uparrow+1}, \ldots, \mathbf{r}_N) \ , \tag{8}$$

where $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ denotes the spatial coordinates of all the electrons. This function is not antisymmetric under exchange of electrons with opposite spins but it can be shown that it gives the same expectation value as $\Psi(\mathbf{X})$ for any spin-independent operator. Note that the use of wave function forms in QMC which allow one to treat non-collinear spin arrangements and the resultant vector magnetization density is an interesting open problem, and we are currently working on developing such an algorithm [28].

The full Jastrow functions that we typically use in CASINO contain one- and two-electron terms and may be inhomogeneous, i.e., depend on the distances of the electrons from the ions. Their functional form is quite complicated and involves sums in Chebyshev polynomials. However just to give you a feel for it, a simple Jastrow function for a homogeneous system such as the electron gas might look like :

$$e^{J(\mathbf{R})} \quad \text{with} \quad J(\mathbf{R}) = -\sum_{i>j} u_{\sigma_i,\sigma_j}(r_{ij}) \quad \text{and} \quad u_{\sigma_i,\sigma_j}(r_{ij}) = \frac{A}{r_{ij}}\left(1 - e^{-r_{ij}/F_{\sigma_i,\sigma_j}}\right) . \tag{9}$$

where r_{ij} is the distance between electrons i and j, and F is chosen so that the electron-electron cusp conditions are obeyed i.e. $F_{\uparrow\uparrow} = \sqrt{2A}$ and $F_{\uparrow\downarrow} = \sqrt{A}$. The value of A, and the coefficients in the Chebyshev expansion in the full version of the Jastrow function, will need to be optimized using, for example, variance minimization.

2.1.3 Optimization of trial wave functions

In our discussion so far we have said nothing about how we actually perform the wave function optimization, and this is clearly a critical step. Our code CASINO, for example, allows optimization of the parameters in the Jastrow factor, of the coefficients of the determinants of a multi-determinant wave function, and of various parameters in specialized wave functions such as pairing parameters in electron-hole gases and Padé coefficients in orbitals in Wigner crystals. Optimizing the orbitals themselves in the presence of the Jastrow factor would be a good thing to be able to do, since it optimizes the nodal surface in some sense and allows improvement of the DMC answer. This remains an active problem, although some progress has been made [29, 30].

There are many approaches to wave function optimization, but as far as our code is concerned, optimization of the wave function is achieved by minimizing the variance of the energy,

$$\sigma_E^2(\alpha) = \frac{\int \Psi^2(\alpha)\,[E_L(\alpha) - E_V(\alpha)]^2\,d\mathbf{R}}{\int \Psi^2(\alpha)\,d\mathbf{R}} , \tag{10}$$

where α is the set of parameters, and E_V is the variational energy. There are a number of reasons for preferring variance minimization over energy minimization (including the fact that the variance has a known lower bound of zero) but the most important is that it appears to show better numerical stability, particularly in large systems [31].

Minimization of σ_E^2 is carried out via a correlated-sampling approach in which a set of configurations distributed according to $\Psi^2(\alpha_0)$ is generated, where α_0 is an initial set of parameter values. The variance $\sigma_E^2(\alpha)$ is then evaluated as

$$\sigma_E^2(\alpha) = \frac{\int \Psi^2(\alpha_0)\,w(\alpha)\,[E_L(\alpha) - E_V(\alpha)]^2\,d\mathbf{R}}{\int \Psi^2(\alpha_0)\,w(\alpha)\,d\mathbf{R}} , \tag{11}$$

where

$$E_V(\alpha) = \frac{\int \Psi^2(\alpha_0)\,w(\alpha)\,E_L(\alpha)\,d\mathbf{R}}{\int \Psi^2(\alpha_0)\,w(\alpha)\,d\mathbf{R}} , \tag{12}$$

and the integrals contain a weighting factor, $w(\alpha)$, given by

$$w(\alpha) = \frac{\Psi^2(\alpha)}{\Psi^2(\alpha_0)} . \tag{13}$$

The parameters α are adjusted until $\sigma_E^2(\alpha)$ is minimized. The advantage of the correlated-sampling approach is that one does not have to generate a new set of configurations every time the parameter values are changed.

In order to create a set of configurations distributed according to $\Psi^2(\alpha_0)$, a VMC 'configuration generation' run must first be carried out. This is just an ordinary VMC run where 'snapshots' of the system are created by writing the current electron positions and associated interaction energies to a file. To perform the actual minimization, we then use an algorithm which performs an unconstrained minimization (without requiring derivatives) of a sum of m squares of functions which contain n variables, where $m \geq n$. Having generated a new set of parameters with this algorithm, we then carry out a second configuration generation run with these parameters followed by a second variance minimization run, and so on. Generally very few such 'iterations' are required before the minimum is approached. The procedure can be, and in CASINO is, thoroughly automated and providing a systematic approach is adopted, optimizing VMC wave functions is not the complicated time-consuming business it once was. This is particularly the case if one requires only the optimized wave function for input into a DMC calculation, rather than being concerned with lowering the VMC energy as much as possible.

2.1.4 VMC conclusions

Although VMC can be quite powerful when applied to the right problem, the necessity of guessing the functional form of the trial function limits its accuracy and there is no known way to *systematically* improve it all the way to the exact non-relativistic limit. In practice therefore, the main use of VMC is in providing the optimized trial wave function required as an importance sampling function by the much more powerful DMC technique, which we now describe.

2.2 Diffusion Monte Carlo

Let us imagine that we are ignorant, or have simply not been paying attention in our quantum mechanics lectures, and that we believe that the wave function of the hydrogen atom looks like a square box centred on the nucleus. If we tried to calculate the expectation value of the Hamiltonian using VMC we would obtain an energy which was substantially in error. What DMC can do, in essence, is to correct the functional form of the guessed square box wave function so that it looks like the correct exponentially-decaying one before calculating the expectation value. This is a nice trick if you can do it, particularly in cases where we have very little idea of what the exact ground state wave function looks like (that is, almost all of them). Clearly the necessary algorithm is rather more involved than the VMC.

Essentially then, the DMC method is a stochastic projector method for evolving the imaginary-time Schrödinger equation,

$$-\frac{\partial\Psi(\mathbf{R},t)}{\partial t} = -\frac{1}{2}\nabla^2\Psi(\mathbf{R},t) + (V(\mathbf{R}) - E_T)\Psi(\mathbf{R},t) \ . \tag{14}$$

Here the real variable t measures the progress in imaginary time and $\mathbf{R}$ is a $3N$-dimensional vector of the positions of the N electrons. $V(\mathbf{R})$ is the potential energy operator, E_T is an energy offset which only affects the normalization of the wave function Ψ, and $\nabla = (\nabla_1, \nabla_2, \ldots, \nabla_N)$ is the $3N$-dimensional gradient operator.

This equation has the property that an initial starting state $\Psi(\mathbf{R}, t = 0)$ decays towards the ground state wave function. In DMC the time evolution of Eq. 14 may be followed using a stochastic technique in which $\Psi(\mathbf{R},t)$ is represented by an ensemble of $3N$-dimensional electron configurations ('walkers'), $\{\mathbf{R}_i\}$. The time evolution of these configurations is governed by the Green's function of Eq. 14. Within the short time approximation the Green's function separates into two processes: random diffusive jumps of the configurations arising from the kinetic term and creation/destruction of configurations arising from the potential energy term.

Unfortunately this simple algorithm suffers from two very serious drawbacks. The first is that we have implicitly assumed that Ψ is a probability distribution, even though its fermionic nature means that it must have positive and negative parts. The second problem is less fundamental but in practice very severe.

The required rate of removing or adding configurations diverges when the potential energy diverges, which occurs whenever two electrons or an electron and a nucleus are coincident. This leads to extremely poor statistical behaviour.

These problems are dealt with at a single stroke by introducing an importance sampling transformation. If we consider the *mixed distribution* $f = \Psi_T \Psi$, where Ψ_T is known as the trial or guiding wave function, and substitute into Eq. 14 we obtain

$$-\frac{\partial f(\mathbf{R},t)}{\partial t} = -\frac{1}{2}\nabla^2 f(\mathbf{R},t) + \nabla \cdot [\mathbf{v}_D(\mathbf{R}) f(\mathbf{R},t)] + (E_L(\mathbf{R}) - E_T) f(\mathbf{R},t) \ , \tag{15}$$

where $\mathbf{v}_D(\mathbf{R})$ is the $3N$-dimensional *drift velocity* defined by

$$\mathbf{v}_D(\mathbf{R}) = \nabla \ln |\Psi_T(\mathbf{R})| = \frac{\nabla \Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})} \ , \tag{16}$$

and

$$E_L(\mathbf{R}) = \Psi_T^{-1} \left(-\frac{1}{2}\nabla^2 + V(\mathbf{R}) \right) \Psi_T \ , \tag{17}$$

is the local energy. This formulation imposes the *fixed-node approximation* [32]. The nodal surface of a wave function is the surface on which it is zero and across which it changes sign. The nodal surface of Ψ is constrained to be the same as that of Ψ_T and therefore f can be interpreted as a probability distribution. The time evolution generates the distribution $f = \Psi_T \Psi$, where Ψ is the best (lowest energy) wave function with the same nodes as Φ_T. The problem of the poor statistical behaviour due to the divergences in the potential energy is also solved because the term $(V(\mathbf{R}) - E_S)$ in Eq. 14 has been replaced by $(E_L(\mathbf{R}) - E_T)$ which is much smoother. Indeed, if Ψ_T was an exact eigenstate then $(E_L(\mathbf{R}) - E_T)$ would be independent of position in configuration space. Although we cannot in practice find the exact Ψ_T it is possible to eliminate the divergences in the local energy by choosing a Ψ_T which has the correct cusp-like behaviour whenever two electrons or an electron and a nucleus are coincident [33]. The fixed-node approximation implies that we solve independently in different nodal pockets, and at first sight it appears that we have to solve the Schrödinger equation in every nodal pocket, which would be an impossible task in large systems. However, the *tiling theorem* for exact fermion ground states [34, 35] asserts that all nodal pockets are in fact equivalent and therefore one only need solve the Schrödinger equation in one of them. This theorem is intimately connected with the existence of a variational principle for the DMC ground state energy [35].

A DMC simulation proceeds as follows. First we pick an ensemble of a few hundred configurations chosen from the distribution $|\Psi_T|^2$ using VMC and the standard Metropolis algorithm. This ensemble is evolved according to the short-time approximation to the Green function of the importance-sampled imaginary-time Schrödinger equation (Eq. 15), which involves biased diffusion and addition/subtraction steps. The bias in the diffusion is caused by the importance sampling which directs the sampling towards parts of configuration space where $|\Psi_T|$ is large. After a period of equilibration the excited state contributions will have largely died out and the configurations start to trace out the probability distribution $f(\mathbf{R}) / \int f(\mathbf{R}) \, d\mathbf{R}$. We can then start to accumulate averages, in particular the DMC energy, E_D, which is given by

$$E_D = \frac{\int f(\mathbf{R}) E_L(\mathbf{R}) \, d\mathbf{R}}{\int f(\mathbf{R}) \, d\mathbf{R}} \approx \sum_i E_L(\mathbf{R}_i) \ . \tag{18}$$

This energy expression would be exact if the nodal surface of Ψ_T was exact, and the fixed-node error is second order in the error in the nodal surface of Ψ_T (when a variational theorem exists [35]). The accuracy of the fixed node approximation can be tested on small systems and normally leads to very satisfactory results. The trial wave function limits the final accuracy that can be obtained because of the fixed-node approximation and it also controls the statistical efficiency of the algorithm. Like VMC, the

DMC algorithm satisfies a zero-variance principle, i.e., the variance of the energy goes to zero as the trial wave function goes to an exact eigenstate.

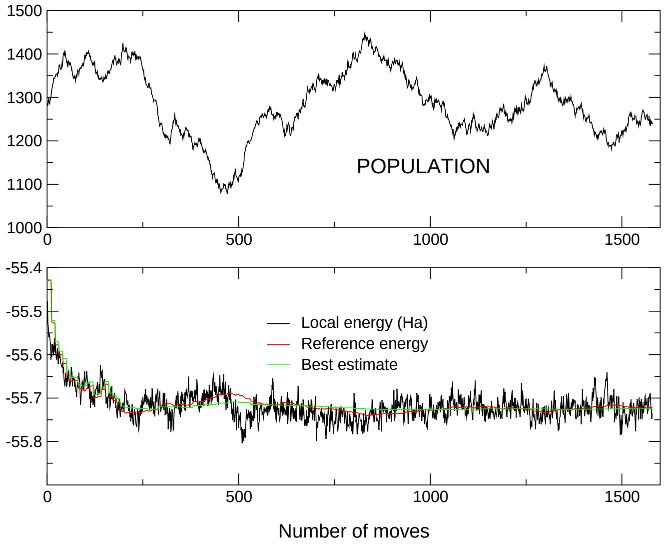

Figure 1: *DMC simulation of solid antiferromagnetic NiO. In the lower panel, the noisy black line is the local energy after each move, the green (or possibly grey) line is the current best estimate of the DMC energy, and the red (slightly different grey) line is E_T in Eqn. 15 which is varied to control the population of configurations through a feedback mechanism. As the simulation equilibrates the best estimate of the energy, initially equal to the VMC energy, decreases significantly then approaches a constant - the final DMC energy. The upper panel shows the variation in the population of the ensemble during the simulation as walkers are created or destroyed.*

3 Miscellaneous issues

In this section I will discuss some practical issues related to VMC and DMC.

3.1 More about trial wave functions

Single-determinant Slater-Jastrow wave functions often work very well in QMC calculations. For example, in the ground state of the carbon pseudo-atom, single determinant HF theory retrieves about 98.2% of the total energy. The residual 1.8% is the correlation energy, amounting to 2.7 eV in this case, which is very important for an accurate description of chemical bonding. A determinant of HF orbitals gives the lowest energy of all single-determinant wave functions and DFT orbitals are often very similar to them. These orbitals are not optimal when a Jastrow factor is included, but it turns out that the Jastrow factor does not change the detailed structure of the optimal orbitals very much, and the changes are well described by a fairly smooth change to the orbitals, which is conveniently included in the Jastrow factor.

How might we improve on the HF or DFT orbitals in the presence of the Jastrow factor? Direct optimization of the whole Slater-Jastrow wave function including both the orbitals and Jastrow factor has not been performed for large systems due to the computational cost. A promising technique [29, 30] is to optimize the potential that generates the orbitals rather than the orbitals themselves. Grossman and Mitas [36] have used a determinant of the *natural orbitals* which diagonalize the one-electron density matrix. It is not immediately clear why this should be expected to work in QMC, but the motivation appears to be that the convergence of configuration interaction expansions is improved by using natural orbitals instead of HF orbitals. However, the calculation of reasonably accurate natural orbitals is computationally demanding, and this approach is not attractive for large systems.

Another approach is to introduce 'backflow' correlations which were originally derived from a current conservation argument by Feynman and Cohen [37] to provide a picture of the excitations in liquid ^{4}He, although they are also helpful in fermionic systems. In the backflow trial function the electron coordinates $\mathbf{r}_i$ appearing in the Slater determinants of Eq. (8) are replaced by *quasiparticle coordinates*,

$$\bar{\mathbf{r}}_i = \mathbf{r}_i + \sum_{\substack{j=1 \\ (j \neq i)}}^{N} \eta(r_{ij})(\mathbf{r}_i - \mathbf{r}_j) \ , \tag{19}$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. The optimal function $\eta(r_{ij})$ may be determined variationally. Kwon, Ceperley, and Martin [38] found that the introduction of backflow significantly lowered the VMC and DMC energies of the three-dimensional uniform electron gas at high densities (it is expected to be even more significant in two dimensions). However, the use of backflow wave functions significantly increases the cost of QMC calculations because one can no longer move the electrons one at time, which is a significant saving in the standard algorithm. The basic scaling of the algorithm with backflow is thus N^4 rather than N^3.

In some cases it is necessary to use multi-determinant wave functions to preserve important symmetries of the true wave function. In other cases a single determinant may give the correct symmetry but a significantly better wave function can be obtained by using a linear combination of a few determinants. Multi-determinant wave functions have been used successfully in QMC studies of small molecular systems and even in periodic calculations such as the recent study of the neutral vacancy in diamond due to Hood *et al.* [39]. It is widely believed that a direct expansion in determinants (as used in configuration interaction calculations) converges very slowly because of the difficulty in describing the strong correlations which occur when electrons are close to one another. These correlations result in cusps in the wave function when two electrons are coincident, which are not well approximated by a finite sum of smooth functions [40]. However, this is not the whole story, and Prendergast *et al.* [41] have pointed out that the cusp is energetically less important, and that the slow convergence of determinant expansions has a lot to do with the description of medium-range correlations. In any case the number of determinants required to describe the wave function to some fixed accuracy increases exponentially with the system size. Practically speaking, this rules out the possibility of retrieving a significant extra fraction of the correlation energy with QMC in large systems via an expansion in determinants. Methods in which only local correlations are taken into account might be helpful, but overall an expansion in determinants is not a promising direction to pursue for making QMC trial wave functions for large systems, and the backflow technique, while costly, is more likely to be useful.

3.2 Basis set expansions : how to represent the orbitals?

The importance of using good quality single-particle orbitals in building up the Slater determinants in the trial wave function is clear. The determinant part accounts for by far the most significant fraction of the variational energy. However, the evaluation of the single-particle orbitals and their first and second derivatives can sometimes take up more than half of the total computer time, and consideration must therefore be given to obtaining accurate orbitals which can be evaluated rapidly at arbitrary points in space. It is not difficult to see that the most critical thing is to expand the single-particle orbitals in a basis set of *localized* functions. This ensures that beyond a certain system size, only a fixed number of the localized functions will give a significant contribution to a particular orbital at a particular point. The cost of evaluating the orbitals does not then increase rapidly with the size of the system. Note that 'localized basis functions' can (1) be strictly zero beyond a certain radius, or (2) can decrease monotonically and be pre-screened before the calculation starts, so that only those functions which could be significant in a particular region are considered for evaluation.

An alternative procedure is to tabulate the orbitals and their derivatives on a grid, and this is feasible for small systems such as atoms, but for periodic solids or larger molecules the storage requirements quickly become enormous. This is an important consideration when using parallel computers as it is much more efficient to store the single-particle orbitals on every node. Historically a very large proportion of condensed matter electronic structure theorists have used plane-wave basis sets in their DFT calculations. However in QMC, plane-wave expansions are normally extremely inefficient because they are not localized in real space ; every basis function contributes at every point, and the required number of functions increases linearly with system size. Only if there is a short repeat length in the problem are plane waves not totally unreasonable. Note that this does not mean that all plane-wave DFT codes are useless for generating trial wave functions for CASINO; a post-processing utility can be used to reexpand a function expanded in plane-waves in another localized basis before the wave function is input into CASINO. The usual thing here is to use some form of localized spline functions on a grid such as those used by the Lawrence Livermore group [15], or the 'blip' functions used by Mike Gillan's group [42] and implemented in CASINO by Dario Alfè [43].

Another pretty good way to do this is to expand the orbitals in a basis of Gaussian-type functions. These are localized, quick to evaluate, and are available from a wide-range of sophisticated software packages. Such a large expertise has been built up within the quantum chemistry community with Gaussians that there is a significant resistance to using any other type of basis. A great many Gaussian-based packages have been developed by quantum chemists for treating molecules. The most well-known of these are the various versions of the GAUSSIAN package [44]. In addition to the regular single determinant methods, these codes include various techniques involving multi-determinant correlated wave functions (although sadly, not QMC!). This makes them very flexible tools for developing accurate molecular trial wave functions. For Gaussian basis sets with periodic boundary conditions, the CRYSTAL program [45] can perform all-electron or pseudopotential Hartree-Fock and DFT calculations both for molecules and for systems with periodic boundary conditions in one, two or three dimensions, which makes it very useful as a tool for generating trial functions for CASINO.

3.3 Pseudopotentials

Pseudopotentials or effective core potentials are commonly used in electronic structure calculations to remove the inert core electrons from the problem and to improve the computational efficiency. Although QMC scales very favourably with system size it has been estimated that the scaling of all-electron calculations with the atomic number Z is approximately $Z^{5.5-6.5}$ which effectively rules out applications to atoms with Z greater than about ten. The use of a pseudopotential serves to reduce the effective value of Z and although errors are inevitably introduced, the gain in computational efficiency is sufficient to make applications to heavy atoms feasible.

Accurate pseudopotentials for single-particle theories such as DFT or Hartree-Fock theory are well developed, but pseudopotentials for correlated wave function techniques such as QMC present additional challenges. The presence of core electrons causes two related problems. The first is that the shorter length scale variations in the wave function near a nucleus of large Z require the use of a small time step. This problem can be significantly reduced (in VMC at least) by the use of acceleration schemes [46, 47]. The second problem is that the fluctuations in the local energy tend to be large near the nucleus because both the kinetic and potential energies are large.

The central idea of pseudopotential theory is to create an effective potential which reproduces the effects of both the nucleus and the core electrons on the valence electrons. This is done separately for each of the different angular momentum states, so the pseudopotential contains angular momentum projectors and is therefore a non-local operator.

It is convenient to divide the pseudopotential for each atom into a local part $V_{\rm loc}^{\rm ps}(r)$ common to all angular momenta and a correction, $V_{{\rm nl},l}^{\rm ps}(r)$, for each angular momentum l. The electron-ion potential energy term in the full many-electron Hamiltonian of the atom then takes the form

$$V_{\rm loc} + \hat{V}_{\rm nl} = \sum_i V_{\rm loc}^{\rm ps}(r_i) + \sum_i \hat{V}_{{\rm nl},i}^{\rm ps} \, , \tag{20}$$

where $\hat{V}_{{\rm nl},i}^{\rm ps}$ is a non-local operator which acts on an arbitrary function $g(\mathbf{r}_i)$ as follows

$$\hat{V}_{{\rm nl},i}^{\rm ps}\, g(\mathbf{r}_i) = \sum_l V_{{\rm nl},l}^{\rm ps}(r_i) \sum_{m=-l}^{l} Y_{lm}(\Omega_{\mathbf{r}_i}) \int Y_{lm}^*(\Omega_{\mathbf{r}_i'})\, g(\mathbf{r}_i')\, d\Omega_i' \, , \tag{21}$$

where the angular integration is over the sphere passing through the $\mathbf{r}_i$. This expression can be simplified by choosing the z-axis along $\mathbf{r}_i$, noting that $Y_{lm}(0,0) = 0$ for $m \neq 0$, and using the definition of the spherical harmonics to give

$$\hat{V}_{{\rm nl},i}^{\rm ps}\, g(\mathbf{r}_i) = \sum_l V_{{\rm nl},l}^{\rm ps}(r_i)\, \frac{2l+1}{4\pi} \int P_l\left[\cos(\theta_i')\right]\, g(\mathbf{r}_i')\, d\Omega_i' \, , \tag{22}$$

where P_l denotes a Legendre polynomial.

It is not currently possible to construct pseudopotentials for heavy atoms entirely within a QMC framework, although progress in this direction was made by Acioli and Ceperley [48]. It is therefore currently necessary to use pseudopotentials generated within some other framework. Possible schemes include HF theory and local density functional theory (DFT), where there is a great deal of experience in generating accurate pseudopotentials. There is evidence to show that HF pseudopotentials give better results within QMC calculations than DFT ones, although DFT ones work quite well in many cases. The problem with DFT pseudopotentials appears to be that they already include a (local) description of correlation which is quite different from the QMC description. HF theory, on the other hand, does not contain any effects of correlation. The QMC calculation puts back the valence-valence correlations but neglects core-core correlations (which have only an indirect and small effect on the valence electrons) and core-valence correlations. Core-valence correlations are significant when the core is highly polarizable, such as in alkali-metal atoms. The core-valence correlations may be approximately included by using a 'core polarization potential' (CPP) which represents the polarization of the core due to the instantaneous positions of the surrounding electrons and ions. Another issue is that relativistic effects are important for heavy elements. It is still, however, possible to use a QMC method for solving the Schrödinger equation with the scalar relativistic effects obtained within the Dirac formalism incorporated within the pseudopotentials. The combination of Dirac HF pseudopotentials and CPPs appears to work well in many QMC calculations. CPPs have been generated for a wide range of elements (see, e.g., Ref. [49]).

Many HF pseudopotentials are available in the literature, mostly in the form of sets of parameters for fits to Gaussian basis sets. Unfortunately many of them diverge at the origin, which can lead to significant time step errors in DMC calculations [50]. We have concluded that none of the available sets are ideal for QMC calculations, and that would be helpful if we generated an on-line periodic table of smooth non-divergent HF pseudopotentials (with relativistic corrections). This project is well on its way to completion.

Recent developments have been made that allow the use of all-electron QMC calculations for much heavier atoms than has previously been the case, based on reducing the fluctuations in the local energy near the nucleus. These developments will be described in the following section.

4 Recent developments

In this section I will describe some recent improvements to the basic algorithms that improve the ability of QMC to (1) treat heavier atoms with all-electron calculations, and (2) to treat larger systems by improving the scaling behaviour. Both these features have recently been implemented in the CASINO code.

4.1 All-electron QMC calculations for heavier atoms

At a nucleus the exact wave function has a cusp so that the divergence in the potential energy is cancelled by an equal and opposite divergence in the kinetic energy. If this cusp is represented accurately in the QMC trial wave function therefore, then the fluctuations in the local energy referred to in the previous section will be greatly reduced. If the wave function is formed from one or more determinants of single-particle orbitals expanded, for example, in a Gaussian basis set, then there can be no cusp in the wave function since Gaussians have zero gradient at $r = 0$. The local energy thus diverges at the nucleus. In practice one finds that the local energy has wild oscillations close to the nucleus which can lead to numerical instabilities in DMC calculations. To solve this problem we can make small corrections to the single particle orbitals close to the nuclei which impose the correct cusp behaviour. Such corrections need to be applied at each nucleus for every orbital which is larger than a given tolerance at that nucleus.

It is likely that a number of other researchers have developed such schemes, but within the literature we are only aware of the scheme developed by Manten and Lüchow [51], which is rather different from ours [52]. Our scheme is based on the idea of making the one-electron part of the local energy for each orbital, $\frac{\hat{H}_{oe}\phi}{\phi}$, finite at the nucleus. $\hat{H}_{oe}$ is given by

$$\hat{H}_{oe} = -\frac{1}{2}\nabla^2 - \frac{Z}{r}, \tag{23}$$

where r is the distance to the nucleus of charge Z. The scheme need only be applied to the s-component of orbitals centred at the nuclear position in question. Inside some radius r_c we replace the orbital expanded in Gaussians by $\phi = sgn[\psi(r=0)]\exp[p]$, where $sgn[\psi(r=0)]$ denotes the sign of the Gaussian orbital at $r = 0$ and p is a polynomial in r. Therefore $\ln|\phi| = p$ and the local energy is given by

$$E_L = \frac{\hat{H}_{oe}\phi}{\phi} = -\frac{p'}{r} - \frac{p''}{2} - \frac{p'^2}{2} - \frac{Z}{r}. \tag{24}$$

We impose five constraints, that $p(r_c)$, $p'(r_c)$, and $p''(r_c)$ are continuous, that $p'(0) = -Z$ (to satisfy the cusp condition), and that $E_L(0)$ is chosen to minimize the maximum of the square of the deviation of $E_L(r)$ from an 'ideal curve' of local energy versus radius.

To see the cusp corrections in action, let us first look at a hydrogen atom where the basis set has been made to model the cusp very closely by using very sharp Gaussians with high exponents. Visually (top left in Figure 2) the fact that the orbital does not obey the cusp condition is not immediately apparent. If we zoom in on the region close to the nucleus (top right) we see the problem: the black line is the orbital expanded in Gaussians, the red (or light grey if you've scrimped on the colour printing) line is the cusp-corrected orbital. The effect on the gradient and local energy is clearly significant. This scheme has been implemented within the CASINO code both for finite and for periodic systems, and produces a significant reduction in the computer time required to achieve a specified error bar, as one can appreciate from Figure 3.

In order to understand our capability to do all-electron DMC calculations for heavier atoms, and to understand how the necessary computer time scales with atomic number, we are currently carrying out a series of calculations on the various noble gas atoms [53]. So far it has proved to be perfectly possible to produce converged DMC energies with acceptably small error bars for atoms up to Z=36. It seems that even xenon (Z=54) can be done (although this is still running as I write this).

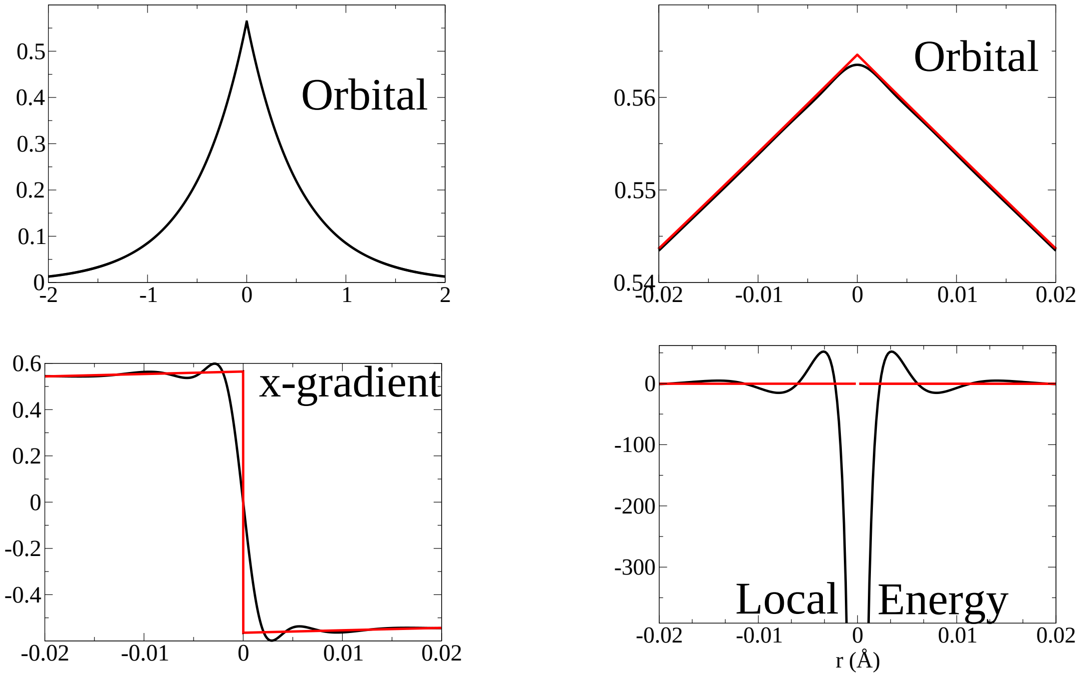

Figure 2: *Cusp corrections in the hydrogen atom.*

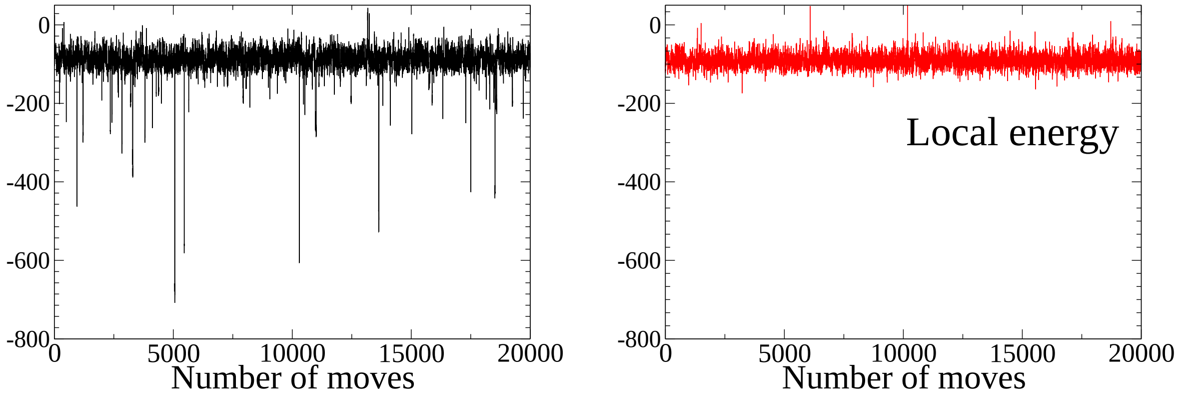

Figure 3: *Local energy as a function of move number in a VMC calculation for a carbon monoxide molecule with a standard reasonably good Gaussian basis set. The cusp corrections are imposed only in the figure on the right. The reduction in the local energy fluctuations with the new scheme is clearly apparent.*

4.2 Improved scaling algorithms

Let us now consider in more detail how QMC calculations scale with system size, and what one might do in order to improve the scaling behaviour. QMC methods are stochastic and therefore yield mean values with an associated statistical error bar. We might want to calculate the energy of some system and compare it with the energy of a different arrangement of the atoms. The desired result might be a defect formation energy, an energy barrier, or an excitation energy. These are evidently energy differences which become *independent of the system size* when the system is large enough. To perform such a calculation we therefore require an error bar ΔE on the energy of the system which is independent of system size, a feature denoted here by $\Delta E = \mathcal{O}(1)$. There are other quantities such as cohesive energies, lattice constants, and elastic constants, for example, in which both energy and error bar may be defined *per atom* or *per formula unit*, in which case the error bar on the whole system is allowed to scale linearly with system size, i.e., $\Delta E = \mathcal{O}(N)$.

How does the computational cost C of a QMC calculation, yielding an error $\Delta E = \mathcal{O}(1)$, scale with the system size, measured by the number of electrons N? The result for the standard algorithm is $C = AN^3 + \epsilon N^4$, where ϵ is very small [4]. In current solid simulations $N \leq 2000$, and the first term in this expression dominates, giving an N^3 scaling for the standard algorithm: double the system size and the cost goes up eightfold. What is the best scaling we could possibly achieve? As is well known, the best possible scaling for conventional (non-stochastic) single-particle methods such as DFT is $\mathcal{O}(N)$ [54]. A considerable effort has been made over the previous decade to design DFT codes which (a) scale linearly with system size, (b) are faster than the regular cubic scaling algorithm for reasonable system sizes, and (c) are *as accurate* as codes using the regular algorithm, with the latter two problems being the most difficult. In wave function-based QMC, these additional problems do not occur ; with the improved scaling algorithms described here the speed benefit is immediate and there is essentially no loss of accuracy. However, for the scaling one cannot do better than $\mathcal{O}(N^2)$ in general, unless the desired quantity is expressible as an energy per atom. Why is this so? One still has the 'near-sightedness' in the many-body problem which is exploited in linear scaling DFT algorithms, but the difference is the stochastic nature of QMC. The statistical noise in the energy adds incoherently over the particles, so the variance in the mean energy increases as N (and thus the error bar as $\sqrt{N}$). Since the variance is inversely proportional to the number of statistically independent configurations in the calculation, we see that to obtain $\Delta E = \mathcal{O}(1)$ we must therefore evaluate the energy of $\mathcal{O}(N)$ configurations, each of which costs $\mathcal{O}(N)$ operations. This accounts for the 'extra' power of N in the cost of a QMC calculation. However, $\mathcal{O}(N^2)$ scaling is still a vast improvement over $\mathcal{O}(N^3)$ scaling when N can be of the order of a few thousand, and clearly the scaling is improved further for properties which can be expressed in terms of energies per atom. The primary task is thus to reduce the AN^3 term to AN^2. The operations which make up this term are (1) evaluation of the orbitals in the Slater determinants, (2) evaluation of the Jastrow factor, and (3) evaluation of Coulomb interactions between particles.

The first of these operations is by far the most costly. As in $\mathcal{O}(N)$-DFT methods, the solution is to use *localized orbitals* instead of the delocalized single-particle orbitals that arise naturally from standard DFT calculations. The number of such orbitals contributing at a point in space is *independent of* N which leads to the required improvement in scaling. In fact, our collaborators at Lawrence Livermore have recently shown that this approach is extremely effective in molecular QMC calculations using maximally-localized Wannier function orbitals in the CASINO code [15]. We are currently working in collaboration with them to develop these methods and are testing the applicability of the method in various finite and periodic systems. One might expect this method to be more efficient for insulators than metals because the orbitals can be made more localized, but in practice a large efficiency gain in metals also seems to be achievable.

For the Jastrow factor all that is required to achieve the improved scaling is that it be truncated at some distance which is independent of system size. Because the correlations are essentially local it is natural to truncate the Jastrow factor at the radius of the exchange-correlation hole. Of course, truncating the Jastrow factor does not affect the final answer obtained within DMC because it leaves the nodal surface of the wave function unchanged, although if it is truncated at too short a distance the statistical noise increases. The scaling of the Coulomb interactions can be improved using an accurate scheme which exploits the fact that correlation is short-ranged to replace the long-range part by its Hartree contribution (in the style of the Modified Periodic Coulomb (MPC) interaction [23]).

For extremely large systems, the notionally ϵN^4 term might begin to be significant. This arises from N updates of the matrix of cofactors of the inverse Slater matrix (required when computing the ratio of new to old determinants after each electron move), each of which takes a time proportional to N^2, plus the extra factor of N from the statistical noise. In CASINO this operation has been significantly streamlined through the use of sparse matrix techniques and we have not yet found a system where it contributes substantially to the overall CPU time.

Method	Si	Ge	C	BN
LSDA	5.28[a]	4.59[a]	8.61[a]	15.07[e]
VMC	4.38(4)[c]	3.80(2)[b]	7.27(7)[d]	12.85(9)[e]
	4.82(7)[d]		7.36(1)[f]	
	4.48(1)[g]			
DMC	4.63(2)[g]	3.85(2)[b]	7.346(6)[f]	
Exp.	4.62(8)[a]	3.85[a]	7.37[a]	12.9[h]

Table 1: Cohesive energies of tetrahedrally bonded semiconductors calculated within the LSDA, VMC and DMC methods and compared with experimental values. The energies for Si, Ge, and C are quoted in eV per atom while those for BN are in eV per two atoms. References : *a.* Farid and Needs [55], and references therein. *b.* Rajagopal *et al.* [19], *d.* Fahy, Wang, and Louie [56]. Zero-point energy corrections of 0.18 eV for C and 0.06 eV for Si have been added to the published values for consistency with the other data in the table. *e.* Malatesta, Fahy, and Bachelet [57], *f.* Hood *et al.* [39], *g.* Leung *et al.* [58], *h.* Estimated by Knittle *et al.* [59] from experimental results on hexagonal BN.

Taken together the localization algorithms described above should speed up continuum fermion QMC calculations significantly for large systems, but we can view it in another light - as an *embedding* algorithm in which a QMC calculation could be embedded within a DFT one. The idea is to use the higher accuracy of QMC where it is most needed, such as around a defect site or in the neighbourhood of a molecule attached to a solid surface. Developments along the lines of those described here might allow such QMC/DFT embedding calculations to be performed for the first time. This is quite simple in VMC although a practical DMC embedding scheme would be more difficult.

5 Applications

Time and space preclude me from presenting a long list of applications, but here are some cohesive energies of tetrahedrally-bonded semiconductors to be going on with.

6 The CASINO code

CASINO [1, 2] is a program package developed in Cambridge by the group of Richard Needs for performing quantum Monte Carlo electronic structure calculations for finite and periodic systems. The philosophy behind it involves generality, speed, portability and ease-of-use. Generality in this sense means that one ought to be able to create a trial wave function for any system, expanded in any of a variety of different basis sets, and use it as input to a CASINO QMC calculation. Clearly the wave functions must be generated by an external electronic structure program, and this must in the past have been persuaded to write out the wave function in a format that CASINO understands, either all by itself, or through the transformation of its standard output using a separate CASINO utility. This is one of the main reasons that producing a QMC code is somewhat labour intensive. Maintaining these interfaces as codes evolve, and persuading their owners that this is a good idea in the first place, is a difficult and sometimes frustrating task. It is nevertheless part of the philosophy that CASINO should support a reasonably wide range of the most popular electronic structure codes, and at the present time this list includes CRYSTAL95/98/03 [45], GAUSSIAN94/98/03 [44], CASTEP [60], ABINIT [61], PWSCF [62], ONETEP [63], TURBOMOLE [64] and JEEP.

The most important current capabilities of CASINO are as follows :

- Variational Monte Carlo (including variance minimization of wave functions).

- Diffusion Monte Carlo (branching DMC and pure DMC).

- Use of Slater-Jastrow wave functions where the Slater part may consist of multiple determinants of spin orbitals.

- Trial wave functions expanded in plane waves or Gaussian basis sets (s, sp, p, d, f or g functions centred on atoms or elsewhere) produced using DFT, HF, or various multideterminant methods).

- Trial wave functions expanded in various kind of spline functions generated by post-processing plane-wave DFT solutions.

- Numerical atomic calculations with the orbitals and their derivatives interpolated from a radial grid.

- 2D/3D electron phases in fluid or crystal wave functions, with arbitrary cell shape/spin polarization/density (including excited state capability).

- 2D/3D electron-hole phases with fluid/crystal/pairing wave functions with arbitrary cell shape/spin polarization/density (including excited state capability). Variable electron-hole mass ratio. 2D layer separation between holes and electrons possible.

- Improved 'linear scaling' mode through use of Wannier orbitals and localized basis functions.

- Computation of excitation energies corresponding to either promotion or addition/subtraction of electrons.

- Computation of distribution functions such as the pair correlation function and density matrices (electron and electron-hole systems only for the moment).

- Calculation of electron-electron interactions using either Ewald and/or our 'modified periodic Coulomb interaction' [23] which is faster and has smaller Coulomb finite size effects.

- Written in strict compliance with the Fortran90 standard using modern software design techniques.

- Parallelized using MPI—tested in parallel on Hitachi SR2201, Cray T3E, SGI Origin 2000, SGI Altix, IBM SP3, Fujitsu Primepower, Alpha servers and SunFire Galaxy, Linux PC clusters. Also set up for workstation use on DEC Alphas, SGI Octane and O2, Linux PC with various compilers. MPI libraries not required on single processor machines.

- Flexible input with full documentation and interactive help system.

It is worth sketching a brief history of the CASINO code. Its development was inspired by a Fortran77 development code (known simply as 'the QMC code') written in the early 1990s in Cambridge by Richard Needs and Guna Rajagopal, assisted by many helpful discussions with Matthew Foulkes. This was later extended by Andrew Williamson up to 1995 and then by Paul Kent and Mike Towler up to 1998. Various different versions of this were able to treat fcc solids, single atoms and the homogeneous electron gas. By the late 1990s it was clear that a modern general code capable of treating arbitrary systems (e.g. at least atoms, molecules, polymers, slabs, crystals, and electron phases) was required, not only for the use of the Cambridge QMC group, but for public distribution. At that time, a user-friendly general publically available code did not exist, at least for periodic systems, and it was felt to be a good thing to create one to allow other researchers to join in the fun. So beginning in 1999 a new Fortran90 code, CASINO, was gradually developed in the group of Richard Needs largely by Mike Towler, considerably assisted from 2002 by Neil Drummond (some routines from the old code were retained, translated and reused, although most were gradually replaced). Various additional contributions have been made over the years by Andrew Porter, Randy Hood, Dario Alfè, Andrew Williamson, Gavin Brown, Chris Pickard, Rene Gaudoin, Ben Wood and others. The main aims of the new code were generality, speed, ease-of-use and transferability over a wide range of computational hardware. It is hoped that these objectives have been largely attained, but the code continues to be actively developed.

6.1 Availability of CASINO

We are making CASINO available to a number of groups now. However the technology of QMC can hardly be said to be mature, and largely for this reason it has been decided not to distribute the code under a GNU public licence in the admirable way that, for example, the ABINIT [61] project is run. We do not ask for any payment for academic use of the code, but we ask users to sign an agreement concerning its use. The practical upshot of this is that users may not redistribute the code, they may not incorporate any part of it into any other program system, nor may they modify it in any way whatsoever without prior agreement of the Cambridge group.

The CASINO distribution comes with extensive documentation and examples but clearly it remains a research code and learning how to use it is a significant task. This is particularly the case if the user does not have relevant experience such as familiarity with VMC and DMC calculations and knowledge of band structure methods for solids and DFT/molecular orbital theory. Available manpower is sufficiently limited that we find supporting users can take a large amount of our time and so we have to limit the number of such groups that we can work with directly. We find that most people need quite a lot of help and the project turns into a collaboration, but of course we cannot enter into too many projects of this type as our time is limited. We do have people visiting Cambridge to learn about the codes and how to do calculations, and this seems to work well.

7 Discussion and conclusions

In this article I have provided a very brief review of the VMC and DMC methods, highlighted some recent innovations, and introduced our implementation in the CASINO code. I have tried to make the case that QMC is a useful addition to the toolbox of the computational electronic structure theorist.

That said, it's important to be honest about the problems with QMC. If it is such a wonderful technique, why doesn't everyone use it? As an example of why not, see the web site of David Ceperley's group `archive.ncsa.uiuc.edu/Science/CMP/topten/topten.html` where there is a well-known page entitled 'Top Ten List of reasons why quantum Monte Carlo is not generally used in chemistry'. The list contains the following twelve reasons.

1. We need forces, dummy!
2. Try getting O_2 to bind at the variational level.
3. How many graduate students lives have been lost optimizing wavefunctions?
4. It is hard to get 0.01 eV accuracy by throwing dice.
5. Most chemical problems have more than 50 electrons.
6. Who thought LDA or HF pseudopotentials would be any good?
7. How many spectra have you seen computed by QMC?
8. QMC is only exact for energies.
9. Multiple determinants. We can't live with them, we can't live without them.
10. After all, electrons are fermions.
11. Electrons move.
12. QMC isn't included in Gaussian 90. Who programs anyway?

This apparently first appeared on the web in 1996, so it might be worth examining whether any progress has been made in these areas in the last seven years. Here is an attempt at a commentary :

1. *We need forces, dummy!*

Of course it is true that for QMC to be considered a general method, one ought to be able to calculate forces (i.e., derivatives of the energy with respect to nuclear displacements) in order to optimize structures or to perform dynamical simulations. In fact almost all QMC calculations up to the present time have been done within the Born-Oppenheimer approximation. The nuclear positions are thus fixed during the calculation and the wave function depends parametrically on the nuclear coordinates. The fixed nuclear positions are normally taken from geometry optimizations done with alternative methods such as DFT, on the principle that DFT is more reliable for geometries than for total energy differences. Calculating forces using a stochastic algorithm is a difficult thing to do. A straightforward application of the Hellmann-Feynman theorem (where the force is given by the gradient of the potential energy surface with respect to nuclear positions) leads to estimators with a very large variance. While a convincing general algorithm has yet to be demonstrated for QMC calculations, some progress has been made. The literature contains a variety of interesting contributions to this problem, which may be roughly classified into three groups :

- finite differences using correlated sampling techniques which take advantages of correlations between statistical samples to reduce the overall statistical error, e.g. [65].

- methods which use the standard Hellmann-Feynman formula. This is not normally useful in QMC as the Hellmann-Feynman estimator (at least with bare nuclei) has an infinite variance associated with it. One way of getting round this is to use some renormalized expression for the force, see e.g. [66]. Furthermore, the Hellmann-Feynman expression does not give the exact derivative of the DMC energy if the nodal surface is not exact and depends on the nuclear positions. This is due to an additional nodal term rising from the action of the kinetic-energy operator on the discontinuity in the derivative of the wave function at inexact nodal surfaces [67].

- direct attempts to calculate analytic derivatives, see e.g. [68].

Currently one cannot calculate accurate forces for large systems with QMC. However, some progress has been made and one has to be reasonably optimistic that a better general method for calculating forces will be devised in the near future. Also worth mentioning is the interesting recent attempt to design a coupled QMC and DFT molecular dyanmics algorithm by Grossman and Mitas [69].

2. *Try getting O_2 to bind at the variational level.*

I haven't managed to do so either. However, one can choose not to be overly concerned with QMC calculations done at the variational level. The binding energy of the oxygen molecule comes out very accurately in DMC [70, 71].

3. *How many graduate students lives have been lost optimizing wavefunctions?*

To give a feel for the time scale involved in optimizing wave functions, I can tell you about the weekend recently when I added the entire G2-1 set [72, 73] to the examples included with the CASINO distribution. This is a standard set of 55 molecules with various experimentally well-characterized properties intended for benchmarking of different quantum chemistry methods see e.g. Ref.[74]. Grossman has published the results of DMC calculations of these molecules using pseudopotentials [70], while we are doing the same with all-electron calculations [71]. It took a little over three days using only a few single-processor workstations to create all 55 sets of example files from scratch including optimizing the Jastrow factors for each molecule. While if one concentrated very hard on each individual case one might be able to pull a little more energy out of a VMC simulation, the optimized Jastrow factors are all perfectly good enough to be used as input to DMC simulations. I suggest that the process is sufficiently automated these days that graduate students are better employed elsewhere; certainly we have not suffered any fatalities here in Cambridge.

4. *It is hard to get 0.01 eV accuracy by throwing dice.*

With modern computers and efficient computer codes, there are a great many systems where one can get sufficient accuracy in a reasonable time. Obviously this becomes increasingly difficult for heavier atoms and large systems, but as discussed previously, satisfying the electron-nuclear cusp condition accurately in all-electron calculations or using pseudopotentials helps a lot.

5. *Most chemical problems have more than 50 electrons.*
QMC calculations for several thousand electrons (per simulation cell) have been published, and this number will only increase with the new improved scaling techniques currently being introduced, and with the increasing power of available computational hardware.

6. *Who thought LDA or HF pseudopotentials would be any good?*
Very accurate QMC results using LDA/HF pseudopotentials have been published. Such pseudopotentials seem to work best for *sp*-bonded systems, and it is not clear that particularly good results can be obtained in systems containing, for example, transition elements. As previously explained, we are developing an on-line periodic table containing a new set of smooth non-divergent Dirac-Hartree-Fock pseudopotentials expected to be particularly satisfactory for QMC calculations.

7. *How many spectra have you seen computed by QMC?*
Almost none. The calculation of excited state properties is a difficult problem for most other methods ; one can sometimes compute the energies of individual excited states pretty accurately with QMC, but the calculation of complete spectra is too difficult for the moment. It is very difficult in general to treat frequency-dependent properties.

8. *QMC is only exact for energies.*
The problem here is to find unbiased expectation values of operators that do not commute with the Hamiltonian. In standard DMC, the time evolution generates the mixed distribution $f(\mathbf{R}) = \Psi_T(\mathbf{R})\Psi_0(\mathbf{R})$, where $\Psi_0(\mathbf{R})$ is the best (lowest energy) wave function with the same nodes as the trial function $\Psi_T(\mathbf{R})$. To obtain the exact energy with respect to the distribution $\Psi_0^2(\mathbf{R})$ it is necessary to project by means of a mixed estimator, which in practice just involves summing the local energies over the positions generated in the DMC simulation:

$$E_{DMC} = \frac{\int \Psi_0(\mathbf{R})\hat{H}\Psi_T(\mathbf{R})\, d\mathbf{R}}{\int \Psi_0(\mathbf{R})\Psi_T(\mathbf{R})\, d\mathbf{R}} \approx \frac{1}{M}\sum_{i=1}^{M} E_L(\mathbf{R}_m) \tag{25}$$

If another operator $\hat{O}$ commutes with the Hamiltonian, then any eigenstate of $\hat{H}$ is (or may be chosen to be) an eigenstate of $\hat{O}$ and the same mixed estimator can be used to work out its expectation value. If $\hat{O}$ and $\hat{H}$ do not commute, then the mixed estimator does not give the ground state eigenvalue of $\hat{O}$. It is a good approximation to it however, and normally lies somewhere between the variational estimate and the exact value.

In general, the best thing to do to improve the expectation value of an operator that does not commute with the Hamiltonian is to improve the trial wave function. One may additionally use the extrapolation method [75] which approximates the true estimator as a linear combination of the mixed and variational ones, but it is not aesthetically pleasing and may not be particularly accurate in all cases. Note however that if the operator is just a simple local function of $\mathbf{R}$ and not, for example, a differential operator, then various methods can be used to obtain the ground state eigenvalue exactly. Among them are the future-walking algorithm (clearly explained in Ref. [3]) based on estimating the ratio $\frac{\Psi_0}{\Psi_T}$ using the asymptotic offspring of the DMC branching term, and the related time-correlation method [76]. Both of these methods are somewhat delicate however, and lead to signal-to-noise ratios that decay to zero at large time. Neither are likely to prove useful for large systems. More recently introduced bilinear methods [77] show promise but have not yet been fully developed into a practical general scheme. Probably the best scheme for the moment is the 'reptation QMC' method of Baroni and Moroni [78].

9. *Multiple determinants. We can't live with them, we can't live without them.*

As we have seen, multiple determinants are occasionally required to preserve important wave function symmetries, but more often one sees that using a linear combination of a few determinants can give a significantly lower DMC energy. Clearly this is because the nodal surface of this wave function is in some sense closer to the true one than that of the single determinant trial function. This is a problem not least because most electronic structure codes are not capable of generating optimized multiple determinant wave functions using e.g. the multi-configuration self-consistent field (MCSCF) method. Of the eight codes in the list supported by CASINO, only two (GAUSSIAN and TURBOMOLE) support multideterminant calculations, and to my knowledge there is no periodic code that does so. In an earlier section we observed that the number of determinants likely to be required in large systems effectively rules this out as a general solution. Orbital optimization and the backflow method are likely to prove more useful.

10. *After all, electrons are fermions.*
The solution to the fermion sign problem, which in this context means finding a way to bypass the fixed-node approximation in DMC, is one of the most interesting and important problems in computational physics. A solution to this would allow one to provide exact numerical solutions to the many-electron Schrödinger equation for fermionic systems (such as those containing electrons). It might seem strange to say that a stochastic or Monte Carlo method could solve such a problem exactly, since there is always a statistical error associated with the result, but we rely on the central limit theorem to provide an estimate of the probability that the exact results lies within a given interval. If we need to have the error to be less than this amount, this implies that the computer time will scale proportional to one over the square of the error.

We have seen that in DMC random walks serve to filter out the higher energy modes of some initial distribution, so that for very large imaginary time, the probability distribution of the random walkers is given by the ground state. The problem is that the ground state in question is actually the *bosonic* ground state which has the same sign everywhere in configuration space. It is only by imposing an additional boundary condition for the electronic Hamiltonian in the form of the fixed nodal surface that we are able to prevent collapse to the bosonic state, and maintain the positive and negative regions which are required for an antisymmetric wave function. The simplest methods which allow diffusing configurations to cross nodes and change the nodal surface, such as release-node Monte Carlo [79], are very inefficient because the 'signal' quickly becomes overwhelmed by the 'noise'. Methods which overcome this problem, such as fermion Monte Carlo [7, 8, 9] have been shown to be apparently stable for small test systems, but suffer from scaling problems with system size. It should never be forgotten that a genuine solution to the fermion sign problem in the context of continuum Monte Carlo methods must not only give the exact answer, but must also scale as some low-order polynomial with system size, and work generally rather than just for certain special cases. No proposed solution (and there are many in the literature) has all these characteristics. Recall that in some sense we already know how to solve the Schrödinger equation exactly for any system. One can in principle just do, for example, a full CI expansion in a complete basis set. The only trouble is it would take forever to compute and so this is not a viable solution.

That said, the fixed-node approximation is a good one, and one can normally recover well in excess of 95% of the correlation energy from a DMC calculation. For most problems this turns out to be accurate enough. Another approach - which is not a genuine solution to the sign problem but which might be the best practical thing to do - would be to optimize the nodal surface in some way, e.g., by optimizing the orbitals in the Slater part of the trial wave function (recalling that in some cases more than one determinant might be required for symmetry purposes). This ought certainly to be feasible and work is under way to develop an appropriate algorithm and implement such a facility in our CASINO code.

11. *Electrons move.*
Quite so.

12. *QMC isn't included in Gaussian 90. Who programs anyway?*

Nor in Gaussian94, '98 or '03. Neil Drummond and I and some of our collaborators like programming.

So, quite a lot of progress has been made in the theory and practical implementation of quantum Monte Carlo over the last few years, but certainly many interesting problems remain to be solved. For its most important purpose of calculating highly accurate total energies, the method works well and currently has no serious competitors for medium-sized and large systems. The CASINO program [1, 2] has been designed to allow researchers to explore the potential of QMC in arbitrary molecules, polymers, slabs and crystalline solids and in various electron and electron-hole phases.

Acknowledgements

I would like to thank the Royal Society [80] for the award of a research fellowship, to acknowledge the underlying contributions to this article of Richard Needs, Neil Drummond, Matthew Foulkes and Paul Kent, and to thank all our various collaborators.

References

[1] R.J. Needs, M.D. Towler, N.D. Drummond, and P.R.C. Kent, CASINO version 1.7 User Manual, University of Cambridge, Cambridge (2003).

[2] CASINO web site : `www.tcm.phy.cam.ac.uk/∼mdt26/casino.html`

[3] B.L. Hammond, W.A. Lester, Jr., and P.J. Reynolds, *Monte Carlo Methods in Ab Initio Quantum Chemistry* (World Scientific, Singapore, 1994).

[4] W.M.C. Foulkes, L. Mitas, R.J. Needs, and G. Rajagopal, *Rev. Mod. Phys.* **73**, 33 (2001).

[5] D.M. Ceperley and E.L. Pollock, *Phys. Rev. Lett* **56**, 351 (1986).

[6] C. Pierleoni, D.M. Ceperley, B. Bernu, and W.R. Magro, *Phys. Rev. Lett.* **73**, 2145 (1994).

[7] M.H. Kalos and K.E. Schmidt, *J. Stat. Phys.* **89**, 425 (1997).

[8] F. Pederiva and M.H. Kalos, *Comp. Phys. Commun.* **122**, 445 (1999).

[9] M.H. Kalos and F. Pederiva, *Phys. Rev. Lett.* **85**, 3547 (2000).

[10] D.M. Ceperley and B.J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).

[11] Y.S.M. Wu, A. Kuppermann, and J.B. Anderson, *Phys. Chem. Chem. Phys.* **1**, 929 (1999).

[12] G. Ortiz, M. Harris, and P. Ballone, Phys. Rev. Lett. **82**, 5317 (1999).

[13] D. Alfè, M.J. Gillan, M.D. Towler and R.J. Needs, to be published.

[14] M.D. Towler, R. Maezono and R.J. Needs, to be published.

[15] A.J. Williamson, R.Q. Hood, and J.C. Grossman, *Phys. Rev. Lett.* **87**, 246406 (2001).

[16] S. Manten and A. Lüchow, *J. Chem. Phys.* **119**, 1307 (2003).

[17] E. Schrödinger, *Ann. Phys.* **79**, 361 (1926).

[18] N.W. Ashcroft and N.D. Mermin, *Solid State Physics*, (Saunders, 1976), p.330.

[19] G. Rajagopal, R.J. Needs, A.J. James, S.D. Kenny, and W.M.C. Foulkes *Phys. Rev. B* **51**, 10591 (1995).

[20] G. Rajagopal, R.J. Needs, S.D. Kenny, W.M.C. Foulkes and A.J. James *Phys. Rev. Lett.* **73**, 1959 (1994).

[21] P.P. Ewald, Ann. Phys. **64**, 25 (1921).

[22] M.P. Tosi, in *Solid State Physics*, Vol. 16, edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1964), p. 1.

[23] L.M. Fraser, W.M.C. Foulkes, G. Rajagopal, R.J. Needs, S.D. Kenny, and A.J. Williamson, *Phys. Rev. B* **53**, 1814 (1996) ; A.J. Williamson, G. Rajagopal, R.J. Needs, L.M. Fraser, W.M.C. Foulkes, Y. Wang, and M.-Y. Chou, *Phys. Rev. B* **55**, R4851 (1997).

[24] W. Kohn, *Rev. Mod. Phys.* **71**, 1253 (1999).

[25] N.D. Drummond, First Year Ph.D. Report, University of Cambridge.

[26] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.M. Teller, and E. Teller, *J. Chem. Phys.* **21**, 1087 (1953).

[27] R.J. Jastrow, *Phys. Rev.* **98**, 1479 (1955).

[28] Z. Radnai, N.D. Drummond, M.D. Towler, and R.J. Needs, unpublished.

[29] S. Fahy, in *Quantum Monte Carlo Methods in Physics and Chemistry*, Nato Science Series C: Mathematical and Physical Sciences, Vol. 525, edited by M.P. Nightingale and C.J. Umrigar (Kluwer Academic, Dordrecht, The Netherlands, 1999), p. 101.

[30] C. Filippi and S. Fahy, *J. Chem. Phys.* **112**, 3523 (2000).

[31] P.R.C. Kent, R.J. Needs, and G. Rajagopal, *Phys. Rev. B* **59**, 12344 (1999).

[32] J.B. Anderson, *J. Chem. Phys.* **63**, 1499 (1975).

[33] T. Kato, *Commun. Pure Appl. Math.* **10**, 151 (1957).

[34] D. Ceperley, *J. Stat. Phys.* **63**, 1237 (1991).

[35] W.M.C. Foulkes, R.Q. Hood, and R.J. Needs, *Phys. Rev. B* **60**, 4558 (1999).

[36] J.C. Grossman and L. Mitas, *Phys. Rev. Lett.* **74**, 1323 (1995).

[37] R.P. Feynman and M. Cohen, *Phys. Rev.* **102**, 1189 (1956).

[38] Y. Kwon, D.M. Ceperley, and R.M. Martin, *Phys. Rev. B* **58**, 6800 (1998).

[39] R.Q. Hood, P.R.C. Kent, R.J. Needs, and P.R. Briddon *Phys. Rev. Lett.* **91**, 076403 (2003).

[40] W. Kutzelnigg and J.D. Morgan, III, *J. Phys. Chem.* **96**, 4484 (1992).

[41] D. Prendergast, M. Nolan, C. Filippi, S. Fahy, and J.C. Greer, *J. Chem. Phys.* **115**, 1626 (2001).

[42] E. Hernandez, M.J. Gillan, and C.M. Goringe *Phys. Rev. B* **55**, 13485 (1997).

[43] D. Alfè and M.J. Gillan, to be published.

[44] Gaussian 03, Revision B.03, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, and J.A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

[45] V.R. Saunders, R. Dovesi, C. Roetti, R. Orlando, C.M. Zicovich-Wilson, N.M. Harrison, K. Doll, B. Civalleri, I. Bush, Ph. D'Arco and M. Llunell, CRYSTAL2003 User's Manual (University of Torino, Torino, 2003).

[46] C.J. Umrigar, *Phys. Rev. Lett.* **71**, 408 (1993).

[47] M.L. Stedman, W.M.C. Foulkes, and M. Nekovee, *J. Chem. Phys.* **109**, 2630 (1998).

[48] P.H. Acioli and D.M. Ceperley, *J. Chem. Phys.* **100**, 8169 (1994).

[49] E.L. Shirley and R.M. Martin, *Phys. Rev. B* **47**, 15413 (1993).

[50] C.W. Greeff and W.A. Lester, Jr., *J. Chem. Phys.* **109**, 1607 (1998).

[51] S. Manten and A. Lüchow, *J. Chem. Phys.* **115**, 5362 (2001).

[52] M.D. Towler and R.J. Needs, unpublished.

[53] M.D. Towler, A. Ma, and R.J. Needs, to be published.

[54] S. Goedecker, *Rev. Mod. Phys.* **71**, 1085 (1999).

[55] B. Farid and R. J. Needs, *Phys. Rev. B* **45**, 1067 (1992).

[56] S. Fahy, X.W. Wang, and S. G. Louie, *Phys. Rev. B* **42**, 3503 (1990).

[57] A. Malatesta, S. Fahy, and G.B. Bachelet, *Phys. Rev. B* **56**, 12201 (1997).

[58] W.-K. Leung, R.J. Needs, G. Rajagopal, S. Itoh, and S. Ihara, *Phys. Rev. Lett.* **83**, 2351 (1999).

[59] E. Knittle, R. Wentzcovitch, R. Jeanloz, and M.L. Cohen, *Nature* **337**, 349 (1989).

[60] M.D. Segall, P.L.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, and M.C. Payne, *J. Phys.: Cond. Mat.* **14** 2717 (2002).

[61] *First-principles computation of material properties: the ABINIT software project*, X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, Ph. Ghosez, J.-Y. Raty, D.C. Allan. *Computational Materials Science* **25**, 478-492 (2002).

[62] S. Baroni, A. Dal Corso, S. de Gironcoli, and P. Giannozzi, `http://www.pwscf.org`.

[63] C.K. Skylaris, A.A. Mostofi, P.D. Haynes, O. Diéguez, M.C. Payne, *Phys. Rev. B* **66**, 035119 (2002) ; A.A. Mostofi, P.D. Haynes, C.K. Skylaris and M.C. Payne, *J. Chem. Phys.* **119**, 8842 (2003).

[64] R. Ahlrichs, M. Bär, M. Häser, H. Horn, and C. Kölmel, *Chem. Phys. Lett.* **162**, 165 (1989).

[65] C. Filippi and C.J. Umrigar, *Phys. Rev. B* **61**, 16291 (2000).

[66] R. Assaraf and M. Caffarel, *J. Chem. Phys.* **113**, 4028 (2000).

[67] K.C. Huang, R.J. Needs and G. Rajagopal, *J. Chem. Phys.* **112**, 4419 (2000).

[68] J. Vrbik and S.M. Rothstein, *J. Chem. Phys.* **96**, 2071 (1992) ; P. Belohorec, S.M. Rothstein and J.Vrbik, *J. Chem. Phys.* **98**, 6401 (1993).

[69] J.C. Grossman and L. Mitas, to be published.

[70] J.C. Grossman, *J. Chem. Phys.* **117**, 1434 (2002).

[71] M.D. Towler, unpublished.

[72] J.A. Pople, M. Head-Gordon, D.J. Fox, K. Raghavachari, and L.A. Curtiss, *J. Chem. Phys.* **90**, 5622 (1989).

[73] L.A. Curtiss, C. Jones, G.W. Trucks, K. Raghavachari, and J.A. Pople, *J. Chem. Phys.* **93**, 2537 (1990).

[74] L.A. Curtiss, K. Raghavachari, P.C. Redfern, and J.A. Pople, *J. Chem. Phys.* **106**, 1063 (1997).

[75] P.A. Whitlock, D.M. Ceperley, G.V. Chester, and M.H. Kalos, *Phys. Rev. B* **19**, 5598 (1979).

[76] D.M. Ceperley and B. Bernu, *J. Chem. Phys.* **89**, 6316 (1988).

[77] F. Arias de Saavedra and M.H. Kalos, *Phys. Rev. E* **67**, 026708 (2003) ; S.W. Zhang and M.H. Kalos, *J. Stat. Phys.* **70**, 515 (1993).

[78] S. Baroni and S. Moroni, *Phys. Rev. Lett.* **82**, 4745 (1999).

[79] D.M. Ceperley and B.J. Alder, *J. Chem. Phys.* **81** 5833 (1984).

[80] Royal Society web site : `www.royalsoc.ac.uk`.