Ψ_k Newsletter

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

Number 67 February 2005

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E-mail: psik-coord@dl.ac.uk

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1 Editorial

We start this newsletter with information on the LaTeX document class of all the newsletters up to date, including templates for various possible contributions to them. We would be very grateful if those templates could be followed at least approximately so that our work could be simplified. Unfortunately, we are not able to accept the MS Word documents, as we have no secretarial help.

In the section of the RTN on "Computational Magnetoelectronics" we publish scientific highlights of the four years' activity of this network, which finished last December. In the section of the RTN on "f-electrons" we have a report on the mid-term review meeting and workshop of this network, including abstracts of presented papers. Following this, is the announcement of the workshop by RTN "Exciting" on "Excited-state Properties of Solids". In the section of the ESF Psi-k Programme there are reports on two recent workshops, with abstracts of presented papers, plus one announcement of a hands-on course on the KKR-bandstructure code, to be held in Munich in June. Also the section of the UK's CCP9 Programme has a report on its conference held last November at Daresbury Laboratory, UK. The conference was associated with the Max Born lecture by and the prize presented to Professor Matthias Scheffler (FHI Berlin). The abstracts of presented papers are also included. A number of workshop/position announcements can be found in the two subsequent sections, followed by the abstracts of recent or newly submitted papers. In the section "Presenting Other Programmes/Initiatives" readers can find some information on the "FRAMES Software Framework Project". The newsletter is finished with a scientific highlight by M.-H. Lee, J.-S. Lin (Cambridge and Taipei), M.C. Payne, V. Heine, V. Milman (Cambridge), and S. Crampin (Canbridge and Bath) on **"Kinetic energy tuning for optimising pseudopotentials and projector reduction"**.

Please see the 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 2005 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@dl.ac.uk	**messages to the coordinators, editor & newsletter**
psik-network@dl.ac.uk	**messages to the whole Ψ_k community**

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

2 General News

2.1 Contributions to Psi-k Newsletters

In order to make our services to the community more efficient and to improve the flow of information, as well as help us with putting Psi-k Newsletters together, we would like to remind you that all the contributions to the newsletters should be e-mailed to

psik-coord@dl.ac.uk

while all the information that you wish to be distributed across the Psi-k mailing list should be sent to

psik-network@dl.ac.uk

The Psi-k mailing list is moderated and all e-mails need to be approved to prevent spreading SPAM and other similar material. To make this most efficient both for you and the owners of the Psi-k mailing list we would appreciate very much if you tried to follow the above advice, also stating clearly in the subject line of your e-mail its content, for example: ’`Postdoctoral position, University of ... , country`’ or ’`To join Psi-k mailing list`’, etc.

Similarly, we would be greatful if in submitting your contributions to the Psi-k Newsletters you could observe the Psi-k Newsletter’s LaTeX style as given below. Following this we also give a reminder of the abstract template, as well as the templates for the workshop reports and announcements, position announcements, and scientific highlights. All the other contributions may follow one of the templates, depending on what it is and how the contributor sees it fit to adapt them. We would just like to see that the guidelines were approximately followed, so that our work could be speeded up since we have no secretarial help available to convert contributions to the correct style or indeed to LaTeX. Unfortunately, we are not at the stage yet when we may be able to accept also the MS Word documents.

2.1.1 LaTeX Document Style of Psi-k Newsletters

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%  Template for the LaTeX Document Style of Psi-k Newsletters  %%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
\documentclass[11pt]{article}
\usepackage{graphicx}
\usepackage{epsfig}
```

```
\usepackage{graphicx,colordvi}
\usepackage[dvips]{color}
\usepackage{amssymb}
\usepackage{amsmath,amsfonts}
\usepackage{url}
\usepackage{bm}
\usepackage{longtable}
%%%%%%%%%%%%%%  other packages may be added above if necessary %%%%%%%%%%%%

\parindent 0pt
\topmargin -2cm
\hoffset -1.5cm
\textheight 25cm
\textwidth 16 cm
\renewcommand{\baselinestretch}{1.2}
\def\ni{\noindent}
\begin{document}
\parskip 1ex

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
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2.1.2 Abstract Template

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%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%  abstract number  %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
\newpage
\null
\vskip 2em
\begin{center}
\Large{\bf  T i t l e  \par}
\vskip 1.5em
{\large \lineskip .5em \begin{tabular}[t]{c}
A u t h o r s \\
{\it  A f f i l i a t i o n s  }\\
\end{tabular}\par}
\end{center}
\begin{abstract}
  T e x t   o f   t h e   a b s t r a c t
\end{abstract}
%
\noindent
```

```
(Submitted to  J o u r n a l  )\\
Contact person:  H i s/h e r   e - m a i l   a d d r e s s   \\

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
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2.1.3 Template for Reports on Workshops/Conferences

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%       Report on Workshop .....................   %%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
\newpage
\null
\begin{center}

\subsection{Report on Workshop ... }

\vspace{0.2cm}
{\large{\bf   P l a c e    \\[3mm]

              D a t e      \\[3mm]

              S p o n s o r s   \\[3mm]

              O r g a n i z e r s   \\[3mm]

              W e b   P a g e   i f   a v a i l a b l e  }}
\end{center}

\vspace{0.5cm}
\noindent

T e x t   o f   t h e   r e p o r t   h e r e   f o l l o w e d   b y:

P r o g r a m m e

A b s t r a c t s   o f   p r e s e n t e d   p a p e r s

L i s t   o f   p a r t i c i p a n t s

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
```

2.1.4 Template for the Workshop/Conference Announcements

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%       Workshop/Conference on  .....................  %%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
\newpage
\null
\begin{center}

\subsection{Workshop on ... }

\vspace{0.2cm}
{\large{\bf   P l a c e   \\[3mm]

              D a t e   \\[3mm]

              S p o n s o r s   \\[3mm]

              O r g a n i z e r s   \\[3mm]

              W e b   P a g e   i f   a v a i l a b l e }}
\end{center}

\vspace{0.5cm}
\noindent
T e x t   o f   t h e   a n n o u n c e m e n t   h e r e .

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
```

2.1.5 Template for Position Announcements

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%  Postdoctoral/Ph. D/Lecturer, etc., Positin at ....   %%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
\newpage
\null
\begin{center}
{\Large{\bf Postdoctoral/Ph. D/Lecturer/... Position \\[3mm]

Institution, Town, Country}}
```

```
\end{centre}

\vspace{0.5cm}
\noindent

Main body of announcement here.

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
```

For the scientific highlights the document class, margins, etc., should be the same as for the rest of the newsletter, as given above. Please do try to follow those to save us unnecessary work, for which, as mentioned above, we have no secretarial help.

2.1.6 Template for the Scientific Highlights

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%                                                                      %
%                Scientific Highlight of the Month                     %
%                                                                      %
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
\documentclass[11pt]{article}
\usepackage{graphicx}
\usepackage{epsfig}
\usepackage{graphicx,colordvi}
\usepackage[dvips]{color}
\usepackage{amssymb}
\usepackage{amsmath,amsfonts}
\usepackage{url}
\usepackage{bm}
\usepackage{longtable}
%%%%%%%%%%%%%%  other packages may be added above if necessary %%%%%%%%%%%%

\parindent 0pt
\topmargin -2cm
\hoffset -1.5cm
\textheight 25cm
\textwidth 16 cm
\renewcommand{\baselinestretch}{1.2}
\def\ni{\noindent}

\begin{document}
\parskip 1ex
```

```
\begin{center}
\section{SCIENTIFIC HIGHLIGHT OF THE MONTH}
\end{center}

\vspace{0.3cm}
\rule{16.0cm}{1mm}
\vspace{2mm}
\setcounter{section}{0}
\setcounter{figure}{0}

\begin{center}

Title

Authors

Affiliations

\end{center}


\begin{abstract}

Text of the abstract here.

\end{abstract}


Main body of the highlight here.

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
```

3 News from the RTN on "Computational Magnetoelectronics"

COMPUTATIONAL MAGNETOELECTRONICS

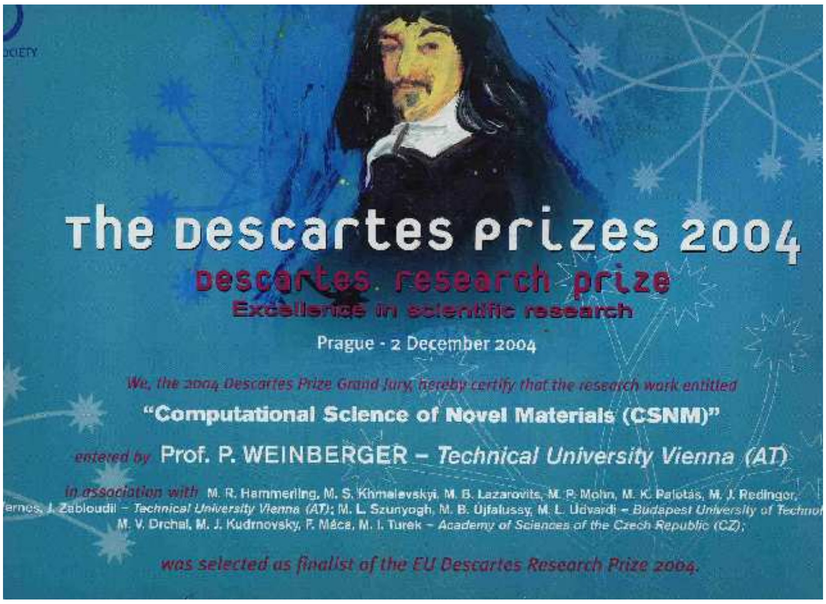
3.1 Final Report on the Scientific Activities

The RTN on "Computational Magnetoelectronics" finished its four years' existence at the end of September 2004. Below we present the scientific highlights of the Periodic Progress and Final Report of this network. The full report can be downloaded from the Network's web site

`http://psi-k.dl.ac.uk/index.html?magnetoelectronics`.

Awards and Distinctions

Four nodes of our Network were honoured in the past year. Firstly, the experimental member Albert Fert from Orsay received the "2003 Medaille d'Or du CNRS" (Gold medal of the CNRS) for the discovery of the Giant Magneto-Resistance (GMR) and his contributions to the development of the field of magneto- or spinelectronics. The CNRS-gold medal is extremely prestigious and only one medal is given each year for all fields of science. In 2004 Albert Fert was elected to the French Academy of Science.



The Descartes Prizes 2004

Descartes research prize

Excellence in scientific research

Prague - 2 December 2004

We, the 2004 Descartes Prize Grand Jury, hereby certify that the research work entitled

"Computational Science of Novel Materials (CSNM)"

entered by Prof. P. WEINBERGER – *Technical University Vienna (AT)*

in association with M. R. Hammerling, M. S. Khmelevskyi, M. B. Lazarovits, M. P. Mohn, M. K. Palotás, M. J. Redinger,
ernes, J. Zabloudil – *Technical University Vienna (AT)*; M. L. Szunyogh, M. B. Ujfalussy, M. L. Udvardi – *Budapest University of Technol*
M. V. Drchal, M. J. Kudrnovsky, F. Máca, M. I. Turek – *Academy of Sciences of the Czech Republic (CZ)*;

was selected as finalist of the EU Descartes Research Prize 2004.

Secondly, this Network in Computational Magnetoelectronics can be characterised by its research through strong networking. In particular one wishes to highlight the Austrian-Hungarian-Czech collaboration which was selected as one of the 2004 finalists for the Descartes prize in the subject of Computational Science of Novel Materials.

Already in the beginning of the nineties close scientific relations between research groups in Budapest, Prague (Brno) and Vienna were established, devoted to electronic and magnetic properties of novel materials. The first common publications [J. Kudrnovský, B. Wenzien, V. Drchal and P. Weinberger, 'Electronic structure of disordered overlayers on metal substrates', Phys. Rev. B **44**, 4068 (1991)] between Prague and Vienna appeared in 1991, those with Budapest a year earlier [L. Szunyogh, G. H. Schadler, P. Weinberger, R. Monnier and R. Podloucky, 'Nonstochiometry studies of the Y-Ba-Cu-O system in terms of a real space scattering coherent potential approximation (CPA)', Phys. Rev. B **41**, 1973 (1990)], since at that time the leader of the present Hungarian team was a PhD student in the Viennese research group. Since then not only a remarkable number of common publications appeared, but - because of close interactions - new theoretical approaches and computer codes were developed. These methods and codes are now widely used in the scientific community including for example such different places as the Institute des Solides, Universit Paris Sud or the Nanostructure Center of Oak Ridge National Laboratory. It was in particular the interaction between different approaches and ideas that created a remarkable continental European intellectual atmosphere: by viewing problems from different angles and in communicating in colourful English.

Up to the very recent past the majority of activities was located at the Center of Computational Materials Science (CMS) in Vienna, now in Budapest as well as in Prague similar institutions exist. In the 4-th framework programme of the European Union the Czech and Hungarian scientists took part as "special guests" of the Austrian node, in the 5-th framework they already formed separate nodes, collaborating now partially via the present RT-network with the corresponding Austrian node. It is reassuring to see that independent of proposal calls or changes in national conditions the Austrian, Czech and Hungarian researchers continue to pursue a particular kind of research: computational science in novel materials. In this sense the Center of Computational Materials Science in Vienna added in a very special manner to the unification in Europe.

Scientific Highlights

Evidence for intrinsic ferromagnetism in Co-doped ZnO semiconductors

K. Rode, A. Anane, F. Petroff, J.-L. Maurice, V. Cros, J.-P. Contour, A. Fert
Unité Mixte de Physique CNRS/Thales, Domaine de Corbeville, Orsay, France and
Université Paris-Sud, Orsay, France

A breakthrough in the field of new materials for spintronics was the report in 2001 of room temperature ferromagnetism in Co-doped ZnO films. Since then an intensive research has been carried out to assess the intrinsic nature of ferromagnetism in transition metal doped ZnO and rule out the presence of ferromagnetic transition metal clustering as an obvious origin of ferromagnetism. The CNRS-Orsay group of the French node has made significant progress towards this end in the last year of the network. Optimized $Zn_{0.75}Co_{0.25}O$ thin films were grown by pulsed laser deposition on $Al_2O_3(0001)$ substrates at 300 C under an oxygen partial pressure less than 10^{-6} Torr. A detailed study of the local structural and magnetic properties of our films by X-ray diffraction, X-ray absorption spectroscopies (XANES, EXAFS, XMCD) and transmission electron microscopy was carried out. By combining these techniques no evidence of Co clustering was found which confirms the intrinsic nature of ferromagnetism in our $Zn_{0.75}Co_{0.25}O$ films. A further confirmation came from the first experimental evidence of spin polarized tunneling of carriers in tunnel junctions of the type $Zn_{0.75}Co_{0.25}O$/Insulator/Co. Although the results are promising, there is still a lack of understanding of the origin of ferromagnetism in this ferromagnetic semiconductor since the experimental Co magnetic moment per atom is significantly smaller than predicted by theory.

Magnetic Percolation in Diluted Magnetic Semiconductors

L. Berqvist[1], O. Eriksson[1], P. Korzhavyi[1], I, Kudrnovsky [2], I. Turek[3], V. Drchal[2], K. Sato[4,5],
H. Katayama-Yoshida[5], P. H. Dederichs[4]
[1] Department of Physics, University of Uppsala, Sweden
[2] Institute of Physics, ASCR, Praha, Czech Republic
[3] Institue of Physics of Materials, Academy of Sciences of the Czech Republic, Brno
[4] Institute for Solid State Research, Research Center Juelich, Germany
[5] ISIR, Department of Physics, University of Osaka, Japan

Because of their ferromagnetism, the diluted magnetic semiconductors (DMS) represent a new class of materials with potential technological applications in the spintronics. The DMS with Curie temperatures of order of room temperature are needed for practical applications, whereas the currently prepared samples of Mn-doped GaAs exhibit Curie temperatures of about 170 K. Reliable determination of magnetic properties of DMS, in particular the critical temperature, is thus of great importance. By combining first principles calculations of interatomic exchange interactions with a classical Heisenberg model and Monte Carlo treatments of spin-fluctuations as well as the randomness of the underlying lattice, a theory that does not use any adjustable parameters was proposed. We have shown that the observed critical temperatures of a broad range of DMS, involving Mn-doped GaAs without and with As-antisites, Mn-doped GaN as well as Cr-doped ZnTe, are all reproduced with a good accuracy. An agreement between theory and experiment is obtained only when the magnetic atoms are randomly positioned on cation sublattices and when the chemical randomness and spin fluctuations are treated beyond the mean-field approximation. This suggests that the magnetic ordering temperature of diluted magnetic semiconductors is strongly influenced by magnetic percolation, which becomes more important for lower concentrations of magnetic impurities and for systems where the exchange interactions are strongly localized in the real space (Mn-doped GaN) (Phys.Rev.Lett. **93** 137202 (2003), Phys.Rev. B **70**, 201202 (2004)). Our analysis explains the wide interval of experimentally reported ordering temperatures, since the distribution of magnetic atoms on the cation sublattice is critically dependent on how the samples are prepared, resulting in a large range of ordering temperatures. In addition, the developed formalism represents a general scheme that can be applied to a number of other relevant problems in future, e.g., the effect of clustering of the magnetic atoms, the effect of electron correlations beyond the LSDA, the occurrence of magnetic atoms and defects on several sublattices, and many others.

Materials specific transport theory

M. Zwierzycki[1], K. Xia[1], M. Talanana[1], P.J. Kelly[1], G.E.W. Bauer[2], I. Turek[3]
[1] University of Twente, The Netherlands
[2] TU Delft, The Netherlands
[3] Academy of Sciences, Brno, Czech Republic.

A tight-binding muffin-tin-orbital (TB-MTO) transport formalism was developed in Twente in which the scattering states are calculated explicitly, making it possible to perform "channel decomposition" of the scattering induced by specular interfaces, interface disorder etc. 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 TB-MTO basis set allows scattering regions to be handled for which $N^2L \sim 10^6$ and calculations have been carried out for lateral supercells containing 20x20 atoms in order to analyse the interface scattering at disordered Co/Cu and Fe/Cr interfaces in an ongoing collaboration with the Delft node. The scheme has been used to study the influence of interface disorder on the giant magnetoresistance in both CPP and CIP geometries, on the spin-dependent interface resistance between the itinerant ferromagnet Fe and the prototypical semiconductor InAs, and on the suppression of Andreev reflection at interfaces between superconducting Pb and the transition metals Cu, Ni and Co.[PRL**89**, 166603 (2002); PRB**65**, 220401 (2002); PRB**63**, 064407 (2001)]

Transport and magnetic properties of M/X/M heterostructures (M=Fe, Co, or Ni, and X=Si, Ge, GaAs or ZnSe)

P. Vlaic[1], M. Alouani[1], H. Dreyss[1], O. Bengone[1], O. Eriksson[2], I. Turek[3]
[1]IPCMS, Universit Louis Pasteur, Strasbourg, France
[2]Department of Physics, University of Uppsala, Sweden
[3]Institue of Physics of Materials, Academy of Sciences of the Czech Republic, Brno

The magnetic and transport properties of Fe(Co)Si/Fe(Co), Fe/Ge/Fe, Fe(Co)/GaAs/Fe(Co) and Fe/ZnSe/Fe trilayer heterostructures were studied by means of a Green's function technique based on the tight-binding linear muffin-tin method. The interdiffusion at the interfaces is computed using the coherent potential approximation.

For all systems, we obtained a net charge transfer from the magnetic slab to the semiconducting region. The charge transfer, the magnetic moments of M atoms at the M/X interfaces as well as the exchange coupling between the magnetic slabs were found to be sensitive to the value of the lattice constant. In case of GaAs or ZnSe systems, the Fe and Co magnetic moments at the M/X interfaces depend of the terminations of the X semiconducting spacer, i. e., the Fe magnetic moment is higher for a Ga termination than for the As termination, and this difference results from a stronger hybridization between Fe and As atoms. We show that when the interdiffusion is confined to only two layers at the M/X interface the Fe(Co)/X/Fe(Co) (X=Si or Ge) interdiffused systems are instable. To explain the stability of these systems a more sophisticated mechanism resulting in an extended alloy formation at the interface is required. For all systems in the ferromagnetic state, the majority-spin electron conductance is much larger than the spin minority one, and for both spin channels the conductance decreases rapidly to zero with increasing spacer thickness. For the silicon systems, and for a small silicon thickness, negative values of tunnelling magnetoresistance ratio were obtained, in qualitative agreement with some experimental data. The strength of the conductance of the ferromagnetic state seems to be proportional to the sp density of states at the Fermi level, and the latter related to the strength of charge transfer at the M/X interface. Unfortunately, this proportionality does not hold for the the conductance of the antiferromagnetic state making the tunnelling magneto resistance (TMR) hard to predict. Nonetheless the so called metal-induced gap states (MIGS) at the Fermi level which result from the hybridization of the metal states and the sp states of the semiconductor at the interface decrease exponentially in the barrier and might explain the trend of the TMR as a function of the semiconductor spacer. Thus, for the Si semiconducting spacer the MIGS decrease much slower than for systems with Ge or GaAs (ZnSe) spacers, resulting in a much higher value for the TMR ratio for this system.

Electric transport through point contacts

Krisztin Palots[1], Bence Lazarovits[1], Lszl Szunyogh[1,2] and Peter Weinberger[1]
[1]Center of Computational Materials Science, Vienna, Austria
[2]Budapest University of Technology and Economics, Budapest, Hungary

Nanosized contacts between two macroscopic leads with single species (molecules, atoms) at its center attracted recently an intensive research interest. One of the most typical investigations are transport measurements showing, in particular, the by now well-known phenomena of conductance quantization and conductance fluctuations. Such systems are also possible candidates for spintronics devices. We employed a real-space formulation of the Kubo-Greenwood equation based on a Green's function embedding technique combined with the fully relativistic spin-polarized Korringa-Kohn-Rostoker method and performed a detailed investigation of the electrical transport through atomic-scaled contacts between two Au(001) semi-infinite systems. We studied the influence of transition metal impurities (Pd, Fe and Co) placed at various positions near the center of a particular contact and found that the conductance is very sensitive to the position of the magnetic impurities. The mechanism for the occurring relative changes can mainly be attributed to the impurities' minority d-band inducing resonant (Fano like) line-shapes in the s-like DOS at the center of the contact.

Spin-transfer and magnetization-relaxation enhancement in thin magnetic films

M. Zwierzycki[1], P.J. Kelly[1], Y. Tserknovnyak[2], A. Brataas[3] and G.E.W. Bauer[4]
[1] University of Twente, The Netherlands
[2] Harvard University
[3] Trondheim University, Norway and
[4] TU Delft, The Netherlands

The magnetization dynamics of small monodomain ferromagnets are well described by the Landau-Lifshitz-Gilbert (LLG) equation down to the micron scale. On the submicron scale, however, where the magnetization dynamics is no longer a highly coherent process because interfaces are relatively more important in small samples, new effects may play a role. One such effect, depending on the environment into which the ferromagnet is embedded, occurs when a time-dependent ferromagnetic order parameter pumps spin currents that carry angular momentum (and energy) into adjacent conducting materials. This angular-momentum loss is equivalent to a damping torque on the magnetization. It forms an additional, non-local source of ferromagnetic resonance (FMR) line broadening.
We used scattering matrices calculated from first-principles to study spin transfer and magnetization damping in layered systems comprising normal metal and ferromagnetic films. It was shown that the spin-current-induced magnetization torque is an interface effect and that quantum-interference effects are greatly overestimated by free-electron models and do not survive when realistic transition-metal band structures are used, especially when interface disorder is included. We also found that the additional term in the ferromagnetic equation of motion is of the Gilbert-damping form, with only a very small correction to the gyromagnetic ratio (cond-mat/0402088, accepted for publication in PRB).

Ferromagnetic Transition Metal Oxide Insulators

Z. Szotek[1], W. M. Temmerman[1], A. Svane[2], L. Petit[3], G. M. Stocks[3], H. Winter[4], M. Bibes[5], and A. Fert[5]
[1]Daresbury Laboratory, UK
[2]University of Aarhus, Denmark
[3]Oak Ridge National Laboratory, USA
[4]Forschungszentrum Karlsruhe, Germany
[5]Thales Paris, France

The field of spintronics is concerned with search for highly spin-polarized materials for spin-dependent devices and spin-injection into semiconductors. Since true half-metals are extremely difficult to realize in practice, spin filtering can also be exploited to create near 100% spin polarization. The ferromagnetic insulating spinel transition metal oxides may very probably be used as tunnel barriers in spin-filtering devices. The filtering of electrons is dependent on the difference in the gap amplitude between the spin-up and spin-down channels of the barrier. Therefore it is of interest to use compounds for which this difference is greater and in this respect the electronic structure calculations could be of great help in providing guidance to experiments. To facilitate this we have studied the electronic structure of such spinel oxides as $CoFe_2O_4$ and $NiFe_2O_4$. The latter is known to be an inverse spinel system, with the octahedral sites occupied by the divalent Ni- and trivalent Fe-ions, and the tetrahedral sites by the trivalent Fe-ions. Using the first principles SIC-LSD-DFT approach we have concentrated on correlations between structure, valence and magnetism of these compounds and their influence on spin filtering properties. In particular, we have established that for $NiFe_2O_4$ the insulating inverse spinel structure is indeed the ground state, meaning that it is not energetically favourable to place 2+ ions on the tetrahedral sites, although in the normal spinel arrangement of ions, with the divalent Ni-ions on the tetrahedral sites, one observes a substantial increase both in the total spin moment (fourfold) and the spin splitting of the conduction band. This has been in line with recent experiments by A. Fert's group in Paris that has seen a fourfold increase in the total magnetic moment of some thin film heterostructures of $NiFe_2O_4$. For $CoFe_2O_4$, a substantial increase in the conduction band splitting has also been calculated, together with more than twofold increase in the total spin moment, when changing from the inverse to normal spinel structure. However, the ground state in this case has been calculated to be a half-metallic, rather than insulating, state with all Fe- and Co- ions in the trivalent configuration. This finding does not necessarily exclude a possibility that the true ground state might be a mixture of the normal and inverse arrangements of ions, as some experiments might imply. In the normal spinel arrangement of ions, we have found both $NiFe_2O_4$ and $CoFe_2O_4$ to be just insulating, but possibly on the verge of becoming half-metallic.

Are Halfmetallic Heusler Alloys really halfmetallic?

Iosif Galanakis[1,2], Peter H. Dederichs[1], Phivos Mavropoulos[1], and Nikos Stefanou[2]
[1] Institute for Solid State Research, Research Center Juelich, Germany
[2] University of Athens, Athens, Greece

Halfmetallic alloys are hybrids between metals and semiconductors: they show a metallic behaviour for electrons with one spin direction, usually for the majority electrons, but a semiconducting behaviour with a band gap at the Fermi level for the other (minority) electrons. Thus at the Fermi energy they exhibit a 100 % spin polarisation, which makes them prime candidates for applications in spintronics. In a series of articles the authors have investigated the fundamental electronic structure properties of such Heusler alloys, as well as the question, if halfmetallicity, i.e. the band gap in the minority band, survives in real systems. The calculations for the ideal systems show, that (i) the band gap arises from the hybridisation between the d electrons of the magnetic transition metal atom and the non-magnetic one, (ii) the total magnetic moments Mt follow a Slater Pauling rule $M_t = Z_t - 2N_0$ where Z_t is the total number of valence electrons and N_0 the number of occupied minority bands ($N_0 = 9$ for half Heusler alloys and $N_0 = 12$ for full Heuslers). Relativistic calculations show that spin orbit coupling destroys the gap, at least in principle, but that in practice the spinpolarisation remains very high, say 99 %. In addition to the Heusler alloys we have also investigated the structurally similar halfmetallic zincblende compounds like CrAs. An important question is, if the halfmetallic behaviour prevails also at surfaces or at interfaces to semiconductors. The calculations show, that this is normally not the case, since localised dangling bond states appear in the band gap, similar to the behaviour observed at semiconductor surfaces. An exception are alloys containing Cr. Here the enhancement of the Cr local moment at the surface, the interface or in the multilayer can to a large extent preserve the gap, thus restoring the strong spin polarisation at E_F.

The authors are editing at present a book in the Springer series Lecture Notes on Physics with the title "Halfmetallic Alloys: Fundamentals and Applications". Furthermore I.G. has an invitation to write a review article for Reviews of Modern Physics.

Half-Metallic Transition Metal Oxides

Z. Szotek[1], W. M. Temmerman[1], A. Svane[2], L. Petit[3], G. M. Stocks[3], H. Winter[4], V. Cros[5] and A. Fert[5]

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Due to the strongly correlated nature of their electrons, transition metal oxides are typically characterised by the coexistence of different kinds of order, including charge and orbital order, together with superconducting and magnetic order. Many of them are of interest for 'spintronics' applications due to their half-metallic characteristics. The 100 % spin polarisation at the Fermi energy makes them ideal materials for spin-dependent devices and spin injection. Using the SIC-LSD-DFT method we have studied the electronic and magnetic properties of magnetite and such half-metallic double perovskites as Ba_2FeMoO_6, Sr_2FeMoO_6, and Ca_2FeMoO_6. In magnetite, we have concentrated on the half-metal to insulator transition, associated with a lattice distortion from inverse spinel to monoclinic structure and charge order between trivalent and divalent Fe ions, induced on the octahedral sites. Exploring a number of charge order scenarios we have shown that a simple Verwey order is not the lowest energy solution, and the ionic picture is not valid. The calculated charge disproportionation of the half-metallic scenario, with all Fe ions in the trivalent configuration, has been found in good agreement with experiment, unlike that for the insulating Verwey phase, where trivalent and divalent Fe's of the octahedral sites order in the alternating (001) planes. We have concluded that the structural distortions, more than localization/delocalisation correlations, are responsible for the charge disproportionation in the low temperature, monoclinic, phase of magnetite. In the double perovskites we have focussed on the Fe valence and the size and alignment of Fe and Mo spin moments to find contact with XMCD and NMR experiments. Based on the SIC-LSD-DFT calculations we have established that the half-metallic state in the studied double perovskites is driven by the interaction of the localized majority spin moment of the Fe^{3+} ion and an itinerant minority electron with an induced spin moment composed of Fe and Mo t_{2g} and oxygen 2p states. For all the perovskites studied, the calculated spin moments on Mo vary between -0.40 and -0.43 Bohr magnetons, and they are anti-parallel aligned with respect to Fe spin moments for all the compounds. This small variation has been confirmed by recent NMR experiments that have detected small differences in the Mo moments and they behave as we have calculated them, namely in the Ca- and Ba-compounds the Mo moments are smaller than in the Sr-compound.

Magnetic and transport properties of M/Cu/M multilayer systems (M=Fe, Co or Ni)

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The magnetic properties of (semi-infinite Cu)/nM/mCu/nM/(semi-infinite Cu) (M=Fe, Co or Ni and n, m=integer number of M or Cu atomic monolayers) multilayer systems were studied by means of a Green's function technique. The method is based on the tight-binding linear muffin-tin potential method in conjunction with the coherent potential approximation in order to describe the interdiffusion at the M/Cu interfaces. To calculate the transport properties in the ballistic limit in the current perpendicular-to-the plane geometry we used the Kubo-Landauer formalism. In case of Ni systems for smaller thickness of Ni magnetic slabs (n=1 or 2) no stable magnetic solutions were obtained. In case of Fe and Co systems at Fe(Co)/Cu interfaces there is a charge transfer from the magnetic slab to the non-magnetic Cu. At the M/Cu interfaces, there is an enhancement of the Fe magnetic moment while the Ni magnetic moment is reduced. The different magnetic behaviours of M atoms at the interfaces result from the competition between the narrowing of the density of states at the Fermi level due to the reduced coordination number and the decrease of the exchange splitting between majority- and minority-spin 3d sub-bands due to the hybridization between Cu and M states (sp-d and d-d). An oscillatory behaviour of the exchange coupling between ferromagnetic (FM) and antiferromagnetic (AFM) configurations with respect to the Cu spacer thickness was evidenced for all systems. The interlayer exchange coupling is influenced by the interdiffusion at the M/Cu interfaces. Thus in case of (semi-infinite Cu)/1Fe/3Cu/1Fe/(semi-infinite Cu) system a magnetic transition from the AFM to the FM state is obtained for the interdiffusion concentration c $\approx$ 4% while for the (semi-infinite Cu)/1Co/3Cu/1Co/(semi-infinite Cu) the FM state remains more stable in the whole interdiffusion range. For (semi-infinite Cu)/3Ni/5Cu/3Ni/(semi-infinite Cu) system a transition from the FM to the AFM state was obtained for the interdiffusion concentration c $\approx$ 26%. For all systems in the FM states, the transmission amplitude of the majority-spin electrons is found to be much larger compared with the minority-spin ones. The oscillations of the giant magnetoresistance ratio are damped with increasing Cu spacer thickness. These oscillations originate from the oscillations of partial minority-spin conductance in the FM state.

Anomalous magnetic anisotropy of Co monatomic wire at the Pt surface step edge

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Recent progress in fabrication and characterization of the one-dimensional (1D) arrays of 3d metal wires at stepped Pt(111) surface made possible to observe, for the first time, the long-range magnetic order in 1D. Ferromagnetic order was demonstrated on Co wire decorating the Pt(997) surface step edge by Gambardella et al. (Nature (London) **416**, 301 (2002)). Theoretically the Mermin-Wagner theorem (Phys.Rev.Lett. **17**, 1133 (1966)) forbids long-range 1D ferromagnetic order at non-zero temperatures. Nonetheless, ferromagnetism in 1D can be stabilized by a large magnetic anisotropy energy, which creates barriers effectively blocking thermal fluctuations. We performed the first-principles calculations using the relativistic full-potential linearized-augmented-plane-wave (FP-LAPW) method, in which the spin-orbit coupling is included self-consistently using the second-variational procedure (Phys.Rev. B **56**, R14259 (1997)). We used the so-called "magnetic force theorem" to compute the magnetic anisotropy energy (MAE). The key outcomes of our study (Phys.Rev. B **69**, (2004)) are: an easy axis at an odd angle rotated towards the Pt step edge, and an intrinsic noncollinearity between spin and orbital magnetic moments of the ferromagnetic Co wire and Pt substrate. We relate the origin of this novel magnetic behavior to the magnetic symmetry lowering at the surface step edge. We find a fair semi-quantitative agreement between our calculations and experimental data (Nature (London) **416**, 301 (2002)): the calculated MAE difference between the hard and easy axes ≈ 4.5 meV is somewhat bigger than experimentaly derived value of 2 meV/Co at T=45 K, and the calculated easy axis is rotated away from the z axis by the angle of 18 degrees which is smaller than the experimentally observed value of ≈ 43 degrees. Our supercell model is a way too simple comparing with the measured system to expect a true quantitative agreement. For example the effect of structure relaxation near the step edge (not taken into account) can be very important. More realistic calculations are in progress.

Absence of zero-bias anomaly in spin-polarized vacuum tunneling in Co(0001)

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One of the most striking effects in spin-dependent ballistic transport through planar tunnel junctions is the zero-bias anomaly (ZBA): the tunnel magneto-resistance (TMR) shows a pronounced maximum at zero bias voltage, in particular in junctions with oxide spacers. The origin of the ZBA was attributed to scattering at magnons and phonons as well as to scattering at defects while the density of states in the electrodes could be ruled.

In order to check the explanation by scattering at defects in the tunnel barrier, the oxide spacer was replaced by vacuum, thereby removing all scatterers from the spacer. Using a spin-resolved scanning tunneling microscope (Phys.Rev.Lett. **90** (2003) 116603), all other possible effects remain. Indeed, the experimental TMR for Co(0001) shows no ZBA, thus providing strong evidence for the defect hypothesis.

The experimental findings are fully supported by first-principles tunnel calculations within the Landauer-Buettiker theory as formulated in the layer-KKR method. Motivated by ab initio results for jellium, a heuristic potential within the vacuum region was introduced in order to treat a finite bias voltage (Phys.Rev. B **68** (2003) 174430). Superposing the image-charge potential between two metal surfaces and a linear potential drop with applied voltage, its shape is determined by the lead separation and the bias voltage. By this means, the absence of the ZBA in both theory and experiment is traced back to the electronic structure in the leads. Further, a distinct minimum in the experimental TMR at 0.2 eV bias voltage is explained by a majority surface state.

Surface-state electrons in atomic-scale nanostructures

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Surface-state electrons on the close packed surfaces of noble metals form a two-dimensional (2D) nearly free electron gas. An electron in such a state runs along the surface, much like a 2D plane wave. The scattering of the surface-state electrons by adatoms leads to quantum-interference patterns in the local density of states(LDOS) [Phys.Rev.Lett. **90**, 236801 (2003)] and to the long-range oscillatory interaction between adsorbates. These interactions were recently detected by STM and calculated by the ab initio method [Phys.Rev. B **68**, 205410 (2003)] for separations of up to 70 Angstrom. It has been found that the long-range interactions can lead to an atomic self-assembly. In this way, new magnetic nanostructures with fascinating properties can be created [Phys.Rev. B **70**, 075414 (2004)]. We have demonstrated that the controllable modification of the electronic confinement of surface-state electrons in atomically-engineered nanostructures, for example in quantum corrals, could permit to manipulate the exchange interaction between magnetic adatoms at large distances [Phys. Rev. Lett. subm], and could be of a great importance for developing of quantum nano-devices.

Rashba-effect at (magnetic) metallic surfaces

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In semiconductor heterostructures, the Rashba effect allows the manipulation of spin-polarized electrons in a two-dimensional electron gas (2DEG) by an electric field. On metallic surfaces that support surface states, these surface states form a 2DEG that moves in the natural electric field provided by the surface. Using photoemission, the Rashba effect can be observed directly as spin-orbit splitting of surface states on some metal surfaces. This has been observed on Au(111) and H-covered W(110), but recently also on a number of Bi surfaces. Our ab-initio calculations clearly demonstrate that the surface states are indeed split by spin-orbit interaction [Phys.Rev.Lett. **93** 46403 (2004)], and the effects can e.g. be seen analyzing quasiparticle interference patterns on a Bi(110) surface observed with STM [Phys.Rev.Lett. **93** 196802 (2004)].
On magnetic metal surfaces, the 2DEG has additionally an exchange splitting that separates the spin-orbit split branches of the surface state. This allows an easier, spin-resolved observation of the Rashba effect as has been demonstrated for the first time on a magnetic surface, i.e. Gd(0001): In combination with first-principles calculations, this effect also opens up a new possibility to directly observe the magnetism of the surface layer and its modification by adsorbates (like O on Gd) on an atomic scale [Phys. Rev. Lett. submitted; cond-mat/0403405]. Comparing our calculations with experimental data, overall good agreement is found.

Spin-dependent scattering at semiconductor/ferromagnetic metal interfaces

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The holy-grail of "spintronics" is to combine the spin-degree of freedom so effectively used in metal-based magnetoelectronics (Giant MagnetoResistance effect), with the functionality and flexibility of semiconductor-based electronics. To do this requires being able to introduce and manipulate unpaired spins into semiconductors at room temperature. This remains a major challenge.
Attempts to realize this in a straightforward fashion by passing a current through an interface between a ferromagnetic metal and a semiconductor failed. This failure was explained

in terms of the mismatch in the resistivities of metals and semiconductors: the large, spin-independent semiconductor resistivity completely swamps the small, spin-dependent ferromagnet resistivity. However, in this analysis, the interface resistance is neglected. By performing first-principles calculations for an Fe/InAs ohmic contact we showed that ideal interfaces have a spin-dependent resistance which is sufficiently large in absolute terms to make spin-injection possible. By performing calculations including disorder at the interface, it was also shown that the spin-dependence is very sensitive to such disorder. Similar calculations for Fe/GaAs Schottky barriers and for Fe/GaAs/Fe tunnel junctions confirmed this finding. [PRB**67**, 092401 (2003)] In addition to a majority-spin and a minority-spin interface conductance (or resistance), spin-transport through interfaces with ferromagnets are characterized by a complex-valued *mixing* conductance. The real part of the mixing conductance describes the angular momentum transfer to and from the ferromagnet, such as the strength of the spin-current induced magnetization torque or the non-local Gilbert damping. The imaginary part is an effective magnetic field. These parameters can be expressed in terms of our microscopically determined scattering matrices. They were evaluated for the Fe/InAs interface and used to interpret recent experiments in which photoinduced carriers in a semiconductor were polarized by spin-dependent reflection.[PRL**92**, 126601 (2004)]

Magnetism in quantum corrals

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Over the past two decades, electrons in two-dimensional (2D) surface states on closed packed surfaces of noble metals have been at the center of much experimental and theoretical attention. For a pristine surface the energies of such states lay in the 'gap' around the L point of the bulk Brillouin Zone and the wavefunctions are confined to the surface. The most interesting feature of this remarkable state of matter is its response to perturbations such as caused by placing transition metal atoms on the surface. As might be expected, such response displays long range, 'Friedel like', charge oscillations governed by the 2D Fermi 'Surface'. Indeed, one of the iconal experiments in nano-technology has been the fabrication of a circular arrangement of 48 Fe atoms on a Cu(111) surface and the direct observation, by Scanning Tunneling Microscopy (STM), of such oscillations within the circle. We discussed the, as yet unexplored, spin-polarized properties of such quantum corrals. We presented calculations for electronic and magnetic properties of surface states confined by a circular quantum corral built of magnetic adatoms (Fe) on a Cu(111) surface by showing the oscillations of charge and magnetization densities within the corral and the possibility of the appearance of spin-polarized states. In order to classify the peaks in the calculated density of states with orbital quantum numbers we analyzed the problem in terms of a simple quantum mechanical circular well model. This model is also used to estimate the behaviour of the magnetization and energy with respect to the radius of the circular corral.

Ab initio spin dynamics approach to nanostructures

Balázs Újfalussy[1,2], Bence Lazarovits[3], László Szunyogh[3,4] and G. Malcolm Stocks[1]
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[4]Budapest University of Technology and Economics, Budapest, Hungary

Stimulated by the need for ever higher density recording media, atomic scale magnetic devices are presently at the very focus of experimental and theoretical research. Without doubt, understanding and design of the relevant physical properties - magnetic moments, magnetic anisotropy energies, thermal stability, switching - of atomic scaled magnets demand detailed knowledge of their electronic and magnetic structure. In order to search for the magnetic ground state of surface nanostructures we extended *first principles* adiabatic spin dynamics to the case of fully relativistic electron scattering. The method relies on a constrained density functional theory whereby the evolution of the orientations of the spin-moments results from a semi-classical Landau-Lifshitz equation. This approach is applied to a study of the ground state of a finite Co chain placed along a step edge of a Pt(111) surface. The ground state spin orientation tilted with respect to the surface normal is obtained in excellent agreement with the experiment. We also found that this magnetic state is *noncollinear*: a feature that is expected to play a key role in nanostructures having complex geometry.

4 News from the RTN on "f-electrons"

"Ab-initio Computation of Electronic Properties of f-electron Materials"

4.1 Report on the Workshop and Midterm Review of the RTN “f-electrons”

Paris, 8-10 Dec. 2004

Coordinators:

S. Biermann (Ecole Polytechnique, Paris, France)

A. Georges (Ecole Polytechnique, Paris, France)

E. Wimmer (Materials Design, Le Mans)

The two-day workshop "Electronic Structure of Correlated Materials" preceeded the one-day midterm review meeting of the Research Training Network on "Ab initio Computation of Electronic Properties of f-electron Materials", held in Paris on 10th Dec. 2004.

The program of the workshop reflected recent progress on first principles investigations of f-electron materials, such as elemental Pu, Ce, Am or Yb as well as compounds containing f-electrons (e.g. the superconducting PuCoGa5 or CeBiPt). At the same time progress in methodological developments, in particular dynamical mean field techniques were presented.

The workshop included several invited presentations of external speakers, half of which were experimentalists, half theorists. The experimental state of the art in the field of heavy fermions was reviewed by J. Flouquet from Grenoble, recent theoretical advances were covered by G. Zwicknagl (TU Braunschweig). T. Gouder (Karlsruhe) and L.H. Tjeng (Cologne) presented their latest photoemission results, while P. Strange (Keele) talked on the theory of magnetic X-ray scattering from rare earth materials. G. Robert (CEA Bruyeres) showed his first principles study of the phase diagram of Pu and its alloys, and F. Aryasetiawan (Tsukuba) presented the latest developments in relation to the GW method and the calculation of the Hubbard U in correlated materials. The associated node at Rutgers was represented by G. Kotliar and his postdoc P. Sun, who presented recent developments within dynamical mean field theory. A talk by E. Wimmer (Materials Design, Le Mans) put state-of-the-art electronic structure calculations in perspective with respect to industrial applications.

Most of the postdocs employed within the RTN used the opportunity, to give – in addition to their short presentations within the review meeting – a more detailed talk within the workshop.

The workshop ended with a round table discussion, where recent advances and remaining challenges were discussed. The participants agreed on a set of benchmark problems which will serve for validating techniques and codes in the field.

The complete program and all abstracts are included below.

Participants

Abreu Luciano	CPHT, Ecole Polytechnique France
Amadon Bernard	CEA, Service de Physique de la Matire Condense France
Aryasetiawan Ferdi	Research Institute for Computational Sciences, AIST Japan
Biermann Silke	CPHT, Ecole Polytechnique France
Bjorkman Torbjorn	Department of physics, Uppsala University Sweden
Bouchet Johann	PCPM, Universit Catholique de Louvain Belgium
Eloirdi Rachel	Institute for Transuranium Elements Germany
Eriksson Olle	Department of Physics ngstrmlab., Uppsala University Sweden
Flouquet Jacques	CEA, DRFMC, Grenoble France
Georges Antoine	CPHT, Ecole Polytechnique France
Gouder Thomas	EC, Joint Research Centre, Institute for Transuranium Elements Germany
Grechnev Alexei	Department of Physics, Uppsala University Sweden
Jollet Francois	CEA, Service de Physique de la Matire Condense France
Jomard Gerald	CEA France
Katsnelson Mikhail	Institute for Molecules and Materials University of Nijmegen The Netherlands
Kotliar Gabriel	Rutgers University USA
Lebegue Sebastien	Uppsala University Sweden
Lichtenstein Alexander	University of Hamburg Germany
Lueders Martin	Daresbury Laboratory UK
Opahle Ingo	IFW Dresden Germany
Oppeneer Peter	Department of Physics, Uppsala University Sweden
Poteryaev Alexander	CPHT, Ecole Polytechnique France
Pourovskii Leonid	University of Nijmegen The Netherlands
Richter Manuel	IFW Dresden Germany
Robert Gregory	CEA, DCSA, SSA, LPMA France
Rozenberg Marcelo	CPHT, Ecole Polytechnique France
Santi Gilles	Dep. of Physics and Astronomy, University of Aarhus Denmark
Souvatzis Petros	Physics Departement, Uppsala University Sweden
Strange Paul	School of Chemistry and Physics, Keele University UK
Sun Ping	Rutgers University USA
Svane Axel	Dep. of Physics and Astronomy, University of Aarhus Denmark
Szotek Zdzislawa	Daresbury Laboratory UK
Tasnadi Ferenc	IFW Dresden Germany
Temmerman Walter	Daresbury Laboratory UK
Tjeng Liu Hao	II. Physikalisches Institut, University of Cologne Germany
Tomczak Jan	CPHT, Ecole Polytechnique France
Wimmer Erich	Materials Design, Le Mans France
Windiks Ren	Materials Design, Le Mans France
Zwicknagl Gertrud	Institut fuer Mathematische Physik Germany

Program

WEDNESDAY 8th December

9:00	Welcome	
9:10	Th. Gouder	Comparative Photoemission Study of Actinide (Am, Pu, Np and U) metals, nitrides and hydrides
9:50	G. Kotliar	Realistic DMFT calculations of f-electron systems using dynamical mean field theory
10:30	Coffee	
11:00	J. Flouquet	Experimental views on heavy fermion compounds
11:40	G. Zwicknagl	The dual nature of 5f-electrons: Spectral functions, heavy fermions and co-operative phenomena
12:20	E. Wimmer	Industrial Perspectives of Materials with f-electrons
12:40	Lunch	
14:00	B. Amadon	The α-γ transition in Cerium within LDA+DMFT at low temperature
14:20	L. Pourovskii	Local perturbative approach to electronic structure of actinidestems
14:40	A.I. Lichtenstein	Prospects of realistic QMC calculations for f-electron systems
15:00	A. Svane	The Plutonium atom
15:30	Coffee	
16:00	G. Robert	Study of plutonium and phase stability in δ-Pu alloys
16:20	O. Eriksson	Theory of mixed valency for Yb metals
16:40	P. Oppeneer	Electronic structure studies of the Pu-based superconductor PuCoGa$_5$ and of related actinide-115 compounds
17:10	G. Santi	Ab-initio calculations of the electronic structure of PuCoGa$_5$ and implications for superconductivity
17:30	Board meeting	

THURSDAY 9th December

9:00	L.H. Tjeng	The role of spin and orbital degrees of freedom in metal-insulator transitions
9:40	A.I. Poteryaev	Correlation-assisted Peierls Transition in VO$_2$
10:00	F. Lechermann	Inter-orbital charge transfers and the metal-insulator transition of BaVS$_3$
10:20	M. Katsnelson	Exciton effects in intermediate valence and Kondo systems
10:50	Coffee	
11:30	F. Aryasetiawan	Ab initio schemes for correlated electrons and the Hubbard U
12:10	P. Sun	Many-Body Approximation Scheme Beyond GW
12:30	Lunch	

14:00	M. Lueders	Self-interaction correction (SIC) in multiple scattering theory
14:20	P. Strange	Ab-Initio Theory of Resonant X-ray Scattering in Rare Earth Materials
15:00	Z. Szotek	SIC-LSD Description of spintronics materials
15:30	Coffee	
16:00	M. Richter	Field-induced band-structure change in CeBiPt
16:30	I. Opahle	Orbital magnetism of Co impurities in gold
16:50	F. Tasnadi	Approximate solution of the Poisson equation for slab geometry
17:10	Break	
17:30	Round table discussion:	Conclusions and perspectives

Abstracts

Comparative Photoemission Study of Actinide (Am, Pu, Np and U) Metals, Nitrides and Hydrides

T. Gouder

European Commission, JRC, Institute for Transuranium Elements, Postfach 2340, 76125 Karlsruhe

Photoemission spectroscopy has been widely used to study the electronic structure of the actinides. For the early actinides (U up to Pu), the 5f spectra are generally discussed in terms of ground-state density of states. It is implicitly assumed, that these are well itinerant systems, where the final state is similar to the ground-state. Even for Pu with its highly correlated 5f states, which are just at the verge of localization, fairly little attention is given to final state effects, which would effect the photoemission spectra and preclude direct comparison with the ground state DOS. For the neighbouring Am, which has a localized 5f ground-state configuration, spectra are then interpreted in terms of a final state multiplet.

We will present a comparative photoemission study of actinide (Am, Pu, Np and U) metals, nitrides and hydrides, and discuss the extend of ground and final state effects. Starting with the most localized compounds (Am), we will pass to more itinerant Pu, Np and U compounds. We will discuss, how localization effects (satellites, multiplets) slowly fade away giving rise to the band-like features. The sharp transition from itinerancy to localization (Pu to Am) observed in the ground-state, contrasts with the more gradual transition in photoemission. While spectra of Am metal still show some residual 5f hybridization, spectra of most Pu compounds already show pronounced localization effects, appearing as 5f5 and 5f6 multiplets.

Realistic DMFT calculations of f electron systems using Dynamical Mean Field Theory.

Gabriel Kotliar

Center for Materials Theory and Physics Department Rutgers University

Dynamical Mean Field theory is a powerful tool for describing the physics of strongly correlated materials. In this talk we will discuss recent successes of this method in describing physical properties of elements in the Lanthanide and Actinide series. We will describe steps the prospects for further development to make DMFT into a truly first principles and practical electronic structure method.

Experimental views on heavy fermion compounds

J. Flouquet

CEA Grenoble, France

We start with studies on cerium intermetallic compounds , point out that three pressures govern the low temperature properties.We then compare these Ce cases with the Yb situation notably on focusing on LaRh2Si2/ CeRh2Si2/ YbRh2Si2 and on considerations on LDA calculations. That leads to the idea that Ce and Yb examples have drastic differences in the strength of relative parameters such as valence, Kondo temperature,magnetic interactions. Finally we present the recent results obtained on SmS/SmB6/ Tmse and discuss the link betwwen valence magnetism and conduction. We propose a simple interpretation based on the feedback betwwen valence and Fermi temperature

The dual nature of 5f-electrons: Spectral functions, heavy fermions and co-operative phenomena

Gertrud Zwicknagl and Frank Pollmann

Institut f. Mathematische Physik, TU Braunschweig, Mendelssohnstr. 3, 38106 Braunschweig, Germany

We calculate the spectral functions of model systems describing 5f-compounds within Cluster Perturbation Theory. The method which combines exact diagonalization on small clusters with strong-coupling perturbation allows for an accurate treatment of the short-range correlations. The calculated excitation spectra provide evidence for the dual nature of 5f-electrons which has been conjectured previously. The partial localization associated with orbital-selective Mott transitions arises from the competition between Hund's rule type intra-atomic correlations and the anisotropic hopping in the crystal environment. We discuss implications for the formation of heavy fermions and for their interactions which may lead to co-operative phenomena.

Industrial Perspectives of Materials with f-electrons

E. Wimmer

Materials Design, Le Mans, France

This contribution reviews the industrial importance of materials containing f-electrons and connects the industrial needs with the capabilities and research efforts in electronic structure calculations. The scope includes rare earth elements and actinides. Rare earth elements play a critical role in many industrial applications including lighting systems, display technology, permanent magnets, thermoelectrics, catalysts, and pigments. Actinides are of central importance in nuclear technology and the understanding and prediction of their, structural, thermodynamic, and thermomechanical properties are intimately linked with the electronic structure of these systems. Selected examples such as the electronic structure of skutterudites for thermoelectric applications, the electronic properties of cerium compounds, and the thermomechanical properties of actinide compounds will illustrate the value of electronic structure calculations to the industrial scientists and engineers.

The α-γ transition in Cerium within LDA+DMFT at low temperature.

B. Amadon (1) , S. Biermann (2), A. Georges (2) et F. Aryasetiawan (4)

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We present a study of the α-γ transition in Cerium within dynamical mean field theory (DMFT) combined with Density Functional Theory within the Local Density Approximation (LDA). Using an implementation of the LDA+DMFT scheme based on the multiple LMTO method and both a QMC algorithm and a numerically efficient slave-rotor technique for the solution of the DMFT equations, we are able to explore the low-temperature phase diagram and to obtain spectral properties and total energies within a rigorous functional formulation. The alpha-gamma transition is characterized as a Kondo volume-collapse transition and shown to result from a stabilization effect on the kinetic energy due to the formation of a Kondo resonance.

Local perturbative approach to electronic structure of actinide systems

L.V. Pourovskii, A.I. Lichtentein and M.I. Katsnelson

University of Nijmegen, The Netherlands

We have implemented a new technique for realistic electronic structure calculations of f-electron systems with moderate and strong correlations. The technique is based on the dynamical mean field theory (DMFT) with a perturbation treatment of correlations in the effective impurity problem by the combination of the T-matrix and fluctuating exchange approximations (spin-polarized T-matrix + FLEX, SPTF). The SPTF method provides an adequate description of electron correlations in 3d metals, while it is less computationally demanding in comparison with the quantum Monte Carlo technique. Contrary to previous implementations of the SPTF, the present approach allows one to include effects of strong spin-orbit coupling which makes it applicable for actinides and their compounds. We apply our technique in conjunction with the LDA+U method to study magnetic and electronic properties of the δ phase of plutonium as well as the Pu monochalcogenides.

Prospects of realistic QMC calculations for f-electron systems

A. Lichtenstein

University of Hamburg

Realistic description of correlated actinide materials within the local density approximation plus dynamical mean field theory (LDA+DMFT)depends crucially on the efficiency and accuracy of quantum impurity solver. We analyze different possibilities to use a multiband Quantum Monte-Carlo scheme for general Coulomb interactions to perform LDA+DMFT calculations for f-electron systems. As an important example, we investigate the spectral function for fcc phase of Pu. The first-principle LMTO-TB scheme have been used to produced the orthogonal one-electron Hamiltonian. The multi-band Quantum Monte-Carlo method with general spin-density interactions produce an accurate results for the local Green function and density of states for f-electron materials. The efficiency of QMC scheme with non-diagonal Coulomb interactions for the LDA+DMFT calculations will be discussed.

The plutonium atom

Axel Svane

University of Aarhus, Denmark

The multiplet structure of an ion of f^n electronic configuration is calculated in terms of Slater integrals and the spin-orbit coupling parameter. The atom is subsequently embedded in a solid environment using the Hubbard-I approximation, i.e. the atomic self-energy is combined with an LDA Hamiltonian leading to a spectral distribution with combined atomic-like and band-like features. The approach is applied to PuSe, PuSb and δ-Pu.

Study of plutonium and phase stability in δ-Pu alloys

G. Robert

CEA Bruyères-le-Châtel, France

Due to it location in the actinides series, plutonium presents specific properties like peculiar crystalline structures and special behavior in binary alloys. *Ab initio* methods are well designed to calculate the specificities of these compounds for which it is difficult to carry out experimental measurements. Taking into account a magnetic order in GGA approximation (DFT calculations) gives results in agreement with methods using a more specific treatment for $5f$ electrons (LDA+U). Then we are able to treat in a unified way all the allotropic phases of plutonium and our results are consistent with experimental data. We are thus able to evaluate the different contributions of the free energy of plutonium and the essential influence of the chemical short range order in the determination of binary phases diagrams .

O. Eriksson

Theory of mixed valency for Yb metal

University of Uppsala, Sweden

A first principles method for calculatoing the electronic structure and total energy of solids in an intermediate-valence configuration is proposed. The method takes into account correlation effects and many-body renormalization of the effective hybridization. The theory, which is based on the Falicov-Kimbal model, is exemplified by means of a study of Yb metal, and both the observed electronic structure (as given by x-ray absorbtion experiments) and the equation of

state are reproduced with good accuracy.

Electronic structure studies of the Pu-based superconductor $PuCoGa_5$ and of related actinide-115 compounds

Peter M. Oppeneer,[1] Ingo Opahle,[2] Saad Elgazzar,[2] and Alexander B. Shick[3]

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The electronic structure of the novel Pu-based medium-high-T_c superconductor $PuCoGa_5$ is investigated on the basis of *ab initio* density functional theory calculations, employing the local spin-density approximation (LSDA). The electronic structures of various related actinide 115-compounds are investigated as well. The equilibrium lattice parameters within the tetragonal $HoCoGa_5$ crystal structure are well reproduced for $UCoGa_5$, $NpCoGa_5$, as well as for the three isoelectronic Pu-115 compounds ($PuCoGa_5$, $PuRhGa_5$, and $PuIrGa_5$) when we assume delocalized $5f$ states. Our total-energy calculations predict antiferromagnetic order to be favorable for all three Pu-115 materials, which is, however, observed experimentally for $PuIrGa_5$ only. In each of the Pu-115 materials the density of states at the Fermi energy is dominated by the Pu $5f$ contribution, indicating the participation of the Pu $5f$ electrons in the pair formation. For $UCoGa_5$, a comparison of the *ab initio* calculated and the experimental properties clearly supports the picture of delocalized $5f$ electrons. Also for $NpCoGa_5$ the $5f$'s are still delocalized to some extent, whereas for $AmCoGa_5$ the Am $5f$ electrons can be expected to be localized. The possibility of a partial $5f$ localization occurring for $PuCoGa_5$ is investigated through LSDA+U calculations. The inclusion of the intra-atomic Coulomb correlation U leads to a significant reconstruction of the f-states electronic structure, for which the positions of the f-states compare better with the results from photoemission experiments. Implications of strong on-site Coulomb correlations for the electronic structure of $PuCoGa_5$ are considered. The possible origins of the unexpected superconductivity are discussed and new experimental evidence for unconventional d-wave superconductivity is presented. Our investigation particularly reinforces the analogy to the heavy-fermion superconductors $CeCoIn_5$ and $CeIrIn_5$, however, with a stronger coupling strength due to a much stronger $5f$ hybridization.

Ab-initio calculations of the electronic structure of PuCoGa5 and implications for superconductivity

Gilles Santi

Department of Physics and Astronomy, University of Arhus, Denmark

I will present the results of our electronic structure calculations for the 18.5 K superconductor PuCoGa5. We used both the Wien2k FLAPW code (within LDA+U) and the self-interaction-corrected (SIC) LMTO method to inves- tigate the effect of different localisation scenarios on the Fermi surface. We estimated the electron-phonon interaction within the rigid-ion approximation and found that it does not appear to be strong enough to explain the high-Tc observed. This points towards spin-fluctuations mediated superconductivity in this compound, in agreement with reports of unconventionalsuperconductivity.

The role of spin and orbital degrees of freedom in metal-insulator transitions*

L.H. Tjeng and D.I. Khomskii

I. Physikalisches Institut, University of Cologne, Zlpicherstrasse 77, 50937 Cologne, Germany

The metal-insulator transitions (MIT) in early transition metal oxides such as V2O3 and VO2, are considered to be classical examples of Mott transitions in which the interplay between band formation and electron correlation causes the crossover between the metallic and insulating regimes. Despite the large amount of experimental and theoretical work carried out in the last 40 years, several fundamental characteristics of these MIT's seems to have been neglected, one of them being the observation that the transition temperatures are generally orders of magnitude smaller in energy scale than the band gaps that are opened in going from the metallic to the insulating phases. It is only very recently, that with the development of dynamical mean field theories (DMFT) one is beginning to have a handle on this problem [1]: for V2O3, as an example, one is now able to produce out of the metallic state an insulating state with a reasonable band gap by using the realistic small changes in the one-particle band structure parameters. There are, nevertheless, several issues that are not yet dealt with properly. For example, the experimental valence band spectrum of metallic V2O3 reveals an appreciably stronger quasi-particle peak than in the DMFT calculation[2]. Another example is that the insulating phase in VO2 cannot be reproduced by DMFT using realistic band structure parameters [3]. Very recently, we have carried out bulk sensitive photoemission experiments on VO2, and discovered that the spectral weight change across the MIT is in fact much more dramatic than for the V2O3 case, revealing the shortcomings of the DMFT even more clearly. Moreover, the relation of the MIT with the very low transition temperatures has still not been addressed. To understand the spectacular changes in the spectral weight and band gap across the MIT, we infer that it is crucial to consider the k-dependence of the self-energy, and in particular, the inter-site spin-spin correlations. These aspects are essentially neglected in the above mentioned single-site DMFT. On the example of a cluster of two V ions, Park et al. [4] demonstrated the dramatic increase in the effective band widths and decrease of the band gaps that one can obtain if the inter-site spin-spin correlation is switched from antiferromagnetic (AFI) to ferromagnetic (FM) across the MIT. For V2O3, much of the action is expected to take place in the honeycomb lattice of the basal plane (and probably not in the often thought c-axis dimer, since this is already FM in the AFI phase), and for VO2 in the dimer singlet formation. In this respect, it is exciting that using a cluster-DMFT calculation, Biermann et al. [5] were able to reproduce much of the spectral weight changes across the MIT in VO2, thereby supporting these ideas. We would like to remark that the idea of the possible importance of spin-spin correlations for the MIT has been explored early on by Bulaevskii and Khomskii [6]. We infer that to make this mechanism to be effective, it is required that the spin-spin correlations are changed drastically and on a short range scale across the MIT. Spectroscopic measurements on V2O3 [4] and VO2 reveal that across the MIT the orbital occupations of the 3d shell are dramatically altered. This apparently is an effective and quite natural manner to drastically change the spin-spin correlations, and, in turn, the band widths and band gaps.

*This work is done in collaboration with M.W. Haverkort, T. Koethe, Z. Hu, C. Schuler-Langeheine (Univ. Cologne), W. Reichelt (TU Dresden), A. Tanaka (Hiroshima Univ.), O. Tjernberg (KTH-Sweden), F. Venturini, N.B. Brookes (ESRF Grenoble), H.H. Hsieh, H.-J. Lin, T. Chen (SRRC Taiwan) and is supported by the Deutsche Forschungsgemeinschaft through SFB608.

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Correlation-assisted Peierls transition in VO2

A.I. Poteryaev

CPHT, Ecole Polytechnique, Palaiseau, France

A theory of the metal-insulator transition in vanadium dioxide from the high-temperature rutile to the low- temperature monoclinic phase is proposed on the basis of cluster dynamical mean field theory, in conjunction with the density functional scheme. The interplay of strong electronic Coulomb interactions and structural distortions, in particular the dimerization of vanadium atoms in the low temperature phase, plays a crucial role. We find that VO2 is not a conventional Mott insulator, but that the formation of dynamical V-V singlet pairs due to

strong Coulomb correlations is necessary to trigger the opening of a Peierls gap.

S. Biermann, A.I. Poteryaev, A.I. Lichtenstein, A. Georges, Phys. Rev. Lett. in press

Interorbital charge transfers and the metal-insulator transition of BaVS$_3$

Frank Lechermann, Silke Biermann, and Antoine Georges

CPHT, Ecole Polytechnique, Palaiseau, France

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

By combining the Dynamical Mean Field Theory (DMFT) with the Local Density Approximation (LDA) to Density Functional Theory, a powerful many-body approach is provided to tackle the given problem on a realistic level.

Within LDA+DMFT we investigated the multi-orbital $3d^1$ system BaVS$_3$ which is well-known for undergoing three distinct continuous phase transitions with decreasing temperature. In BaVS$_3$, a structural transition at T_S=240 K is followed by a metal-to-insulator transition (MIT) at T_{MIT}=70 K. At around T_X=30 K a final magnetic transition to an incommensurate antiferromagnetic ordered state seems to occur. The highlighted MIT appears to be accompanied by a charge density wave instability[1].

In our study, we concentrate on the MIT and reveal the importance of the interorbital charge transfer between the $3d$-orbitals of the V atoms induced by electronic correlations. Using the LDA density of states as an input, with our DMFT investigations we are able to shed light on the underlying mechanism that drives BaVS$_3$ into the insulating regime.

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Exciton effects in intermediate valence and Kondo systems

V. Yu. Irkhin and M. I. Katsnelson

University of Nijmegen, The Netherlands

Correlation effects in intermediate valence compounds are considered for both coherent case (with f-band formation) and incoherent one (independent scattering of conduction electrons by f-centers). An interplay of the Kondo scattering and exciton effects (d-f Coulomb interaction) in the intermediate valence systems and Kondo lattices is demonstrated to lead to an essential change of the scaling behavior in comparison with the standard Anderson model. In particular, a marginal regime can occur where characteristic fluctuation rate is proportional to flow cutoff parameter. In this regime the "Kondo temperature" itself is strongly temperature dependent which may give a key to the interpretation of controversial experimental data for heavy fermions and related systems.

Ab initio schemes for correlated electrons and the Hubbard U

F. Aryasetiawan

Research Institute for Computational Sciences, AIST, Tsukuba, Japan

In the first part, a recently proposed scheme for treating correlated materials

combining the GW approximation (GWA) and dynamical mean-field theory into a self-consistent scheme is described [1]. The problems with the GWA and what can be expected from the new scheme will be discussed. The feasibility of the schemeis demonstrated by applying it to calculate the electronic structure of nickel.

In the second part, a scheme for calculating the Hubbard U from realistic electronic structure calculations is proposed. The energy-dependent effective interaction among electrons living in a narrow band around the Fermi level can be derived and calculated from first-principles. The scheme allows for calculations of the full U matrix. Results for the 3d transition metal series, as well as for correlated metals Ca/SrVO3, obtained within the random-phase approximation willbe presented.

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*f-aryasetiawan@aist.go.jp

Many-Body Approximation Scheme Beyond GW

P. Sun

Rutgers University

To study strongly correlated electron systems with non-local interactions, we combine Extended Dynamical Mean Field Theory (EDMFT) with the GW Approximation (GWA), with the former sums the local contributions to the self-energies to infinite order and the latter handles the nonlocal ones to lowest order. We benchmark the different levels of self-consistency that can be implemented within this method by comparing to the exact quantum Monte Carlo solution of a finite-size model Hamiltonian.

Self-interaction correction (SIC) in multiple-scattering theory

Martin Lüders[1], Arthur Ernst[2], Markus Däne[3], Dzidka Szotek[1], Axel Svane[4], Diemo Ködderitzsch[3,1], Wolfram Hergert[3], Balazs L. Györffy[5], Walter Temmerman[1]

[1] Daresbury Laboratory, Daresbury, Warrington, UK [2] Max Planck Institut für Mikrostrukturphysik, Halle, Germany [3] Fachbereich Physik,Martin-Luther-Universität Halle-Wittenberg, Germany 06099 [4] Institute of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus, Denmark [5] H.H. Wills Physics Laboratory, University of Bristol, UK

We propose a simplified version of self-interaction corrected local spin-density (SIC-LSD) approximation, based on multiple scattering theory, which implements self-interaction correction locally, within the KKR method. The multiple scattering aspect of this new SIC-LSD method allows for the description of crystal potentials which vary from site to site in a random fashion and the calculation of physical quantities averaged over ensembles of such potentials using the coherent potential approximation (CPA). This facilitates applications of the SIC to alloys and pseudoalloys which could describe disordered local moment systems, as well as intermediate valences. As a demonstration of the method, we study the well-known α-γ phase transition in Ce, where we also explain how SIC operates in terms of multiple scattering theory.

Ab-initio Theory of Resonant X-ray Scattering in Rare Earth Materials

P. Strange, M. Horne, E. Arola, S.J. Stockton, B. Zarychta, W. Winter, Z. Szotek, W.M. Temmerman

(1) School of Chemistry and Physics, Keele University, Staffordshire ST5 5BG, UK (2) Optoelectronics Research Centre, Tampere University of Technology, P.O. Box 692, FIN-33101, Tampere, Finland. (3) INFP, Forschungszentrum Karlsruhe GmbJ, Postfach 3640, D-76021 Karlsruhe, Germany (4) Daresbury Laboratory, Daresbury, Warrington, WA4 4AD, Cheshire,

UK

A first-principles theory of resonant magnetic scattering of x-rays is presented. The scattering amplitudes are calculated using a standard time-dependent perturbation theory to second order in the electron-photon interaction vertex. In order to calculated the cross section reliably an accurate description of the electronic states in the material under investigation is required and this is provided by the density functional theory (DFT) employing the Local Spin Density Approximation combined with the self-interaction corrections (SIC-LSD). The magnetic x-ray resonant scattering (MXRS) theory has been implemented in the framework of the relativistic spin-polarized LMTO-ASA band structure calculation method. The theory is illustrated with two applications. Firstly we will show a series of calculations for praseodymium that display the sensitivity of MXRS to the symmetry of the occupied f-states. Secondly we will make direct contact with experiment with a calculation for holmium that can be compared with recent assymetry ratio measurements from the XMAS beamline at ESRF.

SiC-LSD Description of SPINTRONICS MATERIALS

Z. Szotek

Computational Science and Engineering Department, Daresbury Laboratory, UK

The self-interaction corrected local spin density approximation is applied to study electronic structure and magnetic properties of Mn- and Co-doped III-V and II-VI diluted magnetic semiconductors, magnetite, such spinel ferromagnetic insulators as NiFe2O4 and CoFe2O4, and some f-electron compounds of possible interest to spintronics. In the diluted magnetic semiconductors we concentrate on the understanding and realization of the carrier mediated ferromagnetism. The electronic structure of NiFe2O4 and CoFe2O4 is discussed in comparison with the insulating charge ordered Verwey phase of magnetite. We speculate on the implications for possible technological applications.

Field-induced band-structure change in CeBiPt

M. Richter

IWF Dresden, Germany

A field-induced change of the electronic band structure of semi-metallic CeBiPt will be reported. It is evidenced by electrical-transport measurements in pulsed magnetic fields. Above about 25 T, the charge-carrier concentration increases by 28 a strong increase of the magneto-resistance.

These features are intimately related to the Ce 4f electrons since for the non-4f compound LaBiPt the Fermi surface remains unaffected. Electronic structure calculations reveal a strong enhancement of the Zeeman splitting close to the Fermi level due to 4f-5d intra-atomic exchange. This may lead to a magnetic field-induced Lifshitz-like transition.

Orbital magnetism of Co impurities in gold

Ingo Opahle

IWF Dresden, Germany

The electronic structure of Co impurities inside gold has been calculated in the framework of relativistic density functional theory. In agreement with experimental findings, the orbital moment is strongly enhanced with respect to Co metal. The competing influence of orbital polarization corrections and lattice relaxations is discussed.

Approximate solution of the Poisson equation for slab geometry

F. Tasnadi

IWF Dresden, Germany

The multipole compensation method developed by M. Weinert[1] to solve the Poisson equation for 3-dimensional periodic crystalline systems is extended for slabs, layer symmetric[2] structures. Unlike in Ref.[1] the method assumes localized (compact support), overlapping original charge distributions as introduced in Refs.[3,4] and non-local (no compact support) Ewald density distributions. The Poisson equation is solved with periodic boundary conditions in the plane and with finite voltage boundary condition in the perpendicular (z) direction. For the $K_{||} \neq 0$ case a Fourier transformation helps to calculate the solution in a three dimensional periodic sense. While for the $K_{||} = 0$ case, the required charge neutrality is the starting point to find the solution. The $K_{||} = 0$ solution connects the z directional potential step with the surface density of the dipole z component. For both cases suitable representations of the spherical harmonics[5] are needed to arrive at expressions that are convenient for numerical implementation.

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5 News from the RTN "Exciting"

5.1 Workshop Announcements

5.1.1 EXC!TiNG Symposium on Excited-state Properties of Solids

Maritim Parkhotel Mannheim, Germany, May 16-19, 2005
January 10, 2005: Deadline for abstract submission
February 18, 2005: Acceptance notice
March 14, 2005: Deadline for early registration
Conference website: http://cmt.physik.uni-kl.de/XSM05/

This International Symposium will be organized in Mannheim by the Condensed Matter Theory Group of Kaiserslautern University of Technology within the framework of the European Union Research Training Network "EXC!TiNG", and it should bring together researchers active in the field of excited-state properties of low-dimensional condensed matter systems. Over the past few years, progress has been achieved in combining the field of nanomaterials with first-principles calculations, and this conference will cover the excited-state properties of these materials from both the theoretical as well as the experimental and applicational points of view. Sessions will be centered around the following themes:

-Theory: time-dependent density-functional theory.

-Theory: Hedins GW method and the Bethe-Salpeter Equation.

-Theory: quantum-chemical calculations of excited-state properties.

-Code developments of the "EXC!TiNG" network—overview and examples.

-Materials: nanostructures (magnetic and nonmagnetic), semiconductors, oxides, molecules, superconductors.

-Spectroscopy: Raman scattering, two-photon photoemission, second-harmonic generation.

-Industrial applications.

The presentations at the conference will comprise invited lectures as well as contributed talks and posters (no parallel sessions).

Setting: The city of Mannheim is located about 30 minutes from Frankfurt International Airport and can be reached conveniently by train, plane, or car.

Invited speakers (including):

H. Ebert (Munich)
G. Ju (Seagate)
L. Reining (Palaiseau)
A. Rubio (San Sebastian)
E. Runge (Ilmenau)

Advisory Committee:

C. Ambrosch-Draxl (Graz)
N. E. Christensen (Aarhus)
X. Gonze (Louvain-la-Neuve)
E. K. U. Gross (Berlin)
W. Hübner (Kaiserslautern)
B. Johansson (Uppsala)
E. Molinari (Modena)

Programme Committee:

C. Ambrosch-Draxl (Graz)
T. Andersen (Kaiserslautern)
X. Gonze (Louvain-la-Neuve)
E. K. U. Gross (Berlin)
W. Hübner (Kaiserslautern)

Organizing Committee:

T. Andersen (Secretary General)
M. Frey (Conference Secretary)
W. Hübner (Chair)
G. Lefkidis
O. Ney
Y. Pavlyukh

6 News from the ESF Programme

"Towards Atomistic Materials Design"

6.1 Reports on ESF Workshops/Conferences

6.1.1 Report on Mt. St. Odile Workshop

Workshop on Ab-initio Methods for Correlated Spintronics Materials: Theories and Applications

Monastery of Mont Sainte Odile, Strasbourg, France, September 23-26, 2004

Sponsored by ESF Psi-k Programme and RTN on "Computational Magnetoelectronics"

Coordinators:

M. Alouani (U. of Strasbourg, France)
S. Biermann (Ecole Polytech, Paris, France)
A. Lichtenstein (U. of Hambourg, Germany)

This workshop in condensed matter physics was motivated by recent advances in the treatment of electronic correlation effects, particularly in the context of realistic electronic structure calculations. The workshop attempted to balance two important components: (1) the development of new methods, and (2) applications of these methods to experimentally relevant systems, particularly in spintronics. The main objective was to gain new physical understanding into the working of complex materials. In the last few years alone, a great progress in the field of strongly correlated electrons was made possible due to the new developments of both the dynamical mean-field theory (DMFT) and its combination with realistic band-theory methods. This combined approach was central to this workshop. The realistic implementation of DMFT constituted a great opportunity towards the solution of important problems which remained unsolved using traditional approaches. In particular, significant understanding of the Mott metal to insulator transition, the itinerant ferromagnetism and the behavior of heavy fermions is now better, thanks to this new push towards realistic calculations with the LDA+DMFT and GW+DMFT combined approaches.

Taking advantage of these new developments, we brought together 40 researchers, some using different methodologies for strongly correlated materials, and others from the band theory community who are interested in correlated materials. The workshop sated a new start for further developments in the theory of correlated materials, and was strongly oriented towards the discussion of the physical properties of a large number of specific materials of great current experimental interest in spintronics. The participants shared insights from diverse materials and different calculation methods, distinguished between common aspects and non-universal, material-specific, aspects, hence providing some understanding on what are the new physical principles that govern the behaviour of strongly correlated materials. Rather than search for abstract unifying principles, the participants talked more about the specific physical properties of many interesting materials, and compared them to what can be understood using the quantitative tools under development. This approach depicted a broader picture of the strong correlation problem, and evaluated more accurately the status of theoretical understanding, a key step for further progress. A web page http://www- ipcms.u-strasbg.fr/odile2004 was created and is accessible worldwide. It contains the list of all speakers, the workshop programme, the abstracts, and the pdf files of the talks.

Invited Speakers

B. Amadon (CEA, Bruyeres, France)
O.K. Andersen (MPI Stuttgart, Germany)
B. Arnaud (U. of Rennes, France)
F. Aryasetiawan (JRCAT, Japan)
F. Bruneval (Ecole polytechnique Paris, France)
S. Bluegel (Juelich, Germany)
P. Dederichs (Juelich, Germany)
V. Drchal (Prague, Czech Republic)
A. Ernst (MPI Halle, Germany)
O. Eriksson (Upsalla, Sweeden)
Martin Feldbacher (MPI FKF, Stuttgart)
A. Georges (Ecole Polytechnique Paris, France)
O. Gunnarson (MPI Stuttgart, Germany)
K. Held (MPI Stuttgart, Germany)
M. Katsnelson (Nijmegen, The Netherland)
J. Kortus (Strasbourg, France)
P. Kratzer (Fritz-Haber Institut, Max-Planck, Berlin, Germany)
A. Marini (San Sebastien, Spain)
W. Metzner (MPI Stutgart, Germany)
E. Pavarini (Pavia, Italy)
M. Rohlfing (Augsburg, Germany)
A. Poteryaev (Paris, France)
M. Rozenberg (Buenos Aires, Argentina)
Alexey Rutsov (Moscow, Russia)
T. Saha-Dasgupta (S.N. Bose Centre, India)

A. Schindlmayr (Juelich, Germany)
Z. Szotek (Daresbury, England)
W. Temmerman (Daresbury, England)
R. Zeller (Juelich, Germany)

Participants

Nadjib Baadji (U. of Strasbourg, France)
Alberto Camjayi (Polytechnique, Paris, France)
Hugues Dreyssé (U. Strasbourg) (one day only: night of Friday)
Frank Lechermann (Polytechnique, Paris, France)
Abdel Samir (U. of Strasbourg, France)
Jan Tomczak (Polytechnique, Paris, France)
Atsushi Yamasaki (MPI, Stuttgart, Germany)

WORKSHOP PROGRAM

Friday, September 24, 2004
9:00 to 9:05 Welcome by the organizers
9:05 to 9:40 -Ole K. Andersen, Stuttgart, Germany Downfolding, NMTO, and Wannier functions
9:40 to 10:20 -Peter Dederichs, Juelich , Germany Exchange interactions and Curie Temperatures of Diluted Magnetic Semiconductors
10:20 Coffee break
10:40 to 11:10 -Olle Eriksson, Uppsala, Sweden Electronic structure, magnetism and critical temperatures of diluted magnetic semiconductors
11:10 to 11:40 -Rudy Zeller, Juelich, Germany Progress of the KKR Green-function method for complex electronic systems
11:40 to 12:10 -Jens Kortus, Strasbourg, France Electron transport through a single Co-complex and Co-grids
12:10 to 12:40 -Tanusri Saha-Dasgupta, S.N . Bose Centre, Kolkata, India Na2V3O7: a low-dimensional quantum spin system with nano-tubular structure
12:40 Lunch

14:00 to 14:40
-Antoine Georges, Polytechnique, Paris, France
Electronic Structure of Correlated Materials: an overview of the DMFT approach

14:40 to 15:20
-Misha Katsnelson, Nijmegen, The Netherlands
Nonquasiparticle states in half-metallic ferromagnets

15:20 to 16:00
-Karsten Held, Stuttgart, Germany
Filling of the Mott-Hubbard Gap in (V0.97 Cr0.03)2O3 : Theory and Experiment

16:00 Coffee break

16:30 to 17:10
-Walter Metzner, Stuttgart, Germany
Transport through interacting quantum wires: functional renormalization group computation

17:10 to 17:50
-Olle Gunnarsson, Stuttgart, Germany
Electron-phonon interaction in strongly correlated materials

17:50 to 18:30
.-Vaclav Drchal, Praha, Czech Republic
Electron correlations in diluted magnetic semiconductors

19:00
Diner

Saturday, September 25, 2004

8:30 to 9:10
-Walter Temmerman, Daresbury, UK
Single-Site Self-Interaction Correction in the KKR-CPA

9:10 to 9:50
-Stefan Bluegel, Juelich, Germany
Aspects of correlation in low-dimensional magnetic systems

9:50 to 10:20
-Dzidka Szotek, Daresbury, UK
Electronic Structure of Half-Metallic Ferromagnets and Ferromagnetic Insulators from SIC-LSD

10:20 Coffee break

10:40 to 11:10
-Marcelo Rozenberg, Buenos Aires, Argentina
Modelling resistance random access memory

11:10 to 11:40
-Frank Lechermann, Polytechnique, France
Importance of inter-orbital charge transfers on the metal-insulator transition in BaVS3

11:40 to 12:10
-Eva Pavarini, Pavia, Italy
Mott transition in t2g GdFeO3-type perovskites

12:10 to 12:30
-Alexander Poteryaev, Polytechnique, Paris, France
Non-local Coulomb interactions and metal-insulator transition in lighter transition metal oxides: a cluster LDA+DMFT approach

12:30 Lunch

14:00 to 14:40

-Ferdi Aryasetiawan, JRCAT, Japan

Towards an ab initio scheme for strongly correlated materials

14:40 to 15:15

-Brice Arnaud, Rennes, France

Quasiparticle's lifetimes from first principles

15:15 to 15:50

-Arno Schindlmayr, Juelich, Germany

Quasiparticle Electronic Structure and Energetics of Point Defects on Semiconductor Surfaces

15:50 to 16:30

-Mechael Rohlfing, Augsburg, Germany

Time dynamics of excited electronic states

16:30 Coffee Break

17:00 to 17:30

-Fabien Bruneval, Polytechnique, Paris, France

Electronic Excitations of Cu2O within GW approximation

17:30 to 18:10

Andrea Marini, San Sebastien, Spain

Quasiparticles and excitons in extended systems: Many-Body versus time-dependent density-functional approach

19:00 Diner

Sunday, September 26, 2004

8:30 to 9:10

-Erik Koch, Juelich, Germany

Quasiparticles from quantum Monte Carlo: Effective mass and Wilson ratio for K3C60

9:10 to 9:50

Martin Feldbacher, MPI FKF, Stuttgart, Germany

Projective Quantum Monte Carlo for DMFT

9:50 to 10:30

-Alexy Rubtsov, Moscow University, Russia

Continuous-time QMC for fermions: state of art and perspectives

10:30 Coffee break

10:50 to 11:20

- Peter Kratzer, MPI Berlin, Germany

Theoretical investigations of MnSi and Co2MnSi thin films as spin injectors: Structural, electronic and magnetic properties

11:20 to 12:00

- Arthur Ernst, MPI Halle, Germany

Beyond LDA: GW and SIC implementation in KKR

12:00 Lunch

14:00 to 18:00

Organized Hike

Abstracts

Quasiparticle's lifetimes from first principles

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Today, different techniques like angular resolved photoemission spectroscopy, time resolved two-photon photoemission or scanning tunnelling spectroscopy are used to investigate excitation lifetimes. Up to now, these techniques have been widely used to study quasiparticle's lifetimes in metals and experimental results have been successfully compared with ab initio calculations performed within the GW approximation [1,2,3]. By contrast, no experimental results are available for insulators and very few calculations have been reported. We present our new implementation [4] of the GW approximation based on an all-electron Projector-Augmented-Wave method, where no plasmon-pole model is used to mimic the frequency dependence of the dynamically screened interaction W. Therefore, both the hermitian and non-hermitian part of the self-energy are accessible and spectral functions can be easily computed. Thus, we show the calculated spectral functions of different insulators and discuss the lifetimes of quasiparticles in terms of Auger decay channels, neglecting the electron-phonon scattering mechanisms.

1. P. Echenique, J. Pitarke, E. Chulkov, A. Rubio, Chem. Phys. 251, 1 (2000.
2. R. Keyling, W.-D. Schöne and W. Ekardt, Phys Rev B 61, 1670 (2000.
3. C. D. Spataru, M. A. Cazalilla, A. Rubio and L. X. Benedict, Phys. Rev. Lett. 87, 246405 (2001.
4. S. Lebègue, B. Arnaud, M. Alouani and P.E. Bloechl, Phys Rev B 67, 155208 (2003.

Towards an ab-initio scheme for strongly correlated materials

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S. Biermann and A. Georges
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In the first part, a recently proposed scheme for treating correlated materials combining the GW approximation (GWA) and dynamical mean-field theory into a self-consistent scheme is described (1). The problems with the GWA and what can be expected from the new scheme will be discussed. The feasibility of the scheme is demonstrated by applying it to calculate the electronic structure of nickel.

In the second part, a scheme for calculating the Hubbard U from realistic electronic structure calculations is proposed. The energy-dependent effective interaction among electrons living in

a narrow band around the Fermi level can be derived and calculated from first-principles. The scheme allows for calculations of the full U matrix. Results for the 3d transition metal series, as well as for correlated metals Ca/SrVO3, obtained within the random-phase approximation will be presented (2).

(1) S. Biermann, F. Aryasetiawan, and A. Georges, Phys. Rev. Lett. 90, 086402 (2003.
(2) F. Aryasetiawan, M. Imada, A. Georges, G. Kotliar, S. Biermann, and A. I. Lichtenstein, cond-mat/0401620, (to appear in Phys. Rev. B).

Aspects of correlation in low-dimensional magnetic systems

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Lacking orbital-dependent terms, the local density approximation (LDA) as well as the generalized gradient approximation (GGA) to the density functional theory (DFT) is unable to reproduce correctly orbital moments and magnetocrystalline anisotropy energies (MAE) in low dimensional systems. In this talk systematic studies to overcome this failure of conventional DFT calculations employing the LDA+U method for atoms, adatoms, wires and deposited wires are presented. Including a Hubbard-U, the system no longer possesses a single minimum for the total energy and it is possible to obtain a couple of solutions. To find the global minimum, obtain reasonable values for U, and the extreme sensitivity of the MAE on relaxations still pose serious problems for these calculations. Nevertheless, it seems that the underlying physics in these systems is correctly captured in this model. Electronic Excitations of Cu2O within GW approximation Fabien Bruneval, N. Vast, and L. Reining. Laboratoire des Solides Irradiés, CNRS, CEA, Ecole Polytechnique, Palaiseau, France Cuprous oxide has been extensively studied during the last decades, mainly because of its exciton series in the optical range. Cu_2O is a good starting point to address the fundamental issue of *3d* electrons of metals in oxides. This semiconductor material has indeed a cubic structure, a closed d shell, and is non- magnetic. This is now a very important topic: it is known that density functional theory fails to predict a gap in various insulating oxides like CoO, CuO.We performed band structure calculations on Cu_2O within Density Functional Theory and GW approximation We carefully studied the role of semicore states (3s23p6). Though deep in energy, these states have a large overlap with valence bands. Their influence is slight on the Kohn-Sham band structure. However, we state that the semicore states have to be included in the GW calculation to get meaningful results. Even a GW calculation including semicore states largely underestimates the quasiparticle gap. Further approximations are usually used to perform a “standard” GW calculation: the use of a plasmon pole model to describe the dynamical screening, a first-order perturbation scheme, an assumption that LDA and GW wavefunctions are equal... We extensively discuss many of them and conclude that they are reliable. Then the failure of GW may lie in the neglect of the vertex part of the self-energy. We therefore propose a scheme to include some local vertex corrections, thanks to Time-Dependent DFT.

Exchange interactions and Curie temperatures in dilute magnetic semiconductors

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The magnetic properties of dilute 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). First, the Curie temperatures (Tc) of (Ga, Mn)N, (Ga, Mn)P, (Ga, Mn)As and (Ga, Mn)Sb are estimated from the calculated exchange coupling constants by using the mean-field approximation (MFA). It is found that DMS show different concentration dependences in calculated Tc depending on their electronic structures and are divided into two classes. In one extreme case of (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 (2)). In this case, Tc is proportional to the square root of Mn concentration c and the exchange interaction is short ranged since the wave functionin the gap is exponentially damped and well localized. In the other extreme case of (Ga, Mn)Sb, Mn 3d-states are located deep in the valence band. The valence band polarization due to the hybridization between localized d-states and valence bands gives the effective magnetic field that stabilizes the ferromagnetic states (p-d exchange (3)). In this case, Tc is linear to c and the exchange interaction is long ranged since the extended valence hole states mediate the ferromagnetic coupling. Since the experimentally realistic concentration is about 10particular in double exchange systems where the magnetic coupling is short ranged. To take the percolation effect into account, we perform Monte Carlo simulations for the dilute Heisenberg model with the exchange coupling constants which we calculate from first-principles. It is found that exact Tc value of (Ga, Mn)N is very low due to the percolation effect and the MFA estimations are qualitatively wrong and unreliable in this system. Even in (Ga, Mn)As, where long ranged p-d exchange dominates, the percolation effect is still serious and the MFA overestimates Tc very much.

(1) A. I. Liechtenstein et al., J. Magn. Magn. Mater. 67 (1987) 65.
(2) H. Akai, Phys. Rev. Lett. 81 (1998) 3002.
(3) T. Dietl et al., Science 287 (2000) 1019.

Electron correlations in diluted magnetic semiconductors

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We examine the effect of Coulomb correlations in diluted ferromagnetic III-V semiconductors using the LSDA+U correlated band theory method. We show that Hubbard U plays an important role in determination of Mn d states' interaction with the semiconductor host valence band. We present the results of supercell calculations by the FP-LAPW and TB-LMTO-CPA methods for Ga1-xMnx As and Ga1-xMnx N alloys. For Ga1-xMnxAs, we find a reasonable increase of d-Mn binding energy in agreement with the experiment. For Ga1-xMnxN alloy, an account of the Hubbard U is even more important, moving the sharp d peak from the top into the body of the valence band. Based on the calculated electronic structure, we determine exchange interactions between magnetic moments and discuss the role of electron correlations on Curie temperature. We also discuss the energetics connected with possible aggregation of Mn atoms and its dependence on electron correlations.

Electronic structure, magnetism and critical temperatures of dilute magnetic semiconductors

Olle Eriksson
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The electronic structure and magnetic properties of dilute magnetic semiconductors (DMS) are analysed theoretically and compared to experimental data. It is argued that the effect of defects influences the magnetic properties strongly, where in particular the effect of As anti-sites is to stabilize a disordered local moment (DLM) state. In addition it is shown that the observed critical temperature can be reproduced only when considering a random distribution of Mn (Cr) atoms in GaAs (ZnTe) and it is argued that magnetic percolation is important in DMS systems. The measured spectroscopic properties are analysed by combining ab-initio theory with an atomic multiplet calculation in the Hubbard I approximation.

GW and SIC implementation in the KKR method

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The ab-initio study of semiconductors and insulators as well as systems with strong localized electrons entails great difficulties involved by the treatment of excitation energies and many-body effects. The most successful first principles method, the density functional theory (DFT) within the local spin density approximation (LSDA), is designed for ground state properties and can not provide proper description of band structure of semiconductors and insulators. If some localized electrons are present in the system, like 3d-electrons in the transition metal oxides, the local density approximation can be essentially improved by so-called self-interaction correction (SIC). In this approximation the self-iterations of single particle charges, which are present in the LSDA, can be canceled out for the localized electrons. However, the self-interaction correction within the LSDA is still not sufficient for proper description of the excitation energies and band-gaps. It is possible to do accurately from first principles by solving the Hedin's set of equations for the full Green's function. The implementation of this formalism is very difficult, one neglects commonly the vertex correction (the random-phase approximation), and the self-energy is calculated in this case within so-called GW approximation. The non-self-consistent GW approximation was successfully implemented within several first-principle methods, but most of existing implementations are generally designed for systems with delocalized (fast) electrons. Here we present a general ab-initio approach designed for the study of electronic properties of solids, in which on base of the Korringa-Kohn-Rostoker (KKR) method we implemented the self-interaction correction for strong-localized electrons and the non-self-consistent GW approximation for the inclusion of many-body effects. We illustrate our approach on the electronic structure study of some semiconductors and transitions metal oxides.

Projective Quantum Monte Carlo for DMFT

Martin Feldbacher
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In recent years, there has been a revival of interest in Kondo-like physics, in particular in quantum dot systems and in connection with the dynamical mean field theory (DMFT). The numerical solution of the underlying Anderson impurity models is, however, limited: In the Numerical Renormalization Group treatment the effort grows exponentially with the number of orbitals, allowing not more than two interacting orbitals; the Hirsch-Fye Quantum Monte Carlo (QMC) algorithm on the other hand scales like T-3 (T: temperature) and quickly becomes too expensive in CPU time. This limitation is especially severe when DMFT is used to model materials with strong electron correlations where, in order to observe the physics of interest, low temperatures need to be achieved. We propose a projective QMC algorithm for the Anderson impurity model, which converges rapidly to the ground state. With this new impurity solver, we study the Mott-Hubbard metal-insulator transition in the Hubbard model, demonstrating that it gives reliable "T=0"' DMFT results.

Electronic Structure of Correlated Materials: an overview of the Dynamical Mean-Field Theory approach

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In recent years, Dynamical Mean Field Theory (DMFT) has been combined with electronic structure calculation methods in order to provide a quantitative description of strong correlation effects in a realistic setting. I will review the basic principles of this approach. Functionals of the local density and the local Green's function can be constructed in order to provide a convenient formal framework for LDA+DMFT. These functionals can be extended to the local screened interaction, opening the way to a first-principle treatment of the Coulomb interaction, which brings together the GW approximation and DMFT.Early successes of the DMFT approach at describing physical effects of correlations (such as the Mott transition and the properties of transition metal oxides) will also be briefly reviewed, and new challenges will be emphasized. For a recent review and references, see e.g: A. Georges, Strongly Correlated Electron Materials: Dynamical Mean-Field Theory and Electronic Structure, cond-mat/0403123 (to be published in the Proceedings of the VIII Training Course in the Physics of Correlated Electron Systems and High-Tc Superconductors, American Institute of Physics). georges@cpht.polytechnique.fr

Electron-phonon interaction in strongly correlated materials

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Recent photoemission work suggests a strong electron-phonon coupling in cuprates. These experiments were interpreted in terms of a strong coupling to a half-breathing Cu-O bond-stretching phonon. Neutron scattering experiments show that this phonon has an anomalous softening upon doping, suggesting an appreciable electron-phonon coupling. It is interesting, however, that photoemission experiments were interpreted in terms of a rather strong coupling, 1, while neutron scattering suggest a modest coupling, 0.2-0.3, and LDA calculations a very weak coupling, 0.01. To address this issue, we start from the three-band model of a CuO2 layer and derive a t-J model with electron-phonon interaction, taking into account the modulation of both hopping and Coulomb integrals by phonons. The former is found to be dominant, but the modulation of the Coulomb integrals cannot be neglected. The model is studied using exact diagonalization. It explains the anomalous softening of the half- breathing mode upon doping and a weaker renormalization of the breathing mode. We find that the creation of low-energy excitations in the t-J model is an important reason for the difference from LDA calculations. We next study more generally the electron-phonon interaction in a doped insulator and compare with results for non-interacting electrons. Using exact sum-rules, we find that the effect of the electron-phonon interaction on the phonon self-energy is strongly reduced by correlation effects, while there is no corresponding reduction for the electron self-energy or the phonon induced electron-electron interaction.

Filling of the Mott-Hubbard Gap in (V0.97Cr0.03) 2O3 : Theory and Experiment

Karsten Held
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The combination of band structure theory in the local density approximation (LDA) with dynamical mean field theory (DMFT) [1] was recently applied successfully to V2O3 [2] – a material that undergoes the famous Mott-Hubbard metal-insulator transition upon Cr doping. We will emphasize two aspects of our recent results: (i) The filling of the Mott-Hubbard gap with increasing temperature, a genuine feature of the Mott-Hubbard insulator, was recently observed in photoemission experiments [3], ascertaining the DMFT prediction. (ii) The Mott-Hubbard transition in V2O3 shows peculiarities due to inequivalent orbitals. In particular, the effective mass of the a1g-orbital does not diverge at the Mott-Hubbard transition [2].

[1] For reviews see K. Held et al., Psi-k Newsletter #56 (2003),
p. 5[psi-k.dl.ac.uk/newsletters/News_56/Highlight_56.pdf]; A. I. Lichtenstein, M. I. Katsnelson, and G. Kotliar, to be published in Electron Correlations and Materials Properties 2, ed. A. Gonis (Kluwer, NY).

[2] K. Held et al. Phys. Rev.Lett. 86, 5345 (2001); G. Keller et al., cond-mat/0402133.

[3] S.-K. Mo et al., Phys.Rev. Lett. in print [cond-mat/0403094]. ANOQUANTA (NOE 500198-2).

Nonquasiparticle states in half-metallic ferromagnets

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Anomalous magnetic and electronic properties of the half-metallic ferromagnets (HMF) are discussed. A general concept of the HMF electronic structure hich take into account the most important correlation effects from electron-magnon interactions, that is, the spin-polaron effects, is presented Special attention is paid to the so called non-quasiparticle (NQP), or incoherent, states which are present in the gap near the Fermi level. Manifestations f NQP in electronic density of states, tunneling transport, nuclear magnetic relaxation, core-level spectra and other properties of HMF are considered. irst-principle calculations of the NQP- states for various half-metallic ferromagnets within the local-density approximation plus dynamical mean field theory LDA+DMFT) are reviewed.

Quasiparticles from quantum Monte Carlo: Effective mass and Wilson ratio for K3C60

Erik Koch
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Taking advantage of the fixed-node approximation to stabilize excited states, we calculate quasiparticle energies by uantum Monte Carlo. We apply this approach to a model describing K3C60 and show that it works surprisingly well. We determine how the quasiparticle dispersion changes with increasing correlation and compare to the many-body nhancement of the Pauli susceptibility. While the self-energies for our model seem to depend only weakly on the omentum (and

band-index), we find a Wilson ration that appears to behave qualitatively different from what is expected from dynamical mean-field theory.

Electron transport through a transition metal complexes and grids

Jens Kortus
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Metal organic complexes offer a promising route to the design of magnetic materials, because intramolecular magnetic interactions can be modified through the choice of the bridging ligands and variation of the metal- ions. The [2x2]-grid structures containing 4 metal ions belong to this class, where the transition metal ions are positioned by perpendicular rrays of ligands. We study the electronic and spin degrees of freedom of Fe(2+) and Co(2+) single ions and grids using first- principles ll-electron density-functional calculations. One goal is to identify the orbitals important for transport. Experimentally single Co2+/3+ ion can be fixed between a left and right terpyridine ligand, which can be coupled by functionalized inker molecules to electrodes. It was found experimentally [1] that depending on the type of linker molecules, a strong ondo effect in the current appears. We have investigated the conjecture that the tunnelling is dominated by single atom-like d-orbitals of the ion by electronic structure calculations. We show that microscopically the ligands of this articular complex act as a tunnel barrier due to different symmetry of the highest ligand pi-orbital and Co2+/3+-ion igma-orbitals. The role of the linker molecules connecting the ligands to the electrodes is therefore crucial. For the ow-spin Fe(2+) [2x2] grid we show, that the electrons can move between the ligands through an empty orbital on the etal bridge. This is compared to the Co(2+) [2x2] grid, where the metal bridge contains a localized electron which can nteract with the transported charge.

[1] J. Park et al, Nature 417, 722 (2002).

In collaboration with M.R. Wegewijs, C. Romeike and H. Schoeller Inst. for Theoretical Physics A, RWTH Aachen, Germany

Importance of inter-orbital charge transfers on the metal-insulator transition in BaVS3

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An understanding of the physics of strongly correlated multi-orbital electron systems is one of the key ingredients in order to describe a wide range of novel solid-state compounds. The complex interplay of the crystal structure with the competition between the localized and the itinerant character of the electrons in a manifestly multi-orbital case is giving rise to highly interesting physical phenomena. By combining the Dynamical Mean Field Theory (DMFT) with the Local Density Approximation (LDA) to Density Functional Theory, a powerful many-body approach is provided to tackle the given problem on a realistic level. Within the LDA + DMFT method, we investigated the multi-orbital system BaVS3 that is well known for undergoing three distinct continuous phase transitions with decreasing temperature. In BaVS3, a first structural transition from a hexagonal to an orthorhombic crystal structure at 240 K is followed by a metal-to-insulator transition (MIT) at around 70 K. Close to 30 K a final magnetic transition to an incommensurate antiferromagnetic ordered state seems to occur. The highlighted MIT seems to be accompanied by a charge density wave instability in this partially one-dimensional sulfide [1]. In our study, we concentrate on the MIT and reveal the importance of the inter-orbital charge transfer between the 3d- orbitals of the V atoms induced by electronic correlations. Using the LDA density of states as an input, with our DMFT investigations we are able to shed light on the underlying mechanism that drives BaVS3 into the insulating regime.

[1] S. Fagot, P. Foury-Leylekian, S. Ravy, J.-P. Pouget, and H. Berger, Phys. Rev. Lett. 90, 196401 (2003).

Theoretical investigations of MnSi and Co2MnSi thin films as candidates for spin injectors: Structural, electronic and magnetic properties

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We investigate thin films of Mn intermetallic compounds with the goal to identify materials systems which could be of possible use as spin injectors on a Si(001) semiconductor substrate. In ordered metallic compounds containing both Mn and Si, the Mn atoms often have large spin moments (depending on their local chemical environment), and show various types of magnetic ordering. All calculations presented here have been performed using the spin-polarized generalized gradient approximation to density-functional theory and the all-electron code WIEN2k, using the full-potential LAPW or APW+lo method.One promising candidate for spintronics applications is the ferromagnetic half-metal Co2MnSi, which, in its bulk phase, has a high Curie temperature of 985 K and displays a gap at the Fermi level in the minority spin channel. At surfaces and interfaces, however, it is conceivable that electronic states in the gap arise which modify or destroy the half-metallic properties of this material. To investigate this possibility, we perform electronic structure calculations for the Co2MnSi(001) surface. Analysis of the surface energies of different surface terminations shows that terminations by a layer of only Mn atoms, only Si atoms, or a mixture of both are all thermodynamically stable, depending on the chemical environment used for surface preparation. We find that the surface electronic structure is strongly affected by the type of surface termination; in particular, terminating the surface by a monolayer of Mn atoms preserves the half-metallic gap, while surface states occur for other terminations. We surmise that such details of the atomic structure may as well be crucial for the electronic properties of Co2MnSi semiconductor interfaces. Next, we investigate the properties of ultra-thin films (1-3 monolayers [ML]) grown epitaxially on the Si(001) surface, focussing on the intermetallics MnSi and Co2MnSi. In its bulk P213 phase, MnSi is known to be a weak helical magnet below 30K. However, from our total-energy calculations, we conclude that a novel, CsCl-like crystalline phase of MnSi should be producible as a metastable epitaxial structure on the Si(001) substrate. We find that the Mn atoms in thin films with CsCl-like sandwich structure of alternating Mn and Si layers have sizeable magnetic moments in the range of 1-2B. Moreover, these films show a layered magnetic ground state, with pronounced ferromagnetic coupling between the Mn magnetic moments within the layers. The interlayer coupling is much weaker and leads to a ferromagnetic ground state for the 2 ML film, or a ferrimagnetic ground state for the 3 ML film. For ultra-thin Co2MnSi films on Si(001) we find that the Mn atoms possess magnetic moments in the range of 2.7-3.5B, similar in size as in bulk Co2MnSi, and strong ferromagnetic coupling is found for Mn magnetic moments both within the same layer and between layers. Moreover, we learn from the calculations that the Co2MnSi thin films are stable against decomposition into elementary silicides. Both for the MnSi and the Co2MnSi films, our calculations predict values of 20In summary, our results suggest that Mn-Si-compounds are potentially useful as spin-polarized electrodes on Si(001), and thus deserve further exploration by theoretical and experimental work.

Quasiparticles and excitons in extended systems: Many-body versus time-dependent density-functional approach

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The correct description of the physical properties of quasiparticles and excitons in extended and low– dimensional systems constitute an important test for modern Ab-Initio theories. The commonly used approximation for the DFT exchange–correlation potential and TDDFT kernel based on the Local–Density Approximation, (LDA) fail to describe, among other things, the quasiparticle band structure properties and the excitonic effects in the optical and energy-loss spectra of semiconductors and insulators. In this framework Many–Body perturbation theory has provided successful tools (GW approximation, Bethe–Salpeter equation) to improve the results of the, (simpler) calculations performed within DFT. However, only recently the first principle description of excitons in the optical absorption has been achieved, due to the high complexity and large computational requirements of many–body calculations. Furthermore, to–date, calculations of the absorption spectra of solids beyond time-dependent LDA were performed in semiconductors characterized by weak continuous excitonic effects. Consequently, it remains open whether or not strong electron-hole effects (e.g. bound excitons) in the optical and energy-loss spectra can be described within TDDFT. We present a robust, efficient, frequency dependent and non-local exchange- correlation derived by imposing TDDFT to reproduce the many-body diagrammatic expansion of the Bethe- Salpeter polarization function (1). As illustration, we show the calculated optical spectra of solids (1) and nanostructures (2) characterized by moderate, (diamond) and strong, (LiF and SiO2) electron-hole interaction. In the second part of the talk we will investigate the relation between this novel fxc and the self– energy vertex function fxc . As the polarization function can be easily expressed in terms of both and fxc we will show how to derive a consistent expression of in terms of fxc. We will show that it is possible to obtain a practical and general expression for the three-point vertex function based on the two–point exchange–correlation kernel [3]. Taking LiF as a test case we will study the quasiparticle dynamics of the low–energy conduction states beyond the GW approximation. We will show that excitonic effects in LiF strongly modifies the electronic lifetimes leading to linear scaling with quasiparticle energy (3). As consequence, we will find that, in contrast to previous results for the electron gas, simple metals and semiconductors, vertex corrections in the self–energy and in the screening function do not compensate each other.

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Transport through interacting quantum wires: functional renormalization group computation

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The interplay of electron correlations and impurities in one-dimensional metals leads to striking effects at low energy scales. We compute the conductance of an interacting quantum wire with isolated static impurities by using a recently developed functional renormalization group (fRG) method [1]. The calculation is perturbative in the interaction, but non-perturbative in the impurity strength. Moreover, the method can deal with arbitrary shapes of the impurity potential. A comparison with exact numerical results for finite systems with up to 1000 lattice sites shows that the fRG is surprisingly accurate even for moderate interaction strength [1]. The agreement with exact asymptotic results, such as the scaling function for the conductance through a wire with a single short-ranged impurity [2], is also remarkable. The flexibility of the fRG in dealing with arbitrary impurity potentials and also with complex crossover phenomena becomes particularly useful in the case of resonant tunneling through a double barrier potential. Results for the peak conductance Gp(T) as a function of temperature exhibit non-monotonous behavior for suitable choices of the barrier parameters and distinctive power-laws at different energy scales [3].

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Mott transition in t2g GdFeO3-type perovksites

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Using a first principle downfolding method, we derive a low-energy Hubbard Hamiltonian for strongly correlated t2g Perovskites. We treat Coulomb repulsion effects by means of dynamical mean-field theory and calculate photoemission spectra. We show that cation covalency (GdFeO3-type distortions) is the most important material dependent mechanism. We study the Mott transition for different fillings and show that the interplay of Coulomb repulsion effects and cation covalency control the electronic properties of these materials.

Non-local Coulomb interactions and metal-insulator transition in lighter transition metal oxides: a cluster LDA+DMFT approach

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We present an ab initio quantum theory of the metal-insulator transition in Ti2O3 and VO2. There is a strong competition between local Coulomb interaction and chemical bonding in a M-M pair which results in a small insulating gap of a low temperature phase. The state of the art calculations in the local density approximation (LDA) show that the bonding-antibonding splitting is not enough to open a gap and correlation effects are important. The conventional single site dynamical mean filed theory (DMFT) cannot reproduce an insulating phase for any reasonable values of the local Coulomb interaction since it leads to the reduction of the bonding-antibonding splitting. The new cluster LDA+DMFT scheme is applied to describe the many-body features of these compounds. We have investigated the metal-insulator transition in Ti2O3 and VO2 and have shown that the many body effects related to the non-local Coulomb interactions are essential for a simultaneous description of the low-temperature insulating and high-temperature metallic states.

Time dynamics of excited electronic states

Michael Rohlfing
International University, Bremen, Germany

Ab-initio many-body perturbation theory (MBPT) provides a rigorous approach to excited electronic states. Within MBPT, single-particle excitations (electron states and hole states) are obtained from a GW calculation, which includes electron exchange and correlation effects in terms of the self-energy operator. In addition, coupled electron-hole excitations are obtained from the Bethe-Salpeter equation (BSE), which includes electron-hole interaction. These techniques can be employed to discuss the Spectra of a wide range of systems, from bulk crystals (like silicon or MgO) to molecules and polymers (like PPV or PPP), and from weakly correlated systems to Mott-Hubbard insulators like the one on the SiC(0001) surface. In addition to the spectra obtained from MBPT, recent developments concern the femtosecond dynamics of excited states. As an example, we discuss the initial decay of a molecular excitation (first excited state of CO) due to adsorption of the molecule on an insulator surface (MgO), which leads to a spatial separation of the excited electron and hole.

Modelling resistance random access memory

Marcelo J. Rozenberg
CPHT - Ecole Polytechnique, France

There is a current up surge in research on non volatile two-terminal resistance random access memory (RRAM) for next generation electronic applications. The RRAM is composed of a simple sandwich of a semiconductor (including strongly correlated electron compounds) with two metal electrodes. In this talk we shall: (i) review some of the essential features associated with RRAM behavior, such as hysteresys and multilevel resistance switching. (ii) introduce a basic model for RRAM with the made assumption that the semiconducting part has a non-percolating domain structure. (iii) present and discuss the behavior of the model investigated with numerical simulations that allows to understand the carrier transfer mechanisms in detail, and see how our model captures three key features observed in experiments: multilevel switchability of the resistance, its memory retention and hysteretic behaviour in the current-voltage curve. A very interesting aspect of our investigations is that they suggest that strong correlation effects are crucial for important resistance switching features.

Continuous-time QMC for fermions: state of art and perspectives

A.N. Rubtsov
Moscow State University, Russia

Novel continuous-time algorithm for QMC simulations of the fermionic systems is surveyed. The algorithm is based on the stochastic calculation of the interaction-representation series for quantum mechanical averages. Action is divided into Gaussian and interaction part in a special way to minimize the sign problem and the complexity of calculation. In addition, special reweighting procedures, particularly Wang-Landau sampling, are invoked for the same purpose. No time discretisation is required, therefore there is no any systematic errors in the scheme. No auxiliary fields are introduced, therefore the algorithm operates natively with an interaction nonlocal in time, space, spin or orbital indices. Several test examples are presented, as well as new results for systems with the dynamical screening and rotationally-invariant exchange interaction.

Na2V3O7: a low-dimensional quantum spins system with nano-tubular structure

Tanusri Saha-Dasgupta, R. Valenti, F. Capraro and C. Gros
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Following the recent discussion on the nature of the interactions in the tubular system Na2V3O7, we present a detailed ab-initio microscopic analysis of its electronic and magnetic properties. We show by means of a downfolding study that, due to the special geometry of this material, the edge-sharing V-V hopping interactions are of the same order of magnitude as the corner-sharing paths within a ring and an order of magnitude bigger than the hopping interactions between rings in a tube. We propose an effective model in terms of weakly coupled partially frustrated nine-site rings and calculate the susceptibility behavior by exact diagonalization of the model. Good agreement with experimental observations is obtained.

Quasiparticle Electronic Structure and Energetics of Point Defects on Semiconductor Surfaces

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Point defects strongly influence the transport, electronic, and optical properties of semiconductors in technological applications. In particular, they act as compensation centers and are responsible for Fermi- level pinning. The energetics of transitions between different charge states is hence an important material characteristic. The relevant charge-transition levels contain two energy contributions due to the transfer of electrons between the Fermi level and the defect state, and due to the lattice relaxation. While the latter is accessible in density- functional theory (DFT), the underestimation of the band gap translates into a significant error in the first, dominant term. We therefore use the GW approximation for the electronic self- energy to accurately describe the electronic properties of localized defects. As specific examples we consider anion vacancies on the GaAs(110) and InP(110) surfaces. Concomitant with the opening of the band gap, the charge-transition levels are raised in comparison to DFT-LDA predictions and show improved agreement with the available experimental data.

Electronic Structure of Half-Metallic Ferromagnets and Ferromagnetic Insulators from SIC-LSD

Dzidka Szotek
Daresbury Laboratory, Daresbury, Warrington, WA4 4AD, UK

We discuss electronic structure of materials of relevance to spintronics and among them half-metallic ferromagnets and ferromagnetic insulators, as obtained from the SIC-LSD calculations. Apart from materials containing transition metal elements, we consider also rare earth compounds. In addition, diluted magnetic semiconductors will be briefly discussed.

Self-interaction correction in multiple scattering theory

Walter M. Temmerman
Daresbury Laboratory, Daresbury, Warrington, WA4 4AD, UK

We propose a simplified version of self-interaction corrected local spin-density (SIC-LSD) approximation, based on multiple scattering theory, which implements self-interaction correction locally, within the KKR method. The multiple scattering aspect of this new SIC-LS method allows for the description of crystal potentials which vary from site to site in a random fashion and the calculation of physical quantities averaged over ensembles of such potential using the coherent potential approximation (CPA). This facilitate applications of the SIC to alloys and pseudoalloys which could describe disordered local moment systems, as well intermediate valences. As demonstration of the method, we study the well-known a- phase transition in Ce, where we also explain how SIC operates in terms of multiple scattering theory.

Progress of the KKR Green-function method for complex electronic systems

Rudolf Zeller
Institut fuer Festkoerperforschung, Forschungszentrum Juelich, Germany

The KKR Green-function method is a powerful and accurate tool to solve the Kohn-Sham density- functional equations for spatially complex systems like impurities in bulk crystals and at surfaces and interfaces. The method is based on the concept of a reference system and solves the integral Dyson equation for the Green function by use of multiple scattering theory. In the talk, the basic features of the method will be explained and some recent examples for the calculated electronic structure of impurities at surfaces will be presented. It will be further discussed that the method is not necessarily restricted to local potentials, as used in LDA density-functional calculations, and that generalization to certain types of non- local energy-dependent potentials is possible.

6.1.2 Report on the Workshop on "Ab Initio Phonon Calculations"

Cracow, Poland
2-4 December 2004
Web Page: http://wolf.ifj.edu.pl/workshop/

EXECUTIVE SUMMARY

The Workshop on "Ab initio phonon calculations" was held in Cracow, Poland in the period from **2 to 4 December, 2004**. The 55 participants were comming from 16 countries.

The Workshop has been organized in the frame of the Ψ_k Programme on *Electronic Structure Calculations of Solids and Surfaces Network*. The organization task has been undertaken by the Department of Materials Reserach by Computers of the Institute of Nuclear Phyiscs, PAN, Cracow, and the Institute of Technics of Pedagogical University, Cracow.

The Workshop has been devoted to provide the basic knowledge in the density functional theory (DFT), and the method to calculate phonons and thermodynamical properties of crystalline systems. The DFT approach allows to finds structure, electronic properties, and interatomic forces in temperatureless (T=0K) regime, while the phonons, which can be calculated within the DFT approach, define the dynamical, and thermodynamical properties at finite temperature. Some of the invited talk could be downloaded from the Web Page http://wolf.ifj.edu.pl/workshop/. During the workshop there were tutorials and the participants had a possibility to learn how to use, and what are the peculiatities of the methods and computer codes handling the above quantities.

SCIENTIFIC CONTENT

In the first day of the Workshop there were three tutorial lectures. Georg Kresse gave a review of procedures, which lead the exact calculations of the Hellmann-Feynman forces used in the phonon and molecular dynamics calculations. The necessary conditions were specified for metalic and non-metalic systems. Selection of correct pseudopotential, selection of wave vector sampling, and values of variety of switches were discussed in details. Rules and Tables to select the most relevant pseudopotential were given. Some results for nanotubes, highlighting the accuracy attainable by the VASP code, were presented.

Peter Blaha reviewed the augmented plane wave method (APW), and later modifications introduced by Slater, Andersen, Freedman, Singh and Sjöstedt. The possibilities for structural optimization and atomic force calculations were summarized. Finally, examples to calculate phonons and predicting a structural phase transition including ferroelectric Aurivillius compound, were discussed.

Krzysztof Parlinski reviewed the direct method of calculating force constants from the Hellmann-Feynman forces under confinements imposed by the system space group. The manner to select the supercell shape and size, the necessary displacements for force calculations were specified. Examples of phonon dispersion curves and phonon density of states were shown. The above phonon data allow to derive the thermodynamical functions in harmonic approximation, and to describe the spectra and intensity of inelastic coherent and incoherent scattering of neutrons. The temperature dependences of number of quantities can be then computed within the quasiharmonic approximation, leading frequently to very good results even close to the melting temperature.

At the end of the first day of the workshop there was a tutorial in the Computer Lab, where the participants could exersise the use of the Phonon and MedeA programs, using data of Hellmann-Feynman files already computer by VASP or Wien2k programs. This time was widely used to exchange information, and learn methodological details, which rutinely are not included in published articles. All participants obtained a CD with the Mini-Phonon program, which can be used to perform simple phonon calculations in combination with an *ab initio* program, and can help to illustrate phonon physics in student educational processes.

Poster session was at the same time as the Computer Lab, but posters were displayed all over the Workshop, also during the breaks, therefore, there was enough time to look at them carefully.

In the second day of the workshop three lectures demonstrated the computed phonon and thermodynamical results in several crystalline systems. Many of these results agreed very well with the experimental finding. Mark Johnson showed that inelastic incoherent neutron scattering, and infrared absorption could be well reproduced by the phonon spectra calculated with the ab intio codes. The reported systems were crystalline bithiophene, being an essential block of a conducting polymer, benzoic acid, serving as a model hydrogen-bonded system, molecular fragments of DNA and proteins. Michael Krisch reported some inelastic x-ray scattering results, a method complementary to the coherent inelastic neutron scattering. The x-ray method is well suited for disordered systems, samples only avaliable in small quantities, and materials studied under high pressure. Particularly interesting were the phonon results measured for Pu element, and high-T_c superconductor $Nd_{1.86}Ce_{0.14}CuO_{4+\delta}$. It was shown that by x-rays the surface phonons can also be measured. Walter Wolf refered results obtained by MedeA, which combines the softwares of VASP and Phonon. The applicability of this approach was demonstrated on temperature dependence of free energies, vibrational enthalpies and entropies of solid compounds, in surface reconstraction, phase stability and phase transitions. The method allows to treat molecules on surfaces and find the energy profile essential for diffusion.

The 13 contributed talks provided further examples of aplications of ab initio phonon calculations to variety of phenomena and systems. Among the others, it was shown that phonon contribute to chemical reactions, in which solid reactants are involved. An example of experimental studies of surface phonons on Ag(111) was given. Phonons decide about structural phase transitions. There is increasing interest to analyse atomic vibrations in the disordered systems.

FUTURE DIRECTION OF THE FIELD

A number of topics have been identified as important areas for future research with increasing prospective potential. Phonons will still be using to search for soft modes and identify the structural phase transitions. Phonon calculations will facilitate the analysis of vibrations in crystals, including molecular crystals, and estimate the phonon peak's intensities in the inelastic neutron and x-ray scatterings. Knowledge of phonon vibrations allows in an ab initio way to calculate the thermodynamical functions, which are important in prediction of phase transition, phase diagrams, and some chemical reactions. The mentioned approach can be applied to bulk crystal, crystals with defects, surfaces and multilayers, hence one may study surface and interface phonons.

Number of topics still need additional implementation into the computer codes. Among them is the electron-phonon coupling constant. There is a need to calculate the anharmonic contributions to phonon shift and width, which goes beyond the quasiharmonic approximation. This should allow to include anharmonic contributions to thermodynamical functions, and to compute heat conductivity. There is an interest to study atomic vibrations in disordered and amorphous systems, which can be done, for example, by averaging phonon properties over many atomic configurations, representing the disordered system. Crystals are usually studied under hydrostatic pressure. One should, however, expect new properties, and more complex phase diagrams temperature-stress components when studing the crystals under different stress componets.

FINAL PROGRAM

Wednesday, December 1, 2004

17:00	–	20:00	Registration
19:00	–		Informal reception at Demel Hotel

Thursday, December 2, 2004

9:00	–	9:10	Opening
9:10	–	10:40	Georg Kresse *VASP: Accurate force calculations and the VASP–PAW datasets*
10:40	–	11:10	Coffee break
11:10	–	12:40	Peter Blaha *Electronic structure, atomic forces and structural relaxations by WIEN2k*
12:40	–	14:00	Lunch at Demel Hotel
14:10	–	15:40	Krzysztof Parlinski *Calculations of phonons and thermodynamical properties of crystals by PHONON*
15:40	–	16:10	Coffee break
16:10	–	18:10	Tutorials, Poster Session
18:45			Bus departure from Krakowiak Hotel
18:50			Bus departure from Demel Hotel
19:00	–		Dinner in Modlnica

Friday, December 3, 2004

9:00 – 10:00	Mark Johnson *Phonons in molecular crystals – from ab initio calculations to neutron scattering, x-ray and infrared data*
10:00 – 10:45	Michael Krisch *Inelastic x-ray scattering from phonons at the ESRF: recent results and perspectives*
10:45 – 11:15	Coffee break
11:15 – 12:15	Walter Wolf *Ab-initio vibrational properties and thermodynamics from an automated computational framework*
12:15 – 12:35	Wilfried Wunderlich *Ab-initio calculations for development of* $SrTiO_3$*-based thermoelectric materials*
12:35 – 14:00	Lunch at Demel Hotel
14:00 – 14:20	Sathya Hanagud *First-principles equation of state for energetic intermetallic and metal-metal oxide mixtures*
14:20 – 14:40	Xuezhi Z. Ke *Lattice dynamics of sodium alanate*
14:40 – 15:00	C.F.J. Flipse *Experimental observation of vibrational modes on Ag(111) along* Γ*–M and* Γ*–K directions*
15:00 – 15:20	Akihide Kuwabara *First-principles calculation of lattice vibration and phase transformation in* ZrO_2 *polymorphs*
15:20 – 15:40	Paweł T. Jochym *Phase transitions in* Mg_2SiO_4 *and* $CaCl_2$ *within quasiharmonic approximation*
15:40 – 16:10	Coffee break
16:10 – 17:20	Tutorials
17:20 – 17:40	Svein Stølen *Collective ionic motion through low-energy structural entities*
17:40 – 18:00	H.A. van Laarhoven *Electron- and hole- vibrational coupling in oligoacene singlecrystals studied by spectroscopic methods as well as first principle calculations*
18:00 – 18:20	Imre Bakó *Vibration of small molecules on Pd(111), Pt(111) and Rh(111) surfaces*
18:20 – 18:40	Elwira Wachowicz *First stages of oxidation of the Si-rich 3C–SiC(001) surface*
18:40 – 19:00	Jacek Piechota *First principles study of geometry of Gd: CASTEP vs. VASP*

Saturday, December 4, 2004

9:00	–	9:20	Chris E. Mohn *Genetic mapping of the potential energy surface of disordered materials*
9:20	–	9:40	Krzysztof D. Meisel *Ab initio study of charged polarons in semiconducting polymers*
9:40	–	10:30	Coffee break
10:30	–	11:30	Tutorials
11:30	–	11:45	Discussion
11:45	–	12:00	Closing

TUTORIAL PRESENTATIONS

VASP: Accurate force calculations and the VASP–PAW datasets

Georg Kresse

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I will briefly describe the projector augmented wave method [1] and its advantages in solid state calculations. Particular attention will be given to the implementation of this method in the VASP package [2] and to the PAW potentials distributed with the VASP package. A brief introduction to the VASP package will be presented, emphasizing the underlying algorithms [3], as well as the most important input parameters required to get systematic transferable results [4]. Prerequisites for accurate force calculations for large supercells are discussed in detail, and some results are presented for nanotubes, highlighting the accuracy presently attainable with finite differences using VASP.

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Electronic structure, atomic forces and structural relaxations by WIEN2k

Peter Blaha

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I will give a review on augmented plane wave (APW) methods for the calculation of the electronic structure in solids. Starting with the original concept developed by J. Slater [1] long time ago the history of the developments will be summarized. Key developments were made by O.K. Andersen [2] (linearization of the energy dependence of the radial wave function), A. Freeman *et al.* [3] (full-potential total energy method), D.J. Singh [4] ("local orbitals", to improve the linearization errors) and finally by Sjöstedt *et al.* [5], which introduced the APW+lo method. This latter method combines the superior convergence behavior of the original APW method with the convenience of LAPW [6]. I will then give an overview of the implementation of APW+lo into the WIEN2k code [7] and demonstrate its usage on a simple example. I'll summarize the available features and discuss in particular the possibilities for structural optimizations and atomic force calculations. Finally, selected results connected with PHONON ("Geometric frustration and electronic instabilities in Pyrochlore $Y_2Nb_2O_7$" [8] and "Phase transitions in ferroelectric Aurivillius compounds" [9]) will be discussed in more detail.

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Calculations of phonons and thermodynamic properties of crystals by Phonon

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The description of finite temperature properties of materials, specially crystalline materials, requires to know the lattice vibrations classified as phonons. Vibrating atoms contribute the thermodynamical functions. Phonons can be calculated using ab initio softwares VASP [1] or Wien2k [2], and Phonon [3] software, in which the direct method was implemented. Within the direct method, the Hellmann–Feynman forces generated while displacing one atom, are transformed to the force constants, which, in harmonic approximation, define the dynamical matrix The diagonalization of the dynamical matrix provides the phonon dispersion relations and the phonon density of states (DOS). Next, the DOS can be used to derive temperature dependence of the phonon contribution to the internal energy, entropy, free energy, heat capacity, and mean square displacement at constant volume. Similarly, the coherent and incoherent inelastic double differential scattering neutron, and x-ray cross sections can be computed. The knowledge of phonon frequencies and polarization vectors allow to predict the phonon peak intensities in the neutron, and x-ray scattering experiment ands select the Brillouin zone, in which the phonon peaks are most intense. As a matter of fact, in particular case, phonon peak intensities can act as selection rules which might allow to measure phonon dispersion relations even for complex crystals. The polarization vectors associated with phonons defines atomic displacements involved in the normal modes. Hence, one can specify the irreducible representations of the phonon frequencies at the Γ point. Moreover, the atomic motion involved in a phonon can be animated on the screen.

Several additional options allow better to find harmonic phonon properties. Effective Born charges and electronic part of the dielectric constants lead to description of the LO/TO splitting of infrared active optic modes. Superimposing the translational-rotational invariance conditions, one forces the acoustic modes to start from zero frequency at Γ point. One may restore the crystal symmetry in the case when the supercell shape lowers the crystal space group. Moreover, one may fit the calculated phonon dispersion relations, to a set of experimental frequencies in order to obtain most representative phonon dispersion relations. There are facilities to tune the phonon frequencies by multiple displacements corresponding to a specific selected mode.

Better account for thermal properties can be obtained within the quasiharmonic approximation, in which temperature dependence is found by scalling temperature with negative pressure. This approach permits to calculate thermal expansion, and anharmonic phonon frequency shifts as a function of temperature.

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Phonons in molecular crystals – from ab initio calculations to neutron scattering, x-ray and infra-red data

Mark Johnson
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Vibrations in molecular crystals have traditionally been studied by optical techniques like infrared and Raman in the intermediate frequency range. These vibrations are determined essentially by intra-molecular interactions and accordingly isolated molecule calculations, using for example Gaussian, have been used to analyse spectra. More recently developments in spectroscopic techniques have opened up the low frequency, far infra-red range to experimental investigation and the need for solid state calculations has become apparent. Neutron scattering has always been able to measure the whole spectral range from 0 to 4000 cm^{-1} and modern spectrometers can have a resolution as good as about 1transfer. Furthermore the relatively short wavelength of neutron beams means that the whole Brillouin zone is probed, whereas optical techniques are limited to the Gamma point. Neutron scattering has therefore pushed us towards solid state calculations that include dispersion. Intensities in neutron scattering spectra are simply determined from the eigenvectors of the dynamical matrix and tabulated scattering lengths, which make this experimental technique ideal for validating the phonon calculations. A similar formalism applies to the newer experimental technique of inelastic x-ray scattering (IXS) and we recently studied molecular crystals by this technique at the ESRF (Grenoble, France).

Examples will be shown of vibrational studies of Van der Waals and hydrogen-bonded molecular solids, the latter systems exhibiting strong inter-molecular interactions. The systems range from bithiophene, the building block of an important conducting polymer, to benzoic acid (a model hydrogen-bonded system) and molecular fragments of DNA and proteins. Measured and calculated neutron scattering, inelastic x-ray scattering and infra-red spectra will be shown.

Inelastic x-ray scattering from phonons at the ESRF: recent results and perspectives

Michael Krisch
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Inelastic x-ray scattering (IXS) with meV energy resolution has become a valuable spectroscopic tool, complementing the well established coherent inelastic neutron scattering (INS) techniques in the study of phonon dispersion. IXS is particularly well suited for disordered systems, samples only available in small quantities or materials studied under very high pressure. At the ESRF there are currently two beam lines (ID16 and ID28) dedicated to phonon spectroscopy. After a brief introduction to the technique and its specificities, the present state of the art and future perspectives shall be illustrated.

Ab-initio vibrational properties and thermodynamics from an automated computational framework

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For decades, ab initio calculations have been largely viewed as being restricted to zero temperature, or more precisely, as being condemned to operate without the concept of temperature at all. Nowadays, this major constraint has been lifted, and routine methods to evaluate vibrational properties and temperature dependent thermodynamic functions have become available, at least within the harmonic approximation. In this contribution, the implementation of the so-called direct approach [1,2] to vibrational properties within the MedeA modeling environment [3] is outlined and a number of applications in rather diverse fields are discussed. The MedeA Phonon module (based on the PHONON software package of K. Parlinski [4]) in conjunction with the MedeA VASP module (interfacing to the Vienna Ab-initio Simulation Package VASP [5]) allows the evaluation of vibrational properties in a routinely and highly automated manner on a distributed network of computers. The efficiency and practicability of the MedeA implementation is directly demonstrated on a wide range of rather different applications. Temperature dependent free energies, vibrational enthalpies and entropies of solid compounds are evaluated thus enabling the study of thermochemistry of chemical reactions as well as phase stability from ab initio theory. As will be shown, in particular for hydrogen containing compounds and hydrogen impurities in metals, neglecting zero point vibrations may cause qualitatively wrong answers in many cases. In addition, phonon instabilities of metastable phases may point towards possible phase transformations to other stable phases. Furthermore, vibrational spectra of transition states are well suited for the study of chemical kinetics as well as transport properties, opening the field for simulation of diffusion processes. The methodology is, however, not restricted to the solid state: vibrations of molecules and molecules on surfaces may help to analyze spectral data, and the calculation of surface phonons are well suited to confirm stability of a suggested surface or may reveal possible reconstructions, just to mention some of the rather promising though challenging applications.

[1] K. Parlinski, Z. Q. Li, Y. Kawazoe, Phys. Rev. Lett. 78, 4063 (1997)
[2] G. Kresse, J. Furthm ller, J. Hafner, Europhys. Lett. 32, 729 (1995)
[3] MedeA, Materials Design Inc., Taos, NM (USA). http://www.MaterialsDesign.com
[4] K. Parlinski, Software PHONON (2002)
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ORAL PRESENTATIONS

Vibration of small molecules on Pd(111), Pt(111) and Rh(111) surfaces

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The adsorption of water and other small molecules onto transition metal surfaces is an important issue in electrochemistry, fuel cells, etc. Despite the overwhelming interest there are still unresolved issues beginning from the geometry of the adsorbed species to the correct assignments of different vibrational modes of the molecule on the surface. In order to understand the adsorption processes, we have performed density functional theory (DFT) calculations for small molecules (water, methanol, formic acid, formaldehyde) on Pd(111), Pt(111) and Rh(111) surfaces. We investigated the nature of the metal-ligand bonding of these adsorption processes using electron density difference and PDOS (partial density of states) methods. Ab initio vibration spectra have been calculated for these systems. The effect of the fixed first layer on the vibration spectra was also investigated. The calculation was performed using VASP program package.

Experimental observation of vibrational modes on Ag(111) along GM and GK direction

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We present an off-specular high-resolution electron energy-loss spectroscopy study of the vibrational modes along the GM and GK directions in the surface Brillouin zone of clean Ag(111). We show experimental data of vibrational modes at the K- edge, thereby extending the earlier He-scattering data on the S1 Rayleigh mode and pseudo-Rayleigh mode. In addition, we observed the S3 gap mode and three high-frequency modes along GK. According to our knowledge, this is the first experimental evidence for the existence of these high frequency modes in the (111) surface Brillouin zone of fcc metals. Along GM the experimental dataset of the S2 gap mode is extended to smaller Q//, and for the first time the high-frequency vibrational mode close to the top of the projected bulk phonon band is observed. The HEELS data is analyzed by comparison to theoretical studies previously reported in the literature. This paper presents new experimental data of the surface vibrational structure, which can stimulate theoreticians to refine their modeling and improve the understanding of the Ag(111) surface lattice dynamics.

First-principles equation of state for energetic intermetallic and metal-metal oxide mixtures

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In this paper, the thermodynamically complete equation of state for a intermetallic mixture of nickel, aluminum, and binders, and a metal-metal oxide mixture of aluminum and iron oxide, with porosity, are obtained via first principle (or ab initio) calculations for pressures up to 300 GPa and temperatures up to 3000 K. The calculations for the static-lattice EOS are carried out in the framework of the density functional theory (DFT), using generalized gradient approximations, ultrasoft psuedopotentials and projector augmented wave approach. The phonon modes are calculated by the density functional perturbation theory (DFPT). The lattice thermal contributions are obtained by populating the phonon modes according to the Boltzmann statistics. The electronic thermal contributions are obtained by populating the band structure according to the Fermi-Dirac statistics. First, the EOS for each species is obtained based on ab initio prediction of the electron ground state and thermal excitations. Then, the EOS of the mixtures are obtained using various mixture theories depending on the architecture of the mixture. The effects of the porosity on the EOS are introduced by considering the air as the third component in the mixture. The comparisons of the EOS for nickel and aluminum obtained from existing shock Hugoniot data show good agreement with the theoretical results. In particular, Fe_2O_3, a transition metal oxide, is classified as a strongly correlated system and poses considerable modeling challenges due to the hopping behavior of 3d valence electrons in Fe^{3+}. While exact modeling of electronic behavior in such systems is still an active research area, ultrasoft pseudopotentials (UP) and projector-augumented wave (PAW) potentials within the framework of DFT have been employed to yield reasonably accurate results.

Phase transitions in Mg_2SiO_4 and $CaCl_2$ within quasiharmonic approximation

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One of the fundamental problems with ab-initio treatment of the phase transitions is inclusion of the temperature into the calculations. We are using the quasiharmonic approximation to solve this problem. We will show an example of application of this method to the case of Mg_2SiO_4 mineral in the cubic phase. The thermal expansion and specific heat calculations will be presented.

As an example of the real system with phase transition we have selected the $CaCl_2$ crystal. This crystal exhibits a second order phase transition in moderate temperatures. We have shown that the application of the quasiharmonic approximation based on the DFT calculation of phonons enables one to derive the p–T phase diagram of the crystal even in the seemingly difficult case of the second order phase transition.

Lattice dynamics of sodium alanate

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The electronic properties and lattice dynamics of the sodium alanate phases have been studied by the density functional calculations. The phases include NaAlH4, Na3AlH6, and NaH. The ionic properties of the phases are discussed on the basis of the electronic band structures, the atomic charges, the bond population analysis. The phonon dispersion relations and phonon density of states (DOS) of the phases are calculated by a direct force-constant method using the code PHONON. Based on the integrated phonon DOS, the thermodynamic functions including the heat capacity, the vibrational enthalpy, and the vibrational entropy are calculated. Three decomposition reactions are studied based on the thermodynamic functions.

First Principles Calculation of Lattice Vibration and Phase Transformation in ZrO_2 polymorphs

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Zirconia, ZrO_2, is one of the most important ceramic materials in modern technology. Its versatility is closely related to phase transformations. Although the transformations have been repeatedly investigated by experiments, fundamental aspects of the transformations are still under debate. In the present paper, we have made first principles calculations to study the lattice dynamics of ZrO_2 polymorphs and phase transformation at finite temperatures. Cubic phase shows a soft mode at the X point in Brillouin zone, which should spontaneously induce cubic-to-tetragonal transformation. In tetragonal and monoclinic ZrO_2, all vibrational modes have real frequency. Calculations of Helmholtz free energies show that the tetragonal phase becomes more stable than the monoclinic phase above 1350 K, which is in quantitative agreement with experimental results. This confirms that vibrational entropy contributes to destabilize monoclinic ZrO_2 at the elevated temperatures.

Ab initio study of charged polarons in semiconducting polymers

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We present a novel ab initio method to analyze electron (hole) - phonon interaction and polaron formation in semiconducting polymers. We use an extended Holstein Hamiltonian describing electrons (holes) coupled to optical phonon modes. A minimization of the lowest electronic state of this Hamiltonian with respect to lattice degrees of freedom yields the polaronic ground state. Input parameters of this Hamiltonian are obtained from ab-initio calculations based on density-

functional theory. We calculate optical phonon modes and the coupling constants of these modes to the HOMO and LUMO bands (highest occupied and lowest unoccupied molecular orbitals, respectively). For the studied polymers (polythiophene - PT, poly(phenylenevinylene) - PPV, poly(para-phenylene) - PPP) the polaron binding energy, its size and the lattice deformation as a function of conjugation length have been determined. Self-trapped polarons are found for long conjugation lengths. Energies of prominent PPV modes involved in polaron formation agree with infrared spectra.

Genetic mapping of the potential energy surface of disordered materials

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Methods for determination of the structure and energetics of disordered materials by averaging over a large number of possible local structural configurations are becoming increasingly efficient. Different selections of a limited number of configurations have been compared with the results obtained when considering each of a vast number of possible configurations [1] (using an efficient symmetry routine). The results can be summarized as follows:
A random selection of a small sub-set of the configurations give accurate results when the energy span of the total configurational space is small.
An RDF-approach works better in systems showing large structural relaxations e.g. for systems like SrFeO2.50. Here all configurations are sorted into groups of non-equivalent RDF-configurations. Subsequently, one configuration of each sub-group is picked at random and optimized [2].
The present paper presents an alternative approach in which a genetic algorithm is used to derive a sufficient set of low energy configurations for a disordered material. Although genetic approaches to an increasing degree are used to find the global minimum for a given system [3], we will show that genetic algorithms are very suitable for characterizing the low-energy part of the potential energy spectrum for grossly disordered materials as well.

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[2] E. Bakken et al., Phys. Chem. Chem. Phys. 5 (2003) 2237.
[3] R.L. Johnston, Dalton Trans. (2003) 4193.

First principles study of geometry of Gd: CASTEP vs. VASP

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The results of first principles calculations of the equilibrium lattice constants are presented for gadolinium. Two software packages, CASTEP and VASP were used, and the computations were aimed on the determination of the applicability of different potential approaches, i.e., projector augmented wave and pseudopotentials (norm-conserving and ultrasoft), for studies of the magnetic and nonmagnetic states of Gd. The performance of all potentials is documented for both LDA and GGA formalisms with and without spin polarization, and results are compared to observed properties.

Collective ionic motion through low-energy structural entities

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The complexity of grossly disordered structures tends to hinder fundamental understanding of the functional properties of many classes of advanced materials. Links between the dynamic structure, thermodynamic behavior and ionic conductivity are central themes in contemporary solid-state science and disordered materials remain a challenge both to experiment and theory. The present contribution focuses on fast-ionic conduction and uses $Ba_2In_2O_5$ as a model system. At high temperatures $Ba_2In_2O_5$ has ionic conductivity equal in magnitude to that of the widely used stabilized zirconias. Present models often describe the structures and thermodynamics of this and related materials in terms of random distributions of oxygen atoms and oxygen vacancies on the available oxygen sites and their dynamic behaviour in terms of single or correlated ion-jump mechanisms. In the present study the local and average structure of this grossly disordered oxide is approached using density functional theory. The energies of the different local structural environments have important implications on the ion transport in the material. The conventional vacancy jump mechanism would allow different types of local short-range order that we here show are of high energy and thus make a negligible contribution. The ionic movement is highly restricted by the local symmetry e.g. by the high energy of the square-planar entity compared to a tetrahedral local structure. However, the very nature of the low-energy structural configurations has even more extensive fundamental implications for the ionic conductivity. Transition paths connecting different low-energy crystallographic non-equivalent configurations characterized using the nudge-elastic-band method strongly indicates that collective ion movements are important in fast oxide-ion conductors such as $Ba_2In_2O_5$. We show, by a detailed systematic search of the potential energy hypersurface, that the ionic conduction takes place through collective ion-movements between different local low-energy structural entities.
Mohn *et al.*, Phys. Chem. Chem. Phys. (2004) 6, 3052-3055.

First Stages of Oxidation of the Si-rich 3C-SiC(001) Surface

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Systematic studies of O adsorption on clean and H-saturated Si-rich 3C-SiC(001) 3×2 surface within density functional theory are presented. We investigate O binding energy for a variety of possible adsorption sites on the surface and in subsurface regions for both substrates. We find that the on-surface adsorption sites are preferred over deep adsorption for both substrates although O is more strongly bound on the hydrogenated surface. We explore the dependence between the energy of the adsorption site and the surface reconstruction accompanying it.

Ab-initio calculations for development of $SrTiO_3$-based thermoelectric materials

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Recent experiments on advanced thermoelectric materials showed an increase in the figure-of-merit for Nb-doped $SrTiO_3$ and for natural Ruddlesden-Popper phases $SrTiO_3$–SrO. For the basic understanding of the parameter dependence of the Seebeck coefficient ab-initio calculations using VASP [1] were performed. The effective mass was estimated from the curvature of the electronic bands and showed excellent agreement with the experimental values. The effective mass increases with the doping concentration and in the case of artificial superlattices (SrO)n–($SrTiO_3$)m with n,m =1..2. The bandstructure changes and large values of effective masses are obtained. The other important parameters for thermoelectric properties, like electron phonon scattering are estimated from the phonon band structure of $SrTiO_3$-based materials, as the maximum vibration frequency leads to the minimum thermal conductivity.

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Electron- and hole- vibrational coupling in oligoacene single-crystals studied by spectroscopic methods as well as first principle calculations

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Analysis of intramolecular vibrations by DFT calculations is carried out for single molecules of both pentacene(1) and rubrene(2). These vibrations are compared to HREELS spectra for a multi-layer. THz spectroscopy is used to measure the dielectric response of both photo-induced charges in single-crystal rubrene and pentacene. For the photo-excited state an increase of the response is visible at frequencies corresponding to those shown in ground state absorption plots. From those measurements effects of electron-vibrational coupling are evident. Comparing these results to ab initio calculations of the carrier-vibrational coupling for a single molecule show that also for intramolecular vibrations a pure local (Holstein) model does not give a satisfying description of the coupling and a mixed Holstein-Peierls model is needed.

LIST OF POSTERS

Miroslav Černy and J. Pokluda

Elastic and magnetic stability of crystals under compression

Jan Łażewski, Przemysław Piekarz, and Krzysztof Parlinski
Second-order phase transition in quasiharmonic approximation

Aritz Leonardo, I.Yu. Sklyadneva, and E.V. Chulkov
Electron-phonon interaction and its contribution to electronic lifetimes in metals

A.S. Mikhaylushkin, U. Häussermann, B. Johansson, and S.I. Simak
Fluctuating lattice constants in Indium under high pressure

Przemysław Piekarz, Andrzej M. Oleś, Krzysztof Parlinski, and Paweł T. Jochym
Ab initio study of lattice dynamics in $PuCoGa_5$ superconductor

Paweł Scharoch
The semiempirical method for finding thermal characteristics of simple crystals

Denys A. Semagin
Numerical analysis of atomic motion in the incommensurate phase of quartz (SiO_2) in the vicinity of phase transition

Małgorzata Sternik and Krzysztof Parlinski
The free energy calculations of the cubic, tetragonal and monoclinic phases of zirconia

Tetsuya Tohei, A. Kuwabara, T. Yamamoto, F. Oba, and I. Tanaka
Pressure dependence of soft mode transition in $LaAlO_3$ and related perovskite compounds by first principles calculations

Bartłomiej Wiendlocha and Janusz Tobola
Calculations of the electron-phonon properties of $MgCNi_3$-type superconductors

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STATISTICAL INFORMATION ON PARTICIPANTS

The 55 participants were comming from 16 countries: Austria (2), Czech (2), Estonia (2), Finland (1), France (6), Germany (1), Hungary (1), Japan (5), Netherland (5), Norway (5), Poland (16), Slovakia (1), Spain (3), Sweden(3), Swiss (1), USA (1).

Krzysztof Parlinski

6.2 ESF Psi-k Programme Workshop/Conference Announsements

6.2.1 Hands-on Course: KKR Bandstructure and Spectroscopy Calculations

Organised by:
Hubert Ebert (München) and Walter Temmerman (Daresbury)

Supported by:
ESF Psi-k-Programme and the German
Bundesministerium für Bildung und Forschung

9th - 11th June 2005

Univ. München, Phys. Chem.

`http://olymp.cup.uni-muenchen.de/ak/ebert/Handson_2005/`

Purpose: teach theoreticians **and** experimentalists the use of the
Munich SPR-KKR bandstructure and spectroscopy package.

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

The code will be available free of charge after signing a license agreement.

Registration: Fill in the database at
`http://olymp.cup.uni-muenchen.de/ak/ebert/Handson_2005/registration.html`

Attendance fee: 60 Euros.

Financial support for some participants is possible.

Program:

- Morning: Lectures on DFT, KKR and electron spectroscopies
- Afternoon: use of the program package guided by tutors on:
  xband, SCF, CPA, E($\vec{k}$), DOS, ground state properties,
  XAS, EXAFS, XMO, XRS, XES, VB-XPS, CL-XPS, MCP, APS, AES, ...

Preliminary list of speakers:

K. Baberschke	Berlin
P. H. Dederichs	Jülich
H. Ebert	München
O. Sipr	Prague
W. M. Temmerman	Daresbury
W. Wurth	Hamburg

7 News from UK's CCP9 Programme

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

7.1 Report on the CCP9 Conference

Daresbury Laboratory, UK

29-30 November 2004

http://www.ccp9.ac.uk

Organizers:

James Annett (Bristol University) and Walter Temmerman (Daresbury Laboratory)

This conference, which was hosted at Daresbury Laboratory (UK), mostly brought together the different working groups of the British CCP9 Programme. Including external researchers from Japan, Germany and the USA, the conference was attended by 79 participants, many of them students or post-docs. The highlight of the conference was the Max Born Lecture and the Max Born Prize of the Institute of Physics (IoP) and the Deutsche Forschungs Gesellschaft (DFG), which was awarded to Matthias Scheffler (Fritz-Haber Institut, Berlin), for his outstanding achievements in theoretical surface physics, and in particular the combination of density functional theory and statistical mechanics to model adsorbates and catalytic processes.

Figure 1: Matthias Scheffler and John Beeby, the IoP representative

The conference started with a lecture by Richard Martin, in which he reviewed the developments of electronic structure theory over the last 40 years, leading to the current topics of the field. This talk beautifully set the scene for the subsequent contributions, which reported on the current status of research in different branches of electronic structure theory, ranging from new theoretical developments to applications, allowing to make contact with experimentally accessible quantities. Amongst the theoretical developments concerning electronic correlations, there was the GW approximation. Rex Godby explained the method as such, including a detailed discussion on different levels of self-consistency, while Takao Kotani presented a novel "quasi-particle self-consistent" GW scheme, implemented in the FP-LMTO method, and first results on the band gaps for a number of semiconductors. Mike Towler reported on recent progress in the quantum Monte Carlo methods, highlighting some algorithmic developments, aimed at an all-electron treatment of heavy atoms and presented some applications using the 'CASINO' code. Dzidka Szotek discussed the electronic and magnetic properties of spintronics materials based on the self-interaction corrected local spin density approximation. A generalisation of density-functional theory for superconductors, allowing for first principles calculations of superconducting properties, including first applications to real systems, were presented by Martin Lüders. Another methodological development was the non-local extention of the coherent potential approximation and its implementation within the KKR method by Derwyn Rowlands. Mikhail Katsnelson discussed the effect of incoherent non-quasiparticle states in half-metallic ferromagnets leading to their anomalous magnetic and electronic properties. A central theme of the conference was concerned with the realistic description of large systems. This field was opened by the Max Born lecture, given by Matthias Scheffler, in which he gave an overview of the applied methods and discussed the example of O_2 dissociation on Al(111). Other contributions in this area were the plenary talk of Mike Payne, who introduced two new methods, namely a linear scaling code and a hybrid modelling scheme, which will allow for the calculation of tens of thousands atoms over long time scales. The linear scaling code was described in more detail by Chris-Kriton Skylaris. A different approach to large systems was outlined by David Pettifor, who described the method of constructing analytical bond-order potentials from systematically coarse-graining DFT results via an intermediate tight-binding model. Bob Jones reported on DFT calculations of extended interstitial defects in Si and demonstrated that these complex arrangements of interstitials can be analysed theoretically. A method for predicting magnetic resonance experiments, based on DFT calculations was put forward by Chris Pickard. He also described how the method is used by the experimental community to assist in extracting information from the experimental data.

Apart from the talks there were poster-sessions during the buffet lunches, and a bottle of champagne was awarded to Jan Minar (Munich) for the best poster presentation.

The conference contained a good mixture of overview talks and more specialised contributions. Throughout the whole conference the atmosphere was very lively, and many stimulating discussions took place. To this good atmosphere also contributed the banquet dinner at the Yang Sing restaurant in Manchester, which was held in honour of Matthias Scheffler on the occasion of his Max Born Prize.

The photographs of the conference can be found on the web under the URL:
`http://www.ccp9.ac.uk/data/CCP9Workshop_Photos/index.htm`

Martin Lüders, *Daresbury Laboratory*

Programme of the CCP9 Conference 2004

Monday, 29th November

09.30 - 10.30		Registration and coffee
10.30 - 11.30	**Richard Martin**	Building on the successes of Electronic Structure Theory
11.30 - 11.55	Mike Towler	Recent progress in quantum Monte Carlo
12.00 - 12.25	Dzidka Szotek	Self-interaction corrected Local Spin Density calculations for spintronics materials
12.30 - 14.30		Buffet Lunch and Posters
14.30 - 15.30	**Rex Godby**	The GW approach to spectral, ground-state and transport properties
15.30 - 15.55	Bob Jones	Density functional treatment of extended interstitial defects in Si
16.00 - 16.25	Martin Lüders	Ab-initio theory of superconductivity: Density functional formalism, approximate functionals and first applications
16.30 - 17.00		Coffee
17.00 - 18.00	**Born Prize Presented to Matthias Scheffler**	Statistical Mechanics from First Principles
20.00		Conference Dinner

Tuesday, 30th November

08.45		Coffee and Pastries
09.00 - 10.00	**Mike Payne**	Next Generation Simulation Techniques
10.00 - 10.25	Chris-Kriton Skylaris	Introducing ONETEP: Linear-Scaling Density Functional Theory with Plane Waves
10.30 - 10.55	David Pettifor	Recent Developments in analytic bond-order potentials
11.00 - 11.30		Coffee
11.30 - 11.55	Derwyn Rowlands	First-principles description of disordered metallic systems with short-range order
12.00 - 12.25	Chris Pickard	Interpreting magnetic resonance experiments from first principles
12.30 - 14.55		Lunch and posters
15.00 - 16.00	**Mikhail Katsnelson**	Non-quasiparticle states in half-metallic ferromagnets
16.00 - 17.00	**Takao Kotani**	Quasiparticle self-consistent GW method

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ABSTRACTS:

Talks

Building on the Successes of Electronic Structure Theory

Richard M. Martin

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Understanding of electronic structure of materials has come a long way in the 80 years since 1924 when Prince Louis de Broglie deposited his thesis. From the start electrons have played a key role in the development of quantum theory, and within a few years quantum mechanics provided the underpinnings of present understanding of metals, insulators and semiconductors. Today the field is at a momentous stage, with new algorithms and computational methods, and rapid advances in basic theory. In the 40 years since the advent of density functional theory and the 20 years since the landmark Car-Parrinello paper, the work of many people have brought the field to the point where properties of materials can now be determined directly from the fundamental equations for the electrons [1]. The methods have become standard tools - an essential part of modern materials research. At the same time there have been important developments in many-body theory and methods to treat excitations of correlated, interacting electrons.

This talk is oriented toward the future and the greatest challenges, which are to understand the vast array of phenomena exhibited by the many-body system of interacting electrons in matter. At this point in time there is the opportunity to build upon recent successes to create new approaches that will make possible robust predictions for new phenomena and materials, complex systems, nanostructures, activity of large molecules in solution, magnetism, metal-insulator transitions, transport, and many other areas. Specific examples of recent work show the power of combined independent-particle and many-body methods to provide new predictive capabilities and new insights into important problems in physics, chemistry, and materials science.

[1] An exposition of the basic theory and methods along with extensive references and examples of recent work can be found in "Electronic Structure: Basic theory and practical methods," R. M. Martin, Cambridge University Press (2004), and on-line at `http://ElectronicStructuer.org`.

Recent progress in quantum Monte Carlo

Mike Towler

Theory of Condensed Matter, University of Cambridge, UK

Abstract

In this talk I shall describe certain algorithmic developments in diffusion Monte Carlo simulations which lead to improved scaling with system size and an increased ability to treat heavy atoms without using pseudopotentials. Some applications of this highly-accurate technique using the code 'CASINO' wil be outlined.

Self-Interaction Corrected Local Spin Density Calculations for Spintronics Materials

Z. Szotek

Computational Science and Engineering Department, Daresbury Laboratory, UK

Abstract

Self-interaction corrected (SIC) local spin density (LSD) method is applied to study electronic structure and magnetic properties of III-V and II-VI diluted magnetic semiconductors, magnetite, and such spinel ferromagnetic insulators as NiFe2O4 and CoFe2O4. In the diluted magnetic semiconductors we concentrate on the understanding and realization of carrier mediated ferromagnetism. The insulating charge ordered Verwey phase of magnetite is discussed in relation to the electronic structure of NiFe2O4 and CoFe2O4, and we speculate on the implications for possible technological applications.

The GW approach to spectral, ground-state and transport properties

Rex Godby

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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. It may be thought of as exact exchange (the Hartree-Fock exchange operator), together with an partial inclusion of correlation diagrams through dynamical screening of the Coulomb interaction. From Σ, the one-electron Green's function G may be calculated, from which various spectral and ground-state properties are available. For transport properties (as well as certain other excited-state properties), the two-electron Green's function is required, which may also be formulated at the same level of approximation as GW.

I shall start with a brief review of key applications of GW to spectral properties such as quasiparticle energies and lifetimes for added electrons or holes, including some recent work on metallic clusters [1].

In applying GW to the ground-state total energy, the choice of whether G and/or W are made to be consistent with the Green's function that arises *from* Σ is particularly important: G_0W_0, GW_0 and fully self-consistent GW, where G_0 generally indicates the LDA Green's function. I shall present results for finite and infinite systems at all three levels of self-consistency. These include converged results resulting from the incorporation of self-consistency and GW total-energy techniques into our general-purpose GWST "space-time" supercell code suite [2], 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 [3] to general systems, and opens the possibility of applications to systems whose energetics is not described sufficiently reliably within the usual DFT-based approaches.

I shall also describe our recent formulation [4] of the conductance of a junction between two nanowires in a form which permits the inclusion of electronic correlation effects in a GW-like framework.

[1] "Image States in Metal Clusters", Patrick Rinke, Kris Delaney, P. García-González and R.W. Godby, submitted

[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] "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)

[4] "Conductance and polarization in quantum junctions", P. Bokes and R.W. Godby, Phys. Rev. B **69** 245420 (2004)

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

Density functional treatment of extended interstitial defects in Si

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Abstract

Self-interstitials in silicon, produced by ion-implantation or oxygen precipitation, can aggregate to form extended rod-like-defects (RLDs) with unusual {113} habit planes and having both electrical and optical activity. Although known for over 30 years they remain an enigma. Here, we describe the results of local density functional calculations on the RLDs which reveal their structure and electrical activity. We find that small {113} RLDs are more stable than RLDs condensing onto {111} planes but this reverses for larger defects. We

attribute the electrical activity of {113} RLDs to the bounding dislocations and a pronounced and sharp photoluminescence band to vacant interstitial sites on the RLD. The results of the modelling demonstrate that complex arrangements of interstitials are amenable to theoretical analysis and give hope that the pathways to other extended defects can also be found.

Ab-initio theory of superconductivity: Density functional formalism, approximate functionals and first applications

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Abstract

A novel approach to the description of superconductors in thermal equilibrium is developed within a formally exact density-functional framework. The theory is formulated in terms of three "densities": the ordinary electron density, the superconducting order parameter, and the diagonal of the nuclear N-body density matrix. The electron density and the order parameter are determined by Kohn-Sham equations that resemble the Bogoliubov-de Gennes equations. The nuclear density matrix follows from a Schrödinger equation with an effective N-body interaction. These equations are coupled to each other via exchange-correlation potentials which are universal functionals of the three densities. Approximations of these exchange-correlation functionals are derived using the diagrammatic techniques of many-body perturbation theory. The bare Coulomb repulsion between the electrons and the electron-phonon interaction enter this perturbative treatment on the same footing. In this way, a truly ab-initio description is achieved which does not contain any empirical parameters.

This new formalism is first applied to simple metals, to show the applicability to both weak and strong electron-phonon coupling. Further results for MgB_2, and Al and Li under pressure will be presented.

Statistical Mechanics from First Principles

Matthias Scheffler

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Abstract

This talk sketches the methods and describes recent theoretical work performed with *ab initio* atomistic thermodynamics and *ab initio* statistical mechanics (molecular dynamics as well as kinetic Monte Carlo).

Key examples in this talk concern the puzzle of O_2 dissociation at Al(111), in particular emphasizing the role of the O_2 spin state, and the properties of transition metals in oxygen atmospheres with (T, p) settings ranging from UHV to those encountered at “human” (or higher T, p) conditions.

Analyzing oxidation catalysis at the late transition metals it is found that the surface composition, that is attained under reactive conditions, and the consequential functionality of the surface can be very different from what is found at (or close to) thermodynamic equilibrium.

Next Generation Simulation Techniques

Mike Payne
TCM Group, Cavendish Laboratory,Madingley Road, Cambridge, CB3 0HE, UK

Abstract

In less than twenty years, the plane wave pseudopotential technique has progressed from modelling two atoms of silicon to modelling many hundreds of atoms of any species. However, this technique is still far away, both in terms of accessible lengthscale and more importantly accessible timescale, from being able to address many scientific challenges. In this talk I shall discuss two new techniques which confront these lengthscale and timescale challenges. They are a linear scaling first principles total energy technique, which will be described in greater detail in the talk by Dr. Skylaris, and a hybrid modelling scheme, developed in collaboration with Dr. Sandro De Vita. The linear scaling code provides the same accuracy as the plane wave pseudopotential technique but can be applied to systems containing many thousands of atoms, with the prospect of tens of thousands of atoms in the near future. The hybrid modelling scheme provides the same accuracy as a full quantum mechanical calculation but

allows simulations to be performed on systems containing hundreds of thousands of atoms or more for very long simulation times.

Introducing ONETEP: Linear-Scaling Density Functional Theory with Plane Waves

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Peter D. Haynes, Arash A. Mostofi and Mike C. Payne
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In order to apply first principles quantum mechanical calculations to systems containing thousands of atoms we need linear-scaling techniques. In achieving this goal we must not lose the accuracy, efficiency and flexibility provided by conventional total energy schemes. Plane waves are a popular choice of basis set for many such schemes because their implementation is straightforward and the completeness of the basis set can be controlled systematically with a single parameter. However, the resulting calculations require a computational effort which scales as the cube of the number of atoms in the system, and as a result current simulations are limited to hundreds of atoms.

In this talk I will present ONETEP (Order-N Electronic Total Energy Package), a parallel implementation of our linear-scaling reformulation [1] of the plane wave pseudopotential approach. The linear-scaling is achieved by exploiting the real space localisation of the electronic system that is inherent in non-metallic materials. I will describe the theoretical developments that allow us to optimise with linear cost the strictly localised quantities expressed in terms of a delocalised plane-wave basis. These same localised quantities also lead us to a physical way of dividing the computational effort among many processors to allow calculations to be performed efficiently on parallel machines. It will be shown that the localisation is achieved in a controlled and mathematically consistent manner so that ONETEP provides the same accuracy as conventional cubic-scaling plane-wave approaches, and offers fast and stable convergence. The particular features of our method which result in its success will be highlighted and preliminary results for realistic biological and condensed matter applications will be presented.

[1] C.-K. Skylaris, A. A. Mostofi, P. D. Haynes, O. Diéguez and M. C. Payne, Phys. Rev. B, **66**, 035119 (2002).

Analytic bond-order potentials for modeling the growth of semiconductor films

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Abstract

Robust interatomic potentials for simulating the growth of semiconductor films should be able to describe bond breaking and remaking naturally within their remit. In this paper we outline the derivation of such potentials, the so-called bond-order potentials (BOPs), by performing a systematic coarse graining from the electronic to atomistic modeling hierarchies. First the density functional theory (DFT) electronic structure and binding energy is simplified by introducing the tight-binding (TB) bond model whose parameters are determined directly from the DFT results. Second, this TB electronic structure is coarse grained through atom-centered moments and bondcentered interference paths, thereby predicting the analytic form of the interatomic BOP. We show that these interatomic potentials predict structural energy differences in quantitative agreement with k-space TB calculations and reproduce the experimental structural trends across the sp-valent elements.

First-principles description of disordered metallic systems with short-range order

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Abstract

For many years the coherent potential approximation (CPA) has been widely used to describe the electronic structure of disordered systems. However, as a local mean-field theory of disorder, the CPA is unable to describe important environmental effects such as short-range order in alloys and spin fluctuations in magnets, amongst others. Only recently,

the first satisfactory means of going beyond the CPA has been developed, the non-local coherent potential approximation (NLCPA),[1,2] which has also been derived within the first-principles Korringa-Kohn-Rostoker (KKR) multiple-scattering framework.[3] In this talk I describe the method and illustrate with KKR-NLCPA calculations for the effects of short-range order upon the electronic structure of alloys such as $CuZn$ and $CuNi$.[4] I also discuss future applications such as transport properties, and developments such as combination with density functional theory for ab-initio calculations, which will enable effects such as charge correlations and lattice displacements to be taken into account self-consistently for the first time.

[1] M. Jarrell and H.R. Krishnamurthy, PRB 63, 125109 (2001)

[2] R. Moradian, B.L. Gyorffy, and J.F. Annett, PRL 89, 287002 (2002)

[3] D.A. Rowlands, J.B. Staunton, and B.L. Gyorffy, PRB 67, 115109 (2003)

[4] D.A. Rowlands, J.B. Staunton, B.L. Gyorffy, E. Bruno, B. Ginatempo (to be published)

Interpreting magnetic resonance experiments from first principles

Chris J. Pickard, Jonathan Yates, and Francesco Mauri

Abstract

A method for predicting the results of magnetic resonance (NMR/EPR) experiments will be presented. It is based on the plane wave pseudopotential method, within density functional theory. Using a modified (gauge including) version of the projector augmented wave method, all-electron accuracy can be achieved. I will describe how the method is being adopted by the experimental community to assist in the extraction of the maximum amount of information from their magnetic resonance experiments. The range of applicability of the method will be emphasized, by reference to successful collaborative applications: porphyrin molecules, boron carbides, complex zeolite silicates, zircon, sodium and calcium silicate glasses and hydrogen bonded molecular crystals.

Non-quasiparticle states in half-metallic ferromagnets

Mikhail Katsnelson
University of Nijmegen, The Netherlands

Abstract

Anomalous magnetic and electronic properties of the half-metallic ferromagnets (HMF) are discussed. A general concept of the HMF electronic structure which takes into account the most important correlation effects from electron-magnon interactions, that is, the spin-polaron effects, is presented. Special attention is paid to the so called non-quasiparticle (NQP), or incoherent, states which are present in the gap near the Fermi level. Manifestations of NQP in electronic density of states, tunneling transport, nuclear magnetic relaxation, core-level spectra and other properties of HMF are considered. First-principle calculations of the NQP- states for various half-metallic ferromagnets within the local-density approximation plus dynamical mean field theory (LDA+DMFT) are reviewed.

Quasiparticle self-consistent GW

Takao Kotani, [2]Mark van Schilfgaarde [3]Sergey V. Faleev, and [4]Takashi Miyake

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We present some progress in the development of a semi self-consistent GW method based on the all-electron, full-potential LMTO method. Starting from a trial one-body Hamiltonian H_0 (or bare Green function G_0), we can get the self-energy $\Sigma(\omega)$ and also the Green function G in the usual GW calculation. Then we can define new one-body Hamiltonian H'_0 by fixing the energy-dependence of $\Sigma(\omega)$ (we tested some possibilities), so that H'_0 can well reproduce the quasiparticle (QP) part contained in G. Here we require $H_0 = H'_0$, so as to determine H_0. This is a self-consistentcy requirement taken as **"non-interacting Hamiltonian ≈ QP part of G"**. Thus we call our method as QPscGW. This is a kind of self-consistent perturbation thoery.

This H_0 gives "the *best* bare QP picture", which get to be the independent-particle picture for the weakly-correlated systems. Then QPscGW gives directly the QP density of states (QP-DOS) in the sense of independent-particle picture, which can be justified by the Landau's Fermi liquid theory. The QP bands given by H_0 can be used directly within the independent-particle picture to evaluate quantities, e.g. response functions, transport, and so on.

The "bare QP picture" should be also a rigid starting point even when we try to go beyond the independent-particle picture. The method may be viewed as a way construct the most suitable quadratic part of the full Hamiltonian for many-body perturbation theory. As for the spectrum DOS (SP-DOS), the imaginary part of the full Green function G, it can be calculated by a one-shot GW calculation (or GW +extensions) from the QPscGW result.

This situation is in contrast with the full self-consistent GW method (full scGW), which makes SP-DOS self-consistent. Compared the full scGW, QPscGW is advantageous in two ways:
(1) Numerically easier and more stable. We successfully applied it to wide range of materials.
(2)There is self-consistency in both the QP bands and the dynamically screened Coulomb interaction W (they are obtained at the same time). By contrast, the full scGW give problematic W, which results in poor G.

We applied our QPscGW to metals, semiconductors, oxides, magnetic materials, f-electron materials (in progress) and so on. Our results show very systematic improvement over LDA

compared with experiments. We present two key findings:
(1) large improvements are found for materials where one-shot GW fails.
(2) The discrepancies with experiment are very systematic, and can be explained in terms of what GW theory omits from the exact hamiltonian.
As for semiconductors, not only band gaps but many other properties are improved, such as effective mass. For NiO and MnO, *d*-*d* splitting and relative positions of oxygen 2*p* bands move closer to experimental results. Transition metals show a small, systematic *d*-band width narrowing relative to LDA. We also present recent results for MnGaAs and half-metallic compounds.

Finally, we report some progress on attempts to compute the total energy in RPA without the LDA kinds of approximations.

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Posters

Ab-Initio studies of structure and magnetic structure in YCo3H2.

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Abstract

We present an ab-initio density functional study of magnetic phase transitions in the YCo3H2 system. The APW+lo method as employed in the WIEN2K code is used to predict the structure and electronic structure of this compound. Comparison is made with recent X-ray diffraction and magnetization studies. The calculations suggest that the YCo3H2 system is ferrimagnetic in character. Further, fixed spin moment calculations are used to predict and interpret magnetic phase transitions observed in externally applied magnetic fields.

A relativistic optimized potential method (OPM) for magnetic solids

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Abstract

The optimized potential method is based on a formulation of density functional theory that uses implicit functionals of the exchange-correlation energy with respect to the electronic density. For atoms there are already a number of corresponding investigations in the literature that turned out to be very fruitful. For solids on the other hand most work was done so far on insulators or semiconductors. For these systems the exchanged-only (exact exchange) version of the OPM led to band gaps in much better agreement with experiment than corresponding LDA-based calculations. For metallic ferromagnets, on the other hand, it was found by Kotani and Akai that an appropriate treatment of correlations have to be included. This way very satisfying results for magnetic properties could be obtained. In the case of the core hyperfine fields this seems to be caused primarily by the fact that the OPM leads to a self-interaction free exchange-correlation potential. Motivated by this success a relativistic formulation of the OPM has been developed that is formulated in terms of Green's function. The resulting current density OPM should in particular lead to better results for the spin-orbit induced orbital moments. Furthermore the developed formalism allows a very reliable implementation on the basis of the relativistic spin-polarized KKR-method. First results for he corresponding response functions and other related quantities will be presented.

Influence of correlation effects on the spin-resolved VB-XPS

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Abstract

Calculations of valence band photoemission spectra on the basis of the local approximation to density functional theory have been very succesfully in the past for many transition metal systems. However it is well known that correlation effects play for some materials a rather crucial role. Fortunately, it is often well justified to represent these by a local, i.e. site-diagonal self-energy. In this case correlation effects can straightforwardly be incorporated within calculations based on the one-step model of photoemission. This applies in particular for its spin-polarised relativistic version that allows to deal with the Fano-effect and magnetic dichroism.

Corresponding results will be presented for ferromagnetic Ni, for which the pure Fano-effect, that means the spin-polarisation of the photo-current due to spin-orbit coupling has been investigated. Results of investigations on the spontanous spin-polarisation in the ground-state by means of spin-resolved VB-XPS will be presented for the half-metallic ferromagnet NiMnSb. Within these investigations correlation effects are accounted for via the electronic self-energy calculated by recently proposed LDA+DMFT scheme (DMFT: dynamical mean field theory). As it turn out, taking correlation effects into account the agreement between theory and experiment is significantly improved.

Electronic structure and bonding in (Mo,Cr)(Si,Al) alloys investigated by X-ray photoelectron spectroscopy and density-functional theory

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We have investigated the electronic structure of (Mo,Cr)(Si,Al) alloys at a various range of composition using a combination of valence band X-ray photoelectron spectroscopy (VBXPS) and density-functional theory. We find good agreement between the experimental spectra and calculated total density of states. The observed differences between the VBXPS spectra for (Mo,Cr) Si_2, $(\mathrm{Mo,Cr})_5\mathrm{Si}_3$ and $(\mathrm{Mo,Cr})\mathrm{Si}_3$ are explained in term of the various hybridizations, involving Si p and Mo d states, induced by the structural topology. The changes observed in the VBXPS spectra for $(\mathrm{Mo,Cr})(\mathrm{Si}_(1-x)\mathrm{Al}_x)_2$ alloys with increasing Al concentration are explained by a series of structural transformations and a downward shift of the Fermi energy due to the reduced electron concentration. Using rigid band arguments we discuss how this leads to waekening of the covalent (Mo,Cr)-Si bonds and, hence, to increase ductility.

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Ab initio modelling of high-k oxides.

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Abstract

The aggressive scaling of the Complementary Metal Oxide Semiconductor devices (CMOS) is an essential predicament for the success of the semiconductor industry. The key component of this miniaturization is an increase of a capacitance of the gate stack, which is achieved either through a reduction of the physical thickness of the gate dielectric (currently SiO_2) or/and through the use of new gate materials with higher dielectric constant. The latter approach has been a focus of extensive academic and industrial research since the last publication of the *International Technology Roadmap for Semiconductors* around five years ago [1-3].

Remarkably, the problem of high-k dielectrics has opened both a large scope and a serious challenge for the electronic structure theory. On the one hand, density functional calculations stipulated significant progress in understanding complex interrelations between the stability of high-k films, their polymorphism and their dielectric response [3,4]. On the other hand, calculations exposed serious difficulties in predictive modelling of the interface growth, especially reliable values of the valence and conduction band offsets with silicon, properties of shallow intrinsic and extrinsic defects and the charge trapping associated with them.

We address some aspects of density functional modelling of defects in high-k oxides [4-7]. First, we discuss calculations of charged defects in bulk HfO_2 and at the Si/HfO_2 interfaces. Second, we overview the limitations of static calculations and consider how they can be instructively combined with the ab initio molecular dynamics to get new insight on the defect transformations in the material. Based on our extensive modelling, we discuss several pressing issues in high-k based CMOS technology:

1. Degradation of carrier mobility; 2. Fermi-level pinning and the threshold potential instability;
3. Role of controlled and uncontrolled impurities: water, hydrogen and various forms of nitrogen.

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Dynamical properties of poly para-phenyl vinylene

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Abstract

It is well known that the vibrational spectroscopy of polyconjugated polymers is one of the tools for probing the structural and opto-electronic properties of materials in various phases both in pristine and doped states. The understanding of the relevant features requires a detailed knowledge of the phonon modes.

We present an ab initio investigation of the dynamical properties of the conjugated polymer poly para-phenylene vinylene (PPV) on both isolated chain and crystalline states within density functional perturbation theory (DFPT) framework implemented in the CASTEP plane wave code[1]. It is found that for an isolated PPV chain, most of the vibrational frequencies are previously assigned: the higher frequency phonon modes are due to the C-H stretch; the vinyl C-C stretch mode has a higher energy than the phenyl ring C-C stretch frequencies. Most of the out-of-plane modes are softer than those in-plane, since the former mainly involve bond-length and bond-angle alternation. However, there are several unidentified experimental modes, hence, calculations in the crystalline state allow us to assign the unidentified experimental modes. Also the results of the polarisability and permittivity of the material are reasonable when compared with typical axial values of conjugated polymers. Analyses of the first-order densities provide us insight into the behaviour of the electronic polarisabilities. Dynamical Born effective charges are more appropriate to be used for the study of the dynamics of the system. Notable differences are found in IR absorption spectra obtained for the PPV isolated and crystalline states which can be attributed to the differences to the crystalline packing effects which play a key role in the understanding of lattice dynamics of this system.

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Resolving Discrepencies Concerning the Enthalpy of Formation of Gallium Nitride

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Abstract

In recent years the study of gallium nitride and gallium nitride surfaces from first principles has become increasingly popular. The accuarate study of surface reconstructions relies strongly on knowledge of the enthalpy of formation of the materials concerned as this determines the range of chemical potential for which the surface is stable. For example a phase diagram for hydrogen on GaN surfaces has recently been calculated [1] in which a value of 1.2 eV was taken as the enthalpy of formation of GaN. This was calculated from first principles using density functional theory (DFT) under the local density approximation and employing norm-conserving Kleinmann-Bylander pseudopotentials. This value has previously been considered reasonable as it is in agreement with commonly tabulated experimental values [2]. However more recent experimental results [3], as well as all-electron calculations [4], suggest the value may actually be in the region of 1.6 eV. In our own work presented here we employ projector reduced pseudopotentials [5] within in the CASTEP code [6] and arrive at a value in much better agreement with these results. We have employed these pseudopotentials to re-calculate the phase diagram for hydrogen on GaN surfaces, obtaining results very different to the previously published work [1].

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Generalised Kohn-Sham Theory

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Abstract

Generalised Kohn-Sham (GKS) Theory [1,2] provides a variety of possible generalisations of the well-known Kohn-Sham implementation of density functional theory for the calculation of total energies of systems of interacting electrons such as molecules and solids. We present an assessment of various GKS schemes for a one-dimensional model semiconductor. Comparison is made with previous quantum Monte Carlo calculations [3] and with previous GW calculations within many-body perturbation theory for this system. Further GW calculations suggest a new GKS approach based on a GW formulation of the total energy. which will lead to a new version of density functional theory for efficient practical calculations which circumvents the problem of approximating the usual Kohn Sham exchange correlation energy functional.

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Density functional theory study of fullerenes and endohedral fullerenes

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Abstract

The atomic and electronic structures of fullerenes and endohedral fullerenes have been investigated using density functional theory. We have studied C_{60}, C_{70} and C_{82} fullerenes, and with an endohedral atom inside. A nitrogen atom in C_{60} or C_{70} was found to locate at the centre of the fullerene without chemical bonding to the fullerene, while a scandium atom in C_{82} was stable at close to a hexagonal ring of fullerene cage. The relative stability of nine isomers of C_{82} was changed dramatically by the encapsulation of a scandium atom. The applicability of these materials to quantum computing will be discussed.

Linear-scaling DFT calculations from empirical tight-binding to full plane- wave accuracy

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Abstract

Density functional theory (DFT) has become a standard tool for modelling materials. But conventional methods are very inefficient for large complex systems, because the memory requirements scale as the square of the number of atoms, and the cpu requirement as the cube of the number of atoms. We report recent progress in the development of the CONQUEST code [1-6], which performs O(N) (linear scaling) DFT calculations on parallel computers, and has a demonstrated ability to handle systems of many thousands of atoms [3- 5]. The code is based on the strategy of minimizing the total energy with respect to the Kohn-Sham density matrix, and the practical techniques for implementing this strategy will be briefly summarized. The code can be run at different levels of precision, ranging from empirical

tight-binding, through ab initio tight-binding, to full plane-wave precision, and the way in which this is achieved will be outlined. Illustrations will be given of very recent practical CONQUEST calculations on semiconductor surfaces. The ability to run at all levels of precision up to plane-wave precision will be illustrated by results on the reconstructed Si (001) surface, and the ability handle large complex systems will be illustrated by preliminary results on?three-dimensional reconstructions of Ge overlayers on Si (001) requiring DFT calculations on systems of over 3000 atoms.

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Molecular dynamic calculations of GaN thermodynamic properties

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Abstract

The thermal expansion coefficients of (wurtzite) GaN at low and intermediate temperature are known and experimental data are available [1, 2] but at high temperatures it doesn't happened. Also due to experimental difficulties the GaN melting point is not reliably known and only a few theoretical studies have been made [3]. Based on the NPT (isothermal- isobaric) ensemble, we have carried out a molecular dynamic simulation in the DFT framework to obtain the coefficients of thermal expansion for a single solid phase of GaN from 0 K to high temperatures. An estimation of the melting point temperature Tm at normal pressure (1 Atm) has been made.

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Self-interaction correction (SIC) in multiple-scattering theory

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Abstract

We propose a simplified version of self-interaction corrected local spin-density (SIC-LSD) approximation, based on multiple scattering theory, which implements self-interaction correction locally, within the KKR method. The multiple scattering aspect of this new SIC-LSD method allows for the description of crystal potentials which vary from site to site in a random fashion and the calculation of physical quantities averaged over ensembles of such potentials using the coherent potential approximation (CPA). This facilitates applications of the SIC to alloys and pseudoalloys which could describe disordered local moment systems, as well as intermediate valences. As a demonstration of the method, we study the well-known α-γ phase transition in Ce, where we also explain how SIC operates in terms of multiple scattering theory.

Ab Initio Calculation of Structure and Phonon Vibration in Ices

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Abstract

First principles calculations of ice, and orientational defects in ice have been performed within a framework of DFT [1, 2] using both the plane wave pseudopotential method (CASTEP) [3] and the flexible LCAO method (SIESTA)[4].

The structure, electronic structure and phonon frequencies of ice Ih are calculated using both methods are compared with each other and with experiment. Calculations using the less computationally demanding SIESTA and the DZP basis set are shown to be quantative. Within this computational framework the sensitivity to calculated structural properties including zero point vibrations is estimated and shown to be small even though changes in zero point energies account for a significant fraction of the energy of formation [5].

Further, we have performed calculations of L and D orientational defects in ice within a supercell approach. In an orientational defect the ice rules [6] are broken such that in a D - defect two hydrogens lie between nearest neighbour oxygens, and in a L - defect zero hydrogens lie between nearest neighbour hydrogens [7]. The dynamics of these defects forms the basis of transport properties in ice. The structure and electronic structure of these

defects in a supercell containing both defect types is calculated and compared to the idealised geometry.

Acknowledgement

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Electronic and magnetic properties of the surfaces of hole-doped manganites

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Abstract

The electronic structure and magnetic phases of hole-doped manganite surfaces are investigated in a model calculation. The model incorporates the kinetic energy of the e_g electrons, their coupling through Hund's rule to the core-like S=3/2 t_{2g} spin and the superexchange interaction between the latter [1]. The anisotropy of the transfer integrals leads to important physics at the surface/interface. There is only one finite transfer integral between planes connecting the $3z^2 - r^2$ orbitals. The latter is then much more sensitive to the presence of the surface, which is perpendicular to the $z-$axis, than the $x^2 - y^2$ orbital. As a result, at the surface, the projected DOS for the $x^2 - y^2$ orbital is broader than that of $3z^2 - r^2$ orbital. The effect of the broken cubic symmetry at the surface is to favour the occupation of the $x^2 - y^2$ orbital while in the bulk both orbitals are equally occupied. We added a shift Δ [2] to the onsite energy at the surface in order to mimic the effects of the broken symmetry and of the changes in the type, number and distance to neighbouring atoms at surfaces or

interfaces with other materials. We looked at negative values of Δ added to one orbital or both while the bulk levels are taken as the reference for the energies. We found that the most favourable scenario is to add a small shift Δ to the $3z^2 - r^2$ to enhance the stability of the ferromagnetic (FM) coupling between surface and bulk. A larger Δ would deplete the other orbital and thus would disfavour in-plane FM coupling at the surface which would be detrimental to the tunnelling magnetoresistance (TMR) of manganite-based junctions. This could be achieved by growing the manganite film on an insulating oxide with a lattice parameter such that the distance between the interface Mn ion and the oxygen ion in the next layer is slightly larger than the Mn-O bond in the bulk of the manganite.

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Electronic structure of UO_2 and its point defects: an LSDA+U approach

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Abstract

We have investigated the electronic structure of UO2 using the density functional theory (DFT) calculations within the local spin-density approximation (LSDA)+U approach as implemented in the Vienna Ab initio Simulation Package (VASP). For the bulk UO2, the electronic structures from both the LDA and the LSDA+U approaches are compared in order to elucidate the effect of correlation. The calculated cohesive properties of UO2 are compared with available experimented data. For different point defects in UO2, the formation energy and the defect-induced changes in the electronic structure were investigated.

Ab Initio Modelling of Complex Hydrogen-bonded Structures using Density Functional Theory

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Abstract

This project is looking at the feasibility and accuracy of modelling complex hydrogen bonded systems to obtain information on structure and vibrational spectra. The first system looked at was N-Hydroxyphthalimide (NHP) crystallized in its yellow form. This was modelled using the CASTEP [1] code, a Density Functional Theory (DFT) program using plane wave basis sets and pseudopotentials. The first phonon spectra were calculated in the harmonic approximation using both the finite difference approach and linear response theory. The Structure of yellow NHP, calculated using geometry optimisation, will be shown as well as comparisons of the density of phonon states in the crystalline solid obtained using finite difference and linear response methods. Result from linear response analysed by the a-Climax program [2] will be displayed and compared to experimental neutron scattering data.

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GW and SIC implementation in the KKR method

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B. Györffy
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Abstract

The *ab-initio* study of semiconductors and insulators as well as systems with strong localized electrons entails great difficulties involved by the treatment of excitation energies and many-body effects. The most successful first principles method, the density functional theory (DFT) within the local spin density approximation (LSDA), is designed for ground state properties and can not provide proper description of band structure of semiconductors and insulators. If some localized electrons are present in the system, like $3d$-electrons in the transition metal oxides, the local density approximation can be essentially improved by so-called self-interaction correction (SIC). In this approximation the self-iterations of single particle charges, which are present in the LSDA, can be canceled out for the localized electrons. However, the self-interaction correction within the LSDA is still not sufficient for proper description of the excitation energies and band-gaps. It is possible to do accurately from first principles by solving the Hedin's set of equations for the full Green's function. The implementation of this formalism is very difficult, one neglects commonly the vertex correction (the random-phase approximation), and the self-energy is calculated in this case within so-called GW approximation. The non-self-consistent GW approximation was successfully implemented within several first-principle methods, but most of existing implementations are generally designed for systems with delocalized (fast) electrons.

Here we present a general *ab-initio* approach designed for the study of electronic properties of solids, in which on base of the Korringa-Kohn-Rostoker (KKR) method we implemented the self-interaction correction for strong-localized electrons and the non-self-consistent GW approximation for the inclusion of many-body effects. We illustrate our approach on the electronic structure study of some semiconductors and transitions metal.

Self-interaction correction (SIC) in multiple-scattering theory

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Diemo Ködderitzsch[3,1], Wolfram Hergert[3], Balazs L. Györffy[5], Walter Temmerman[1]

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Abstract

We propose a simplified version of self-interaction corrected local spin-density (SIC-LSD) approximation, based on multiple scattering theory, which implements self-interaction correction locally, within the KKR method. The multiple scattering aspect of this new SIC-LSD method allows for the description of crystal potentials which vary from site to site in a random fashion and the calculation of physical quantities averaged over ensembles of such potentials using the coherent potential approximation (CPA). This facilitates applications of the SIC to alloys and pseudoalloys which could describe disordered local moment systems, as well as intermediate valences. As a demonstration of the method, we study the well-known α-γ phase transition in Ce, where we also explain how SIC operates in terms of multiple scattering theory.

Ab-Initio Theory of Resonant X-ray Scattering in Rare Earth Materials

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[1] *School of Chemistry and Physics, Keele University, Staffordshire ST5 5BG, UK*
[2] *Optoelectronics Research Centre, Tampere University of Technology, P.O. Box 692, FIN-33101, Tampere, Finland.*
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[4] *Daresbury Laboratory, Daresbury, Warrington, WA4 4AD, Cheshire, UK*

Abstract

A first-principles theory of resonant magnetic scattering of x rays is presented. The scattering amplitudes are calculated using a standard time-dependent perturbation theory to second order in the electron-photon interaction vertex. In order to calculate the cross section reliably an accurate description of the electronic states in the material under investigation is required and this is provided by the density functional theory (DFT) employing the Local Spin Density Approximation combined with the self-interaction corrections (SIC-LSD). The magnetic x-ray resonant scattering (MXRS) theory has been implemented in the framework of the relativistic spin-polarized LMTO-ASA band structure calculation method. The theory is illustrated with two applications. Firstly we will show a series of calculations for praseodymium that display the sensitivity of MXRS to the symmetry of the occupied f-states. Secondly we will make direct contact with experiment with a calculation for holmium that can be compared with recent assymetry ratio measurements from the XMAS beamline at ESRF.

First-principles calculation of the effects of structural relaxation on the optical absorption spectra of ruby and alexandrite

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Abstract

The d-d transitions of transition-metal (TM) ions in ionic crystals have been utilized as solid state lasers such as ruby (chromium doped alumina) and alexandrite (chromium doped chrysoberyl). The optical spectra of these materials have been generally analyzed based on the semiempirical ligand field theory. In this approach the parameters are determined by fitting the theoretical multiplet energies to the experimental ones under appropriate assignment of the observed peaks. However, additional parameters are required for consideration of covalency and the number of parameters increases for lower-symmetry systems. Therefore, establishment of non- empirical computational approach is quite important for unambiguous analysis of materials with complicated local structure. In order to establish a nonempirical computational approach for the optical spectra for impurity transition-metal ions or also rare-earth ions, we have recently developed a first-principles relativistic configuration-interaction (CI) calculation program, in which many-electron wave functions are obtained as linear combination of relativistic Slater determinants by direct diagonalization of the many-electron Dirac Hamiltonian. The transition probabilities between the eigenstates are calculated directly using the explicit many-electron wave functions. The TM L2,3-edge X-ray absorption near-edge structures (XANES) for some TM compounds have been calculated by this approach and excellent agreement with the experimental spectra was obtained [1]. For the analysis of optical spectra of impurity ions, it is also important to consider the effects of structural relaxation around them. Therefore, in this work, we have investigated the effects of structural relaxation around the chromium ions on the absorption spectra of ruby and alexandrite by combining the structural optimization using CASTEP code and first-

principles CI calculations using model clusters composed of 63 atoms (ruby) or 60 atoms (alexandrite). In the case of ruby, the reproducibility of the characteristic anisotropy of the absorption spectra was improved both qualitatively and quantitatively by consideration of the structural relaxation. However, in the case of alexandrite, the reproducibility became worse even qualitatively by consideration of the structural relaxation, indicating the difficulty in predicting structural relaxation for lower- symmetry systems.

[1] K. Ogasawara et al., Phys. Rev B 64, 115413 (2001).

First Principles Study of the Kondo Effect

Andrew. I. Duff, J. F. Annett
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Abstract

The Kondo effect is a non-perturbative many-body phenomenon arising for a single magnetic impurity atom in a metal. First principles theory based on DFT LDA does not include the quantum dynamics of the impurity spin, and hence the Kondo effect.

Here the Kondo effect is to be studied from 1st principles. The starting point is DFT calculations of an atom embedded in jellium. The self consistent approach used by Manninen et al [1] is used to look for a magnetic solutions of the system in terms of the two model parameters: the charge of the ion and the charge density of the jellium. In particular, the system of an Iron atom in jellium is studied. Magnetic and non-magnetic solutions are found, and the difference in energy between the solutions is calculated as a function of jellium density. The magnetic moment is also calculated for the range of jellium densities at which it occurs.

The Local Density Approximation (LDA) neglects the quantum correlations which lead to the Kondo effect. To go beyond LDA we are using a Quantum Monte Carlo approach

[1] M. Manninen, R. Nieminen, P. Hautojarvi, and J. Arponen, Phys. Rev. B 12, 4012 (1975)

8 General Workshop/Conference Announcements

8.1 4th Workshop 'Hands-on FPLO' and FPLO Users and Developers Meeting

Dresden, March 30 till April 3, 2005

This workshop/meeting is connected with the 6th annual deMon developers meeting. FPLO is an efficient and accurate tool to solve the Kohn-Sham equations for ordered or chemically disordered systems. Details can be found at

http://www.fplo.de/ .

Registration deadline is March 15. Please note that places are restricted and that we will follow a first-come-first-served policy.

Accomodation should be organized by yourself.
(Recommendation: http://www.city-herberge.de/)

Registration form (please send back by email)

Name:
email:
Address:
Arrival:
Departure:
I am interested in the hand's-on sessions: yes/no/details (specify)
I wish to contribute to the users session: poster/discussion (specify)
I will pay the registration fee of 100 EUR: yes

Manuel Richter

8.2 Pu Futures' Meeting

Summer of 2006, California

Dear Colleagues,

This is a "heads up" that the Pu Futures Meeting will be coming to California in the Summer of 2006.

Plutonium Futures, July, 2006
Organized and Sponsored by LLNL and LANL
2006 Chair: Michael Fluss (LLNL)

For info about past Pu Futures Meetings, please see the following.

Pu Futures 2003 WEB PAGE:

http://www.lanl.gov/orgs/nmt/nmtdo/PuConf2003/PuConf2003.html

I hope to see you there!

With best regards,

Jim Tobin

9 General Job Announcements

Chaired Full or Associate Professorship in Computational Materials Science

Departments of Physics and Applied Science of the College of William and Mary, Williamsburg, VA

The Departments of Physics and Applied Science of the College of William and Mary announce a search for a chaired full or associate professorship in computational materials science with a focus on nanoscale or mesoscale materials as part of its new Materials by Design initiative. The successful candidate is expected to establish an internationally recognized research program and to interact with existing research programs (first-principles computations with density-functional and quantum Monte Carlo methods, high-field NMR, photon-based characterization, carbon nanostructures, and magnetic materials). In addition, William and Mary has a strong tradition of excellent teaching at the graduate and undergraduate levels, and the successful candidate will be expected to play an important role in the educational programs of both the Physics and Applied Science departments.

Applicants should send a curriculum vita, statement of professional interests, and the contact information for at least three references to:

Chair, Computational Materials Science Search
Departments of Physics and Applied Science
Small Hall, Campus Drive
College of William and Mary
P.O. Box 8795
Williamsburg, VA 23187-8795

e-mail: cmssearch@wm.edu.

Review will begin on February 1, 2005 and materials will be accepted until the position is filled. Further information on the W&M Physics and Applied Science Departments and this search can be found at http://www.wm.edu/physics and http://www.as.wm.edu/.

W&M is an EEO/AA employer.

Research Associate: Developing Multiscale Techniques to Connect the Quantum to the Mesoscopic Level
Center for Theoretical Chemistry, University of Bochum, Germany

Applications are invited for a research associate position (full BAT IIa salary including all benefits). The position is available immediately for at least three years.

The ideal candiate would have significant experience in electronic structure theory, mixed quantum/classical simulation, and dynamical multiscale simulation. She or he would work primarily on developing and implementing novel techniques to connect a quantum description (Car-Parrinello) via a microscopic level to a coarse-grain treatment. Although the ultimate goal is to predict properties of soft materials under irradiation, the project focuses heavily on code development in close collaboration with an outstanding partner group. In addition, he/she can also get involved in other challenging research projects including both method development and large-scale applications.

Information on the techniques used and developed at CTC are accessible via

http://www.theochem.rub.de/go/cprev.html.

The Center for Theoretical Chemistry 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 to

Professor Dominik Marx
Lehrstuhl fuer Theoretische Chemie
Ruhr-Universitaet Bochum
44780 Bochum, Germany
Email: office@theochem.rub.de
Fax: ++49 234 32 14045
URL: http://www.theochem.rub.de/

Consideration of candidates will begin immediately and continue until the position is filled. The University particularly welcomes applications from women.

PhD Studentship: Materials Science and Nanotechnology Center for Theoretical Chemistry, University of Bochum, Germany

Applications are invited for a PhD position embedded in our international doctorate study program which gives individual support to our foreign graduate students. The preferred starting date would be spring 2005.

You will learn about state–of–the–art electronic structure and ab initio simulation techniques and apply them to challenging problems at the nanoscale in order to understand complex materials and processes. Candiates should have, or be about to receive, an honors degree in Physics or Chemistry with a solid background in theory.

Information on the techniques used and developed at CTC are accessible via

http://www.theochem.rub.de/go/cprev.html.

The Center for Theoretical Chemistry 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 achievements and interests as well as contact information for academic references to

Professor Dominik Marx
Lehrstuhl fuer Theoretische Chemie
Ruhr-Universitaet Bochum
44780 Bochum, Germany
Email: office@theochem.rub.de
Fax: ++49 234 32 14045
URL: http://www.theochem.rub.de/

Consideration of candidates will begin immediately and continue until the position is filled. The University particularly welcomes applications from women.

Postdoctoral Position
RTN on "Ab-initio Computation of Electronic Properties of f-electron Materials"
Paris/Le Mans, France

A post-doctoral position is available within the European Research and Training Network "Ab-initio Computation of Electronic Properties of f-electron Materials". The research focuses on the application of advanced theoretical/computational approaches including dynamical mean field theory to calculate optical properties of materials containing rare earth elements, such as optoelectronic devices and pigments.

The candidate will work in the group of Prof. Antoine George in Paris in close cooperation with Materials Design in Le Mans, France. The candidate is expected to have experience in electronic structure methods, should be younger than 35 years, and should be a national of a Member State of the European Community (other than France) or of an Associated State or residing in the Community for at least five years prior to the present appointment.

Please send your applications by email to

Erich Wimmer
ewimmer@materialsdesign.com

and a copy to

Antoine George
georges@lpt.ens.fr

Ph. D. Studentship in Cambridge, UK
”Computational Modelling of Redox Reactions in Solution”

A candidate is sought for an EPSRC PhD studentship to work in the group of Professor Michiel Sprik. The project involves a computational study of model redox reactions in aprotic solutions using density functional based ab initio molecular dynamics simulation (”Car-Parrinello”). Combining electronic structure calculation and statistical mechanics the project is part of a wider research programme for the development of computational methods for first principle simulation of electrochemical processes. Further information about research in the Sprik group is given at:

http://www-theor.ch.cam.ac.uk/people/sprikgroup/

Candidates should have, or be about to receive, an honours degree (at least II.1 or equivalent) in chemistry, physics, or a related discipline. Experience with computer simulations is helpful, but not required.

The studentship offers full costs (fees plus stipend) for UK citizens, but will cover only the fees of other EU citizens. The studentship is not available to citizens of non-EU countries. Applications should include a CV and the names of two referees, and should be sent to: Professor Michiel Sprik , Department of Chemistry, Lensfield Road, Cambridge CB2 1EW (tel: 01223 336314; email: ms284@cam.ac.uk)

Closing date for applications is February 18th 2005.

Ph.D. Studentship
Institute of Solid State Research, Research Centre Jülich, Germany

The department Theory I at the Institute of Solid State Research now seeks a motivated Ph.D. student to strengthen its research activities in the field of spintronics. The goal of this project is a quantitative description of the Rashba effect in semiconductors, which does not rely on empirical parameters. In crystals without inversion symmetry, this effect causes the spin orientation to rotate, due to spin-orbit coupling, as electrons traverse the material. As the rotation can be controlled by an applied gate voltage, it thus offers the perspective to efficiently manipulate spin-polarised currents and eventually create fast spin transistors. Since the Rashba effect depends on details of the electronic structure, such as the band gap, the spin-orbit splitting or the strain, the project involves accurate electronic-structure calculations using both density-functional theory and the GW approximation for the electronic self-energy, implemented within the full-potential linearised augmented plane-wave (FLAPW) method. A central task is the proper treatment of relativistic corrections and the spin-orbit interaction.

Candidates should have a Master or Diplom degree in physics or a related subject, excellent academic background and good computational skills. There are no nationality or age restrictions. The position, offered in conjunction with the Fritz-Haber-Institut der Max-Planck-Gesellschaft, is funded for a period of three years through the NANOQUANTA Network of Excellence, an international collaboration selected for special support by the European Commission. The appointed Ph.D. student will have the opportunity to spend a period of time at one of the partner institutions. Part of the work also involves support of integration activities within the network.

Applications for this position and further inquiries should be addressed to

Dr. Arno Schindlmayr
Institut für Festkörperforschung
Forschungszentrum Jülich
52425 Jülich, Germany
Email: A.Schindlmayr@fz-juelich.de

Applications may be submitted electronically and should include a curriculum vitae, a statement of relevant academic experience and addresses of potential referees. The position is immediately available and will be advertised until an appointment is made.

Further information about the group can be found at
http://www.fz-juelich.de/iff/e_th1 .

Post-Doctoral Position in Atomic Scale Simulation
EPFL/IRRMA (Lausanne), Switzerland

There is currently a post-doctoral position available for a talented and motivated individual in Atomic-Scale Simulation at EPFL/IRRMA in Lausanne. The position is available immediately but could also start at a later convened date. The position is for one year and could be extended for a second one. The selected individual will join a research project in computational condensed matter physics. The research activity will concern the investigation of disordered materials by first-principles simulation methods. Previous experience with computational techniques based on density functional theory is requested. The EPFL in Lausanne benefits from outstanding computational facilities.

The interested candidates should send (in PDF-format) their (1) curriculum vitae (including nationality, date of birth, civil state, and achieved degrees), (2) publication list, and (3) one or two reprints representative of previous research. The interested candidate should also express his/her motivation in a cover letter, including the prospected date of availability, and arrange confidential letters of recommendation to be sent to the address below. Only complete applications will be processed.

Alfredo Pasquarello
CSEA-ITP-SB-EPFL
Station 13 / PPH340
CH-1015 Lausanne
Switzerland
Tel : +41 21 693 44 16
Fax : +41 21 693 66 55
E-mail : Alfredo.Pasquarello@epfl.ch

For more details refer to the web-page:

http://irrmawww.epfl.ch/G3.html

POSTDOCTORAL POSITION IN THE FIELD OF DYNAMICAL MEAN-FIELD THEORY

AND ELECTRONIC STRUCTURE CALCULATIONS

Ecole Polytechnique, Palaiseau, France

Applications are invited for a postdoctoral position in the field of Electronic Structure Calculations for Strongly Correlated Materials, and in particular the application and development of Dynamical Mean-Field Theory in the context of electronic structure calculations.

The position, to begin as soon as possible, is in the context of the European Research and Training Network (RTN) on "Ab initio Computation of Electronic Properties of f-electron Materials". Candidates must be nationals of a MEMBER STATE of the EU or of an ASSOCIATED STATE, and must NOT be French citizens.

At this stage, funding is available to support a 12 months position, but possible sources of funding for an extension will be explored with the applicants.

The applicants should have a strong background in solid-state theory, and preferably some experience in electronic structure calculations and codes (DFT-LDA or GW) and/or many-body theory, as well as appropriate computer skills.

Applicants should send a letter of motivation, a curriculum vitae including a list of publications and a summary of current and proposed research, and a list of three references with phone numbers and emails, to:

antoine.georges@cpht.polytechnique.fr

and

silke.biermann@cpht.polytechnique.fr

Reviewing of applications will start immediately and will continue until the position is filled.

For information about the group activities and resources, see:

http://www.cpht.polytechnique.fr/cpht/correl/index.html

10 Abstracts

Epitaxial growth and magnetic properties of half-metallic Fe_3O_4 on GaAs(100)

Y. X. Lu, J. S. Claydon, and Y. B. Xu
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G. van der Laan
CCLRC Daresbury Laboratory, Warrington WA4 4AD, United Kingdom

Abstract

The growth and magnetic properties of epitaxial magnetite Fe_3O_4 on GaAs(100) have been studied by reflection high-energy electron diffraction, x-ray photoelectron spectroscopy, magneto-optical Kerr effect, and x-ray magnetic circular dichroism (XMCD). The epitaxial Fe_3O_4 films were synthesized by *in situ* post growth annealing of ultrathin epitaxial Fe films at 500 K in an oxygen partial pressure of 5×10^{-5} mbar. The XMCD measurements show characteristic contributions from different sites of the ferrimagnetic magnetite unit cell, namely, Fe^{3+} T_d, Fe^{2+} O_h, and Fe^{3+} O_h. The epitaxial relationship was found to be $Fe_3O_4(100)\langle 011\rangle$ // GaAs(100) $\langle 010\rangle$ with the unit cell of Fe_3O_4 rotated by 45° to match that of GaAs(100) substrate. The films show a uniaxial magnetic anisotropy in a thickness range of about 2.0-6.0 nm with the easy axes along the $[0\bar{1}1]$ direction of the GaAs(100) substrate.

Accepted for publication in Physical Review B **70**, 233304 (2004)
Manuscript available from g.van_der_laan@dl.ac.uk

Ballistic anisotropic magnetoresistance in nanowires

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Renat Sabirianov
Department of Physics, University of Nebraska - Omaha, Omaha NE 68182

Abstract

We perform an ab-initio study of the ballistic conductance of very thin ferromagnetic nanowires. We show that significant change of resistance can be produced by changing the orientation of the magnetization from pointing along the axis of the wire to perpendicular to it. The effect is similar to the bulk anisotropic magnetoresistance (AMR) but the underlining mechanism is very different because the conductance is ballistic. Ballistic anisotropic magnetoresistance (BAMR) is a change in the number of channels open for conductance due to a change in the electronic structure of the wire caused by the change in magnetization orientation. In general, when magnetization is along the high symmetry axis the symmetry of the wire is higher than when the magnetization is away of the high symmetry axis. The degeneracies caused by the symmetry are split in the former case by the spin-orbit interaction which can cause a change in conductance if the degenerate levels are close to the Fermi energy. We find that BAMR can be either positive or negative. Similar ballistic magnetoresistance effect can be achieved by mechanical deformation caused for example by strain or magnetostriction.

This work is supported by NSF-MRSEC and Nebraska Research Initiative.

(Submitted to Physical Review Letters)
Contact person: jvelev@unlserve.unl.edu
Latex-file available from

http://xxx.lanl.gov/ftp/cond-mat/papers/0412/0412637.pdf

CO adsorption on a Cu(211) surface: First-principle calculation and STM study

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IBM Research, Zurich Research Laboratory,
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Abstract

Chemisorption of CO on the stepped Cu(211) surface is studied within ab-initio density functional theory (DFT) and scanning tunneling microscopy (STM) imaging as well as manipulation experiments. Theoretically we focus on the experimentally observed ordered (2×1) and (3×1) CO-phases at coverages $\Theta = \frac{1}{3}$, $\frac{1}{2}$ and $\frac{2}{3}$ monolayer (ML). Also, obtain also information for isolated CO molecules found randomly distributed at low coverages, we performed calculations for a hypothetical (3×1) phase with $\Theta = \frac{1}{3}$ ML. The adsorption geometry, the stretching frequencies, the work functions and adsorption energies of the CO molecules in the different phases are presented and compared to experimental data. Initially and up to a coverage of $\frac{1}{2}$ ML CO adsorbs upright on the on-top sites at step edge atoms. Determining the most favorable adsorption geometry for the $\frac{2}{3}$ ML ordered phase turned out to be nontrivial, both from the experimental and the theoretical point of view. Experimentally, both top-bridge and top-top configurations were reported, whereby only the top-top arrangement was firmly established. The calculated adsorption energies and the stretching frequencies favor the top-bridge configuration. The possible existence of both configurations at $\frac{2}{3}$ ML is critically discussed on the basis of the presently accessible experimental and theoretical data. In addition, we present observations of STM manipulation experiments and corresponding theoretical results, which show that CO adsorbed on-top of a single Cu-adatom, which is manipulated to a location close to the lower step edge, is more strongly bound than CO on-top of a step edge atom.

(Phys Rev. B**71**, 035402 (2005))
Contact person: marek.gajdos@univie.ac.at

Electron delocalization and dimerization in solid $C_{59}N$ doped C_{60} fullerene

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Abstract

Electron spin resonance and ab initio electronic structure calculations show an intricate

relation between molecular rotation and chemical bonding in the dilute solid solution. The unpaired electron of $C_{59}N$ is delocalized over several C_{60} molecules above 700 K, while at lower temperatures it remains localized within short range. The data suggest that below 350 K rigid $C_{59}N$–C_{60} heterodimers are formed in thermodynamic equilibrium with dissociated rotating molecules. The structural fluctuations between heterodimers and dissociated molecules are accompanied by simultaneous electron spin transfer between C_{60} and $C_{59}N$ molecules. The calculation confirms that in the $C_{59}N$–C_{60} heterodimer the spin density resides mostly on the C_{60} moiety, while it is almost entirely on $C_{59}N$ in the dissociated case.

(Accepted, Phys. Rev. Lett.)
Contact person: Gábor Csányi (gc121@cam.ac.uk)

Ab-initio calculations of the Optical band-gap of TiO_2 thin films

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Rachid Belkada
Nagoya Institute of Technology, Dept. of Environmental Technology,
Showa-ku, 466-8555 Nagoya

Abstract

Titanium dioxide has been extensively studied in recent decades for its important photocatalytic application in environmental purification. The search for a method to narrow the optical band-gap of TiO2 plays a key role for enhancing its photocatalytic application. The optical band gap of epitaxial rutile and anatase TiO2 thin films deposited by helicon magnetron sputtering on sapphire and on SrTiO3 substrates was correlated to the lattice constants estimated from HRTEM images and SAED. The optical band-gap of 3.03 eV for bulk-rutile increased for the thin films to 3.37 on sapphire. The band gap of 3.20 eV for bulk-anatase increases to 3.51 on SrTiO3. In order to interpret the optical band gap expansion for both phases, ab-initio calculations were performed using the Vienna ab-initio software. The calculations for rutile as well anatase show an almost linear increase of the band gap width with decreasing volume or increasing lattice constant a. The calculated band gap fits well with the experimental values. The conclusion from these calculations is, in order to achieve a smaller band-gap for both, rutile or anatase, the lattice constants c has to be compressed, and a has to be expanded.

(International Journal of Nanoscience, **3** [4 & 5] (2004) 439-445.)
Contact person: Wilfried Wunderlich (wi-wunder@rocketmail.com)

Suitable substrates for rutile TiO2 thin films with narrow band-gap predicted by calculations on atomic scale

Wilfried Wunderlich[1], Lei Miao[2], Masaki Tanemura[2], Sakae Tanemura[2]
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JST-CREST, Chikusa-ku, 464-8603 Nagoya, Japan
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Abstract

The decrease of the rutile band-gap is a recent goal of research in order to improve the efficiency of devices for photocatalytic or photovoltaic applications. Previous ab-initio simulations showed an excellent agreement between calculated and experimental values of the optical band-gap. The prediction for the case of epitaxial thin films is that a compressive strain of the unit cell in c-direction and a tensile strain in a-direction will narrow the band gap. Geometrical calculations on atomic scale were performed considering various substrates, like Al_2O_3, MgO, Al_2MgO_4, $SrTiO_3$, ZrO_2, and other crystals with rutile structure. The lattice spacing of the oxygen sublattice is analyzed for each of these crystals in different low-index orientations. The comparison to the rutile crystal and the matching at the interface provides the criteria for the expected stress tensor at the interface. The results show, that indeed some interface are suitable substrates providing photoactive Titania thin films with higher efficiency.

(Proc. Int.Conf. New Frontiers of Process Sci. Eng. Adv. Mat (PSEA 04), Nov 24-26. Kyoto, Japan, ed. M. Naka, T. Yamane, Part 2, published by High Temperature Society of Japan, JWRI Osaka (2004) p. 1-6)

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Theoretical investigation of the ground state properties of DMTTF-CA: a step toward the understanding of charge transfer complexes undergoing the neutral to ionic phase transition

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Abstract

A detailed theoretical study based on first-principles DFT calculations is reported for the charge transfer complex 2,6-dimethyltetrathiafulvalene-p-chloranil (DMTTF-CA). Charge transfer estimates reveal that no periodic ordering of neutral and ionic layers is obtained in the low temperature phase of DMTTF-CA. Similarities and differences with other mixed-stack charge transfer complexes are discussed with the help of a topological analysis of the electron density. Our results show also that the most popular model in this field - which is based on the balance between the cost of ionization and gain in Madelung energy - should be used with great care. These molecules are far from being point charges and molecular deformation and polarisation should not be ignored.

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Geometry optimization of periodic systems using internal coordinates

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Abstract

A new algorithm is proposed for the structural optimization of periodic systems in internal (chemical) coordinates. Internal coordinates may include in addition to the usual bond lengths, bond angles, out-of-plane and dihedral angles, various “lattice internal coordinates” like cell edge lengths, cell angles, cell volume, etc. The coordinate transformations between cartesian (or fractional) and internal coordinates are performed by a generalized Wilson B-matrix, which in contrast to the previous formulation by Kudin et al. [J. Chem. Phys. 114 (2001) 2919] includes the explicit dependence of the lattice parameters on the positions of all unit cell atoms. The performance of the method, including constrained optimizations, is demonstrated on several examples, like layered and microporous materials (gibbsite and chabazite) as well as the urea molecular crystal. The calculations used energies and forces from the ab initio DFT plane wave method in the projector-augmented wave (PAW) formalism as implemented in the Vienna Ab initio Simulation Package (VASP).

(Accepted for publication in J. Chem. Phys.)
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Active sites for the vapor phase Beckmann rearrangement over mordenite: An ab initio study

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Abstract

The reaction mechanisms of the Beckmann rearrangement (BR) of cyclohexanone oxime to ϵ-caprolactam in the gas phase and catalyzed by mordenite are investigated. For the gas phase reaction, starting with the protonated oxime, the rate-controlling step is the transformation of the N-protonated to an O-protonated species (1,2-H-shift) with an activation energy of 178 kJ/mol. The barriers for the subsequent reaction steps of the transformation to N-protonated ϵ-caprolactam are significantly lower, 10 kJ/mol and 54 kJ/mol N-insertion and hydrolysis of the carbiminium ion. As possible active sites in the zeolite, Brønsted acid (BA) sites, silanol nests, and surface silanol groups are considered. The most favorable reaction path comprising three reaction barriers of 88 kJ/mol, 64 kJ/mol and 40 kJ/mol for the 1,2-H transfer, the N-insertion and the hydrolysis of the carbiminium ion has been found for a BA site. H-bonding is found to play a key role in the reaction catalyzed by weak acid sites. The activation energies for the rate-controlling step of the Beckmann rearrangement increases in order BA site (142 kJ/mol - 1,2-H-shift+N-insertion) $<$ silanol nest (184 kJ/mol - 1,2-H-shift+N-insertion) $<$ H-bonded terminal silanol groups (223 kJ/mol - N-insertion) $<$ isolated silanol group (266 kJ/mol - N-insertion). We have also used harmonic transition state theory to calculate the reaction rates for catalysis by BA sites and silanol nest. Due to the large difference in the activation energies of the individual steps, the BR catalyzed by BA sites or silanol nests behave like simple first-order reactions with effective reaction barriers of 142 kJ/mol and 184 kJ/mol, respectively. The reaction at BA sites is about five orders of magnitude faster than that at a silanol nest. However, the actual turn-over of a reaction catalyzed by BA sites might by slowed down by the relatively high desorption energy of the product, and frequent readsorption and desorption at an increased concentration of BA sites.

(J.Phys. Chem. A, 2004; 108(51); 11388-11397.)

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Strain Induced Deep Electronic States around Threading Dislocations in GaN

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Abstract

Combining through-focus high-resolution transmission electron microscopy and hierarchical multiscale simulations consisting of density-functional theory, analytical empirical potentials, and continuum elastic theory we demonstrate the existence of a new dislocation type in GaN. In contrast with all previously identified or suggested dislocation structures in GaN, all core atoms are fully coordinated; i.e., no broken bonds occur, implying that the dislocation should be electrically inactive. However, as we show, the giant local strain-field around the dislocation core, in combination with the small lattice constant of GaN, causes deep defect states and thus electrically active edge dislocations independent on the specific core structure.

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Chemically ordered $Al_xGa_{1-x}N$ alloys: Spontaneous formation of natural quantum wells

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Abstract

We combine transmission electron microscopy, high-resolution x-ray diffraction, cathodoluminescence, and photoluminescence experiments with first-principles calculations to study the formation, thermodynamic stability, structural, and optical properties of chemically ordered $Al_xGa_{1-x}N$ alloys $0 < x < 1$. Our results reveal that group-III-nitride surfaces exhibit chemically highly sensitive adsorption sites at step edges and that these sites can be used to kinetically engineer chemically ordered $Al_xGa_{1-x}N$ alloys. The ordered alloys have unique properties: (i) the band gap is redshifted up to 110 meV with respect to the disordered alloy of the same composition and (ii) the band gap reduction is caused by localization of the band edge wave functions in the GaN layer. Ordered $Al_xGa_{1-x}N$ thus can be seen as a natural quantum well structure where electrons and holes are localized and confined in monolayer GaN quantum wells.

(submitted to: Phys. Rev. B)

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Density-functional theory study of the initial oxygen incorporation in Pd(111)

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Abstract

Pd(111) has recently been shown to exhibit a propensity to form a sub-nanometer thin surface oxide film already well before a full monolayer coverage of adsorbed O atoms is reached on the surface. Aiming at an atomic-scale understanding of this finding, we study the initial oxygen incorporation into the Pd(111) surface using density-functional theory. We find that oxygen incorporation into the sub-surface region starts at essentially the same coverage as formation of the surface oxide. This implies that the role of sub-surface oxygen should be considered as that of a metastable precursor in the oxidation process of the surface. The mechanisms found to play a role towards the ensuing stabilization of an ordered oxidic structure with a mixed on-surface/sub-surface site occupation follow a clear trend over the late $4d$ transition metal series, as seen by comparing our data to previously published studies concerned with oxide formation at the basal surface of Ru, Rh and Ag. The formation of a linearly aligned O-TM-O trilayered structure (TM = Ru, Rh, Pd, Ag), together with an efficient coupling to the underlying substrate seem to be key ingredients in this respect.

(submitted to: Phys. Rev. B)
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Role of strain relaxation during different stages of InAs quantum dot growth

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Abstract

Recent experiments suggest that InAs quantum dots grown on GaAs (001) undergo a shape transition during growth from 'hut' to 'dome'-like shapes, similar to Ge quantum dots on Si. ¿From a thermodynamic point of view, quantum dot formation is governed by the energetic balance between the energy gain due to strain relief and the energy cost due to formation of quantum dot side facets and edges. In order to account for both contributions, we have developed a carefully parametrized bond-order potential. Its analytical form follows the previous suggestions by Abell and Tersoff, but the newly determined parameters have been fitted to reproduce the elastic constants as well as properties of both GaAs and InAs low-index surface reconstructions obtained from density-functional theory calculations. The potential describes the elastic constants with less than 10 % deviation and the considered surface energies within 10 meV/Å^2. The results of our calculations are helpful in analysing the energetics of different experimentally observed shapes, and of incomplete layer growth on the facets.

(to appear in: Proc. 27th Int. Conf. on the Physics of Semiconductors (ICPS), 2004)

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Structure Determination of Small Vanadium Clusters by Density-Functional Theory in Comparison with Experimental Far-Infrared Spectra

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Abstract

The far-infrared vibrational spectra for charged vanadium clusters with sizes 3 to 15 atoms have been measured using infrared multiple photon dissociation of $V_n^+Ar \longrightarrow V_n^+ + Ar$. Using density-functional theory (DFT) calculations, we calculated the ground state energy and vibrational spectra for a large number of stable and metastable geometries of such clusters. Comparison of the calculated vibrational spectra with those obtained in the experiment allows us to deduce the cluster size specific atomic structures. In several cases, a unique atomic structure can be identified, while in other cases our calculations suggest the presence of multiple isomers.

(submitted to: Journal of Chemical Physics)

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Combining GW calculations with exact-exchange density-functional theory: An analysis of valence-band photoemission for compound semiconductors

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Abstract

We report quasiparticle-energy calculations of the electronic bandstructure as measured by valence-band photoemission for selected II-VI compounds and group-III-nitrides. By applying GW as perturbation to the groundstate of the fictious, non-interacting Kohn-Sham electrons of density-functional theory (DFT) we systematically study the electronic structure of zinc-blende GaN, ZnO, ZnS and CdS. Special emphasis is put on analysing the role played by the cation semicore d-electrons that are explicitly included as valence electrons in our pseudopotential approach. Unlike in the majority of previous GW studies, which are almost exlusively based on groundstate calculations in the local-density approximation (LDA), we combine GW with exact-exchange DFT calculations in the optimised-effective potential approach (OEPx). This is a much more elaborate and computationally expensive approach. However, we show that applying the OEPx approach leads to an improved description of the d-electron hybridisation compared to the LDA. Moreover we find that it is essential to use OEPx pseudopotentials in order to treat core-valence exchange consistently. Our OEPx based quasiparticle valence bandstructures are in good agreement with available photoemission data in contrast to the ones based on the LDA. We therefore conclude that for these materials OEPx constitutes the better starting point for subsequent GW calculations.

(submitted to: New Journal of Physics)
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Aspects of spin-polarized scanning tunneling microscopy at the atomic scale: experiment, theory, and simulation

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Abstract

The principle and method of atomic-scale spin-polarized scanning tunneling microscopy is discussed, and its application to the case of the (0 1 0) surface of η-phase Mn_3N_2 is presented. For this surface, new proofs of the spin-polarized effect are presented, and it is also shown that the spin-polarized effect can turn on and off with small changes to the tip apex which can occur during scanning; this indicates that the tip magnetic density of states can and does change at certain points during the experiment. It is also shown how to model height profle data using spin-polarized local density of states of the sample. As well, it is shown how to relate the equation for the total spin-polarized height profile to those of the separated magnetic and non-magnetic height profiles. Comparison of the experimental height profiles to the simulated height profiles based on spin-polarized local densities of states calculated from first-principles density functional theory is shown. In particular, a comparison is made between the results of using the atom-super-position method vs. a full Tersoff-Hamman simulation method. For the case of the transition metal nitride system here, it is shown that the latter method is crucial for a full understanding due to the directionality of the atomic orbital lobes.

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Dynamical singlets and correlation-assisted Peierls transition in VO_2

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Abstract

A theory of the metal-insulator transition in vanadium dioxide from the high- temperature rutile to the low- temperature monoclinic phase is proposed on the basis of cluster dynamical mean field theory, in conjunction with the density functional scheme. The interplay of strong electronic Coulomb interactions and structural distortions, in particular the dimerization of vanadium atoms in the low temperature phase, plays a crucial role. We find that VO_2 is *not* a conventional Mott insulator, but that the formation of dynamical V-V singlet pairs due to strong Coulomb correlations is necessary to trigger the opening of a Peierls gap.

(Phys. Rev. Lett. 94 026404 (2005))

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11 Presenting Other Programmes/Initiatives

11.1 The FRAMES Software Framework Project

We would be pleased to know your opinion regarding the project described below and if you would be interested in joining the "Groupement De Recherche" (GDR), we are planning to ask the CNRS to support this spring.

This last year, we (a few French Quantum Chemists) decided to build a "quality" Object-Oriented Software Framework, able to satisfy the needs of both the users and programmers, covering various domains of molecular modelling, from electronic structure calculations to molecular mechanics.

By "quality" we precisely mean the six criteria defined by the ISO9126 Norm for software quality, that is : Functionality, Reliability, Usability, Efficiency, Maintainability, Portability.

You can find a more detailed presentation of the project on the following web page:

`http://galileo.lct.jussieu.fr/~PROJETOOQCB/WIKI/mediawiki/index.php/Project_Presentation`

During the four years of the GDR, two different interdependent kinds of tasks will be done simultaneously. On the one hand, there are the designs of the architecture and the object management -not object design- which needs some expertise and are on the way (see:

`http://galileo.lct.jussieu.fr/~PROJETOOQCB/WIKI/mediawiki/index.php/Project_Presentation#Project_Progress`

You are welcome to collaborate to it.

On the other hand, there is the Object Design which has to be undertaken by scientists and with which you may be more concerned. There is no need to have any experience in software development to collaborate to it. It is a task of thinking about what we want to model. We will strive at expressing the "Objects" of our domains in the most precise and rigorous way, using only English words, no programming language (by "Object" we mean any entity entering the models of these domains).We shall describe (i) what kind of operation they can provide to other Objects, (ii) what conditions are required for these operations to work properly, (iii) what logical properties will guarantee that the results will conform to what is expected, (iv) no implementation of any kind will be undertaken.

We shall start from a coarse description of each entity to be modelled. Then, proceeding step by step and iteratively we will "refine" their specifications, until we get codable "Objects". This should take two or three years, to cover a large enough domain.

At the end of this abstract work we shall possess -a unified, precise and unambiguous Glossary covering all the scientific domains for which we could have obtained collaborations -and the Design of all Object Classes necessary to implement, in whatever programming language, the entities of this Glossary. This work is already started. You may have a look at the first sketches at :

`http://galileo.lct.jussieu.fr/~PROJETOOQCB/WIKI/mediawiki/index.php/Glossary.`

In the last year, we shall apply the Management Tools developped in parallel to this Object Design and build a limited Quantum Chemistry software able to produce at least "multi-reference-DFT" properties.

This Objects Design, which is the key for building any reusable software, will be published and, we hope, will be helpful to anyone willing to develop new code. As you can understand, the quality of the Objects Design depends strongly upon the variety of scientific domains represented by our collaborators.

If, as a theoretician or an experimentalist, you are using some modelization software for your everyday work, your contribution would be very helpful with regards to this second aspect of the project.

If you are not directly interested, you can perhaps forward this e-mail to some of your colleagues that may be interested in a collaboration with us.

If you have any questions, please send a message to our mailing list

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For the FRAMES Team

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12 SCIENTIFIC HIGHLIGHT OF THE MONTH

FOREWORD

The following paper from about 1994 is being published in Psi-k Newsletter because Physical Review has twice refused to do so, for reasons that are frankly unacceptable, in spite of meeting all the objections of the first round of refereeing.

Anyway it is not unsuitable for Psi-k Newsletter because some people still use norm-conserving pseudopotentials for a wide range of applications, and anyway the idea of the Q_c tuning is now also being used elsewhere. Also these pseudopotentials are very good, the extra 'tuning' degree of freedom allowing one to match the logarithmic derivative as closely as possible, and to soften the energy cut-off for the plane waves, or to fit to some other empirical quantity such as a lattice constant. They are considerably softer than some pseudopotentials that are widely used, without loss of accuracy.

The paper is also being put on the e-Print archive server (http://arxiv.org/), and the code is freely available (see website http://boson4.phys.tku.edu.tw/qc/).

Kinetic energy tuning for optimising pseudopotentials and projector reduction

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Abstract

We have developed an improved scheme for generating optimised norm-conserving pseudopotentials which is more systematic and more flexible, with a better insight. The control parameter Q_c connected with the kinetic energy of the pseudo wavefunction $\Psi_l(r)$ is used in a new way to tune the pseudopotential. The scheme uses only three constraints and three spherical Bessel functions in the expansion of $\Psi_l(r)$ inside the pseudising radius r_c, compared with four commonly used, which tends to give a somewhat softer pseudopotentials. The fidelity of the pseudopotential as seen in the logarithmic derivative can be improved in a simple and systematic way by tuning Q_c while minimising the energy cutoff $E_{\rm cut}$ necessary in solid state application. The scheme opens the way to tailor-making pseudopotentials for specific requirements useful for large scale *ab initio* calculations, including reducing the number of non-local projectors for speeding up the calculations.

1 Introduction

The present paper concerns a further improvement of earlier schemes for generating norm-conserving pseudopotentials [1, 2, 3]. Soft and accurate pseudopotentials are essential for state-of-the-art large scale *ab initio* simulations for solids using plane-wave basis sets. This is in the context of periodic superlattice calculations based on Density Functional Theory with Local Density Approximation (LDA) for exchange and correlation with possibly a Generalised Gradient Approximation (GGA). Here, a "soft" pseudopotential means that a low energy cut-off, $E_{\rm cut}$, can be used in the planewave expansion of the wavefunction, and the "accuracy" of a pseudopotential can be measured by the agreement between the logarithmic derivatives of pseudo and true wavefunctions in a certain energy range, which is an equivalent characterisation of the scattering property of a pseudopotential in terms of the phase shifts of different incoming waves. We are here concerned with norm-conserving pseudopotentials, as distinct from the super-soft pseudopotentials of Vanderbilt [4] which are not norm-conserving. Although the latter are widely used, we believe there is still a role for norm-conserving pseudopotentials because of certain computational efficiences, e.g. optical properties and stress are easier to implement. In any case it appears that the idea of Q_c tuning can also be applied with advantage to the super-soft pseudopotential [5]. Even with the accuracy and efficiency achieved by a Car-Parrinello type of algorithm [6, 7], the computational cost still requires as soft a pseudopotential as possible to make the largest calculations affordable.

While the advantage of the softness in a pseudopotential can not be over-emphasised, what is equally important is to have a flexible scheme to generate quickly and systematically a new pseudopotential appropriate to a new physical situation, such as short inter-atomic distances in some compounds or at ultra high pressures. Another example would be some structural energy difference where errors cancel, so that one can compromise on convergence properties. A further situation might be one where the energy range over which the logarithmic derivative of the pseudo wavefunction has to be accurate is unusually narrow or wide. Whereas one standard transferable pseudopotential for a given chemical element may be satisfactory for many purposes, this will not be so for some calculations. On the contrary, the flexibility of balancing the accuracy (logarithmic derivative) and the efficiency ($E_{\rm cut}$) of a pseudopotential in its construction will be useful, because then computing effort will not be wasted in achieving unnecessary precision. This utility can not be replaced by simply using an insufficient $E_{\rm cut}$ in exchange for a less accurate result because the quality of computed physical quantities falls very rapidly when decreasing $E_{\rm cut}$ below some point which is essentially determined by the way the pseudopotential is generated. A flexible scheme is therefore to be welcomed if it allows one to regulate the degree of approximation in different parts of a pseudopotential, such as the logarithmic derivative, E_{cut} and a large pseudising radius ("cut-off" radius) r_c to maximise the pseudopotential performance in a given problem without compromising the science. A great computational efficiency has been achieved in a few cases (eg. reference [8]) by what we call 'projector reduction'. A normal pseudopotential consist of a local potential operating on all angular momentum (l, m) components of the pseudo wavefunction, plus a few non-local potentials operating on specific l components only. For a non-transition element such as carbon, the latter would normally be for $l = 0$ and 1, requiring $1 + 3 = 4$ specific projectors in the computations to pick out these components from the total pseudo wavefunction. However using the flexibility of Q_c tuning, we have been able to generate pseudopotentials for some elements where the $l = 1$ component is sufficiently nearly the same as that for $l = 2$ so that it can be taken as the local potential part, thus requiring only one projector for $l = 0$. This is particularly advantagous with the real-space implementation of Kleinman-Bylander form [9] for the non-local part of the pseudopotential [10]. The large dynamic simulation of methanol dissociation in a zeolite [8] could not have been carried out at that time without such projector reduction for carbon and oxygen. In the case of Cu and transition elements, we can achieve a pseudopotential with projectors for $l = 2$ only.

In order to generate a new pseudopotential efficiently, it is a great help to understand how changes in the input parameters affect the pseudopotential that results. Such understanding also helps one to avoid an unrealistic choice of parameters. We present in this chapter a robust way of constructing norm-conserving pseudopotentials which addresses those essential points mentioned above, namely acceptable accuracy, softness, flexibility and understanding, through further improvements to the well established "Optimised Pseudopotentials" approach. [1, 2, 3]. We regard our method as an alternative to the very popular schemes proposed by Troullier and Martins [11], by Vanderbilt [4], and by Blöchl [12]. These schemes all aim to improve the softness and/or the accuracy of pseudopotentials.

Before we describe the technical details of our current scheme, it is necessary to outline previous optimisation methods. The "Optimised Pseudopotentials" proposed by Rappe, Rabe, Kaxiras and Joannopoulos (RRKJ) [1, 2] are recognised as very soft norm-conserving pseudopotentials. Their scheme is very suitable for transition metals and first-row elements which we are interested in and which usually need higher E_{cut} than other elements due to their very localised $3d$ (or $4d$) or $2p$ valence electrons. Based on the RRKJ idea, a modified strategy of generating optimised pseudopotentials was suggested by Lin, Qteish, Payne and Heine (LQPH) [3] in order to simplify the numerical procedure. Although using different options and procedures, the basic formulations in LQPH and the current work are the same as those in the original RRKJ. In all these schemes the pseudo wavefunction $\Psi_l(r)$ of angular momentum l is generated first, and then the pseudopotential $V_l(r)$ is derived from it by inverting the Schrödinger equation [13]. The $\Psi_l(r)$ is expressed in terms of some specially chosen spherical Bessel functions as follows :

$$\Psi_l(r) = \sum_{i=1}^{n} \alpha_i \; j_l(q_i r) \quad \text{for} \quad 0 < \mathrm{r} < \mathrm{r_c}, \quad \text{with} \quad \frac{\mathrm{j_l}'(\mathrm{q_i r_c})}{\mathrm{j_l}(\mathrm{q_i r_c})} = \frac{\phi_{\mathrm{l}}'(\mathrm{r_c})}{\phi_{\mathrm{l}}(\mathrm{r_c})}$$

$$\Psi_l(r) = \phi_l(r) \quad \mathrm{for r} \geq \mathrm{r_c} \tag{1.1}$$

in which the $j_l(q_i r)$ are spherical Bessel functions with $(i-1)$ zeros for $r < r_c$, and $j_l'(q_i r)$ their first derivative with respect to r. The $\phi_l(r)$ is the proper all-electron atomic wavefunction and $\phi_l'(r)$ its first derivative. Since we start with $\phi_l(r_c)$ when generating a new pseudopotential, all the q_i are fixed once the r_c is chosen. The portion of the kinetic energy of the pseudo wavefunction due to the $q > Q_c$ part of its Fourier components is denoted by ΔE_k (in atomic-Rydberg unit) :

$$\Delta E_k(\alpha_1, \alpha_2, ..., \alpha_n, Q_c) \ = \int_{Q_c}^{\infty} d^3q \ q^2 |\Psi_l(q)|^2 \tag{1.2a}$$

$$= \ -\int_0^{\infty} d^3r \ \Psi_l^*(r) \ \nabla^2 \Psi_l(r) \ - \ \int_0^{Q_c} d^3q \ q^2 |\Psi_l(q)|^2 \tag{1.2b}$$

in which the $\Psi_l(q)$ is the Fourier transform of the $\Psi_l(r)$. The central idea for optimising a pseudopotential was that for a given Q_c, the coefficients α_i of $\Psi_l(r)$ in (1.1) can be obtained by minimising ΔE_k in (1.2) with Lagrange multipliers constraining the normalisation and the continuity of the first and second derivatives of the pseudo wavefunction at r_c. Thus a smooth and norm-conserving pseudo wavefunction $\Psi_l(r)$ could be determined. Incidentally, the continuity of the pseudo wavefunction $\Psi_l(r)$ at r_c is not imposed explicitly because the optimisation procedure results in this condition being fulfilled automatically. This can be understood from the definition of the $j_l(q_i r)$ in (1.1). We know that when the constrained minimisation is successful, one has $\Psi_l'(r_c) = \phi_l'(r_c)$: therefore

$$\Psi_l(r_c) = \sum_{i=1}^{n} \alpha_i \ j_l(q_i r_c) = \sum_{i=1}^{n} \alpha_i \cdot \frac{\phi_l(r_c)}{\phi_l'(r_c)} \cdot \ j_l'(q_i r) = \Psi_l'(r_c) \cdot \frac{\phi_l(r_c)}{\phi_l'(r_c)} = \phi_l(r_c) \tag{1.3}$$

which gives the required continuity of $\Psi_l(r)$ from the continuity of $\Psi_l'(r_c)$ due to the special choice of expansion functions in (1.1). Although the mathematical scheme is essentially the same, there are some differences in the way the procedure is used by the previous authors and in the present work. In the RRKJ method, typically 10 or more spherical Bessel function terms in (1.1) were used, with Q_c being varied iteratively such that the ΔE_k is minimised to a pre-chosen tolerance, say 1 mRyd. It appears that using Q_c in that way has the advantage of controlling the quality of the total energy convergence with respect to the energy cut-off used in the calculations. In the LQPH method, the number of spherical Bessel function terms was fixed to be four so that there are four α_i coefficients for the $\Psi_l(r)$ to be determined, making the number of free parameters equal to the number of constraints, namely norm-conservation, continuity of the first and second derivatives of $\Psi_l(r)$ at r_c, and minimisation of ΔE_k. Efficient numerical routines exist for such a problem, and the reasonably small number (four) of terms in $\Psi_l(r)$ helps to stabilise the numerical procedure. In addition to using just four spherical Bessel function terms in $\Psi_l(r)$, the LQPH method always sets Q_c equal to the largest q_n , i.e. q_4 , which avoided the variation of Q_c and therefore made the numerical procedure significantly simpler than that of RRKJ.

We recognise the success of the above mentioned schemes, but the consequences of some of their detailed assumptions, such as the value of Q_c, the number of terms and the choice of constraints, were not fully clear to us. In particular, the role of Q_c in optimising pseudopotentials attracted our attention. From the definition in (1.2), Q_c can be regarded as a kinetic energy filter controlling the constrained minimisation of the kinetic energy of Ψ_l in the range $q > Q_c$. If the minimisation is effective, the resulting k-space pseudo wavefunction $\Psi_l(q)$ will be restricted as far as possible to the range $0 < q < Q_c$, which will subsequently determine the analogous behaviour of the pseudopotential $V_l^{ps}(q)$ in k-space in solid state applications. A unique correspondence is therefore likely to exist between Q_c and the pseudopotential in k-space $V_l^{ps}(q, Q_c)$, which of course also applies to Q_c and $V_l^{ps}(r, Q_c)$ in r-space due to the duality of r and k spaces. Most importantly, the scattering property of such a pseudopotential should also depend on Q_c in some simple manner because it is all in the characteristics of $V_l^{ps}(q, Q_c)$. In the current scheme we therefore vary Q_c to control the phase shift, i.e. logarithmic derivative, as will be demonstrated in Section 2. We shall call this "Q_c tuning" and it will be the crux of the present work. Additionally, from the argument above we expect the Q_c to correspond roughly to E_{cut}. The Q_c therefore controls both the scattering property and the energy convergence of the pseudopotential in our new optimisation scheme.

On investigating the choice of constraints, we realised that it is not necessary to impose strictly the continuity of $\Psi_l''(r)$ at r_c because minimisation of ΔE_k already more or less constrains the higher derivatives of $\Psi_l(r)$ by reducing its high q amplitude. Moreover, dropping unnecessary constraints means that a less restricted and more efficient minimisation can be performed. Thus not only can a softer pseudopotential be obtained but also the resulting pseudopotential will be more sensitive to the choice of Q_c, which enhances the controllability of the pseudopotential by Q_c. We have, in fact, tried applying the Q_c tuning within the four-term/four-constraint framework, and found that both logarithmic derivative and the shape of the pseudopotential do not vary systematically with respect to Q_c, which is presumably due to the extra (unnecessary) constraint which somehow restricts the effect of Q_c tuning.

However with the use of three terms and three constraints, we found that the logarithmic derivative and pseudopotential varied smoothly with Q_c so that one can use Q_c tuning efficiently. This is the main reason for preferring the three-term/three-constraint framework. Incidentally, keeping the number of terms and unknown coefficients in (1.1) equal to the number of constraints is very helpful in maintaining a stable numerical procedure, as found by LQPH. We can also see why the pseudopotential becomes somewhat softer. To a first approximation, $E_{\text{cut}} = Q_c^2$ Ryd. if Q_c is in atomic units as will be assumed hereafter, and Q_c is approximately the maximum q_i. Thus omitting the term $j_l(q_4 r)$ reduces E_{cut}, because $j_l(q_4 r)$ has the maximum number of nodes and hence the highest Fourier components of the $j_l(q_i r)$.

Incidentally, the small discontinuity in $V^{ps}(r)$ at r_c, corresponding to the discontinuity in the second derivative of the pseudo wave-function, does not destroy the energy convergence. At the q relevant to E_{cut}, the $V^{ps}(q)$ is determined by the general shape of $V^{ps}(r)$, by the discontinuity in $V^{ps}(r)$ at r_c given by the discontinuity in second derivative of the pseudo wave-function, and by the wiggles in $V^{ps}(r)$ at r just less than r_c which are seen clearly in Fig. 1 (c) for example. For a good E_{cut}, these need not individually be zero but it is sufficient that they more or less cancel giving a small total $V^{ps}(q)$ over a range of q. In addition the discontinuity may give some very small Fourier components extending to very high q, which can affect the absolute energy convergence of a calculation but which cancel in the calculation of any physical quantity.

To summarise: using a three-term expansion in (1.1) and three constraints gives a stable nu-

Fig.1.(a)

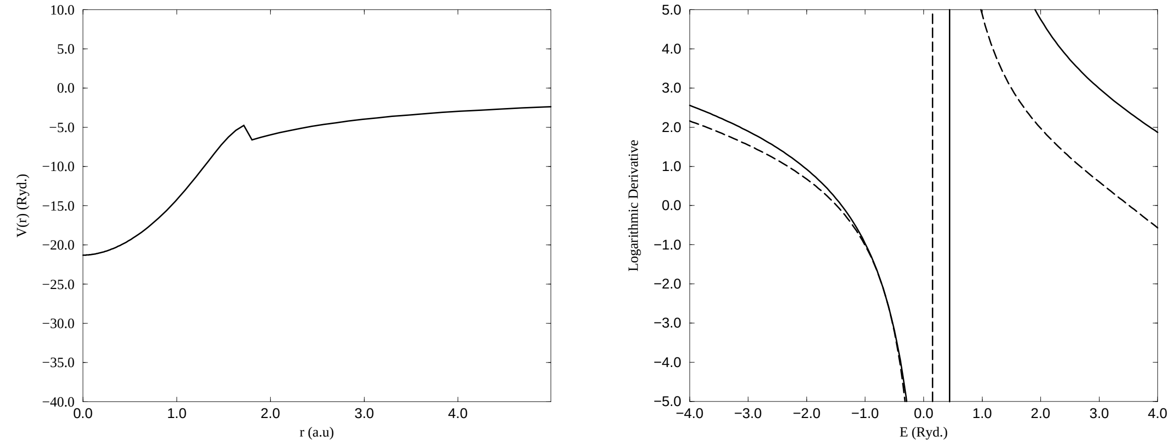

Fig.1.(b)

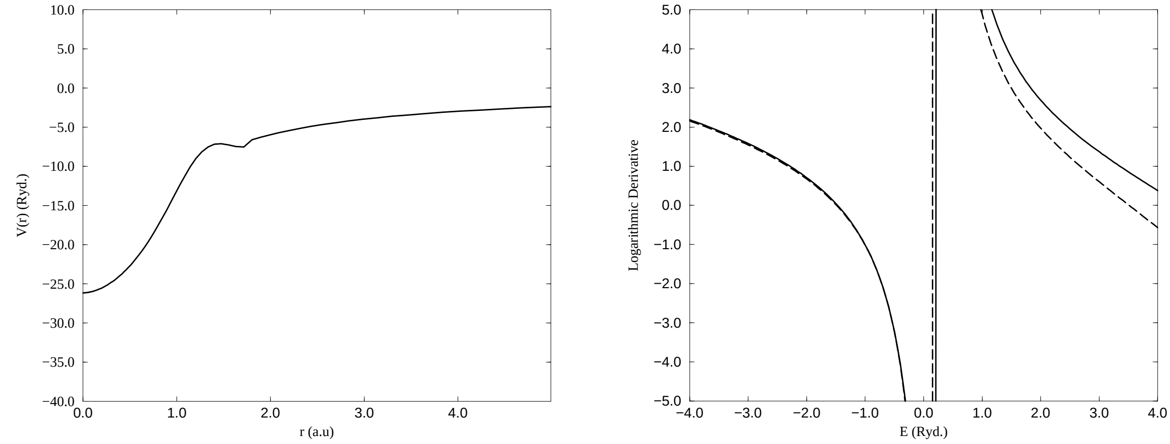

Fig.1.(c)

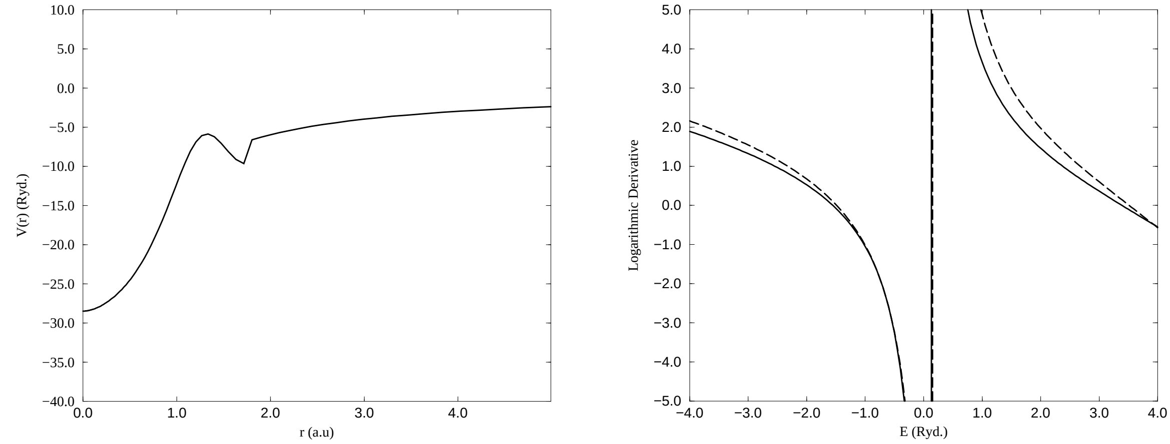

Figure 1: Oxygen $2p$ pseudopotential with r_c =1.8 a.u. showing its variation with Q_c . Left-hand-side panels, $V_{l=1}(r)$: right-hand-side panels, logarithmic derivatives of the true potential (dashed line) and pseudopotential (solid line). (a) $Q_c/q_3 = 0.98$ (b) $Q_c/q_3 = 1.15$ (c) $Q_c/q_3 = 1.20$.

merical procedure allowing a good flexibility in the pseudo wavefunction. It combines well with tuning Q_c to optimise the accuracy of the pseudopotential, which is the main purpose of the present work. The flexcibility can also be used to control the shape of the pseudopotential for different l and hence to reduce the number of projectors required in solid state applications. The limitation to three terms in (1.1) automatically gives a somewhat softer pseudopotential than previously. The effect of Q_c tuning and relevant technical points are discussed in Section 2. In Section 3 some solid state tests of the pseudopotentials will be presented, which is followed by a discussion and conclusion as Section 4.

2 The Q_c Tuning Method

To generate a pseudopotential in the current scheme, as in all *ab initio* pseudopotential generating procedures, an all-electron LDA or GGA atomic calculation is first performed to obtain all the atomic orbitals of a selected configuration : in the present work we just use the LDA. The procedure described in Section 1 is then implemented with three terms in (1.1) and the three constraints already discussed, while Q_c remains as an adjustable input parameter. In Fig. 1 we demonstrate the effect of varying Q_c in the current scheme on the oxygen $2p$ pseudopotential. Three different Q_c were used to generate the corresponding pseudopotentials, and the logarithmic derivative was tested on these pseudopotentials. We can see that for a given atomic configuration and pseudising radius, there is a certain value of Q_c which yields the best agreement with the logarithmic derivative, in this case that shown in Fig. 1(b). We note that the logarithmic derivative curve of the pseudo wavefunction for a larger and a smaller Q_c deviate from the curve with the best possible Q_c in opposite directions, as shown in Fig. 1(a) and Fig. 1(c). In Fig. 1 we also see that the shape of the pseudopotential changes with Q_c, which can be regarded as the reason why the scattering properties of the resulting pseudopotentials are different. The monotonic correspondence between the variation of (a) the Q_c, (b) the shape of the pseudopotential and (c) the logarithmic derivative of the pseudopotential is the most important feature in the current scheme. This feature enables us to establish a systematic procedure for updating Q_c towards the best results judged by the following criterion. As mentioned in Section 1, Q_c controls the softness of a pseudopotential as well as its accuracy because it affects both the E_{cut} and the logarithmic derivative of the wavefunction. If transferability is a higher priority in a particular application, then Q_c should be tuned to obtain the best match between the logarithmic derivatives of the pseudo and true wavefunctions. Depending on the application, one may require a good match over a wide range of energy for broad bands or only a narrower range in the case of narrow bands. If a satisfactory match can be obtained for a range of Q_c, then the smallest Q_c should be used to achieve the lowest E_{cut}.

By removing the constraint on the second derivative of the wavefunction at r_c, we allow our pseudopotential to have a discontinuity there because the kinetic energy, which is proportional to $\Psi''(r)$, is discontinuous across r_c, and hence so is the potential. Although a large discontinuity in a pseudopotential can damage its scattering property, in the current scheme the best possible Q_c is chosen to give the best fit of the logarithmic derivative, which thus guarantees that the discontinuity is harmless. This is also consistent with our observation that whenever the logarithmic derivative agreement is satisfactory, the discontinuity is always small. This can also be understood from the fact that in the current scheme the high q components of the pseudo wavefunction are reduced as much as possible, both because they are expanded using the least possible number of spherical Bessel functions and also because of the minimising procedure imposed on ΔE_k in (1.2). The convergence of a practical calculation is not affected if a suitable E_{cut} is chosen, as already discussed in the previous section. Incidentally, it is generally the case that the Q_c yielding the best fit to the logarithmic derivative of the true potential need not be the Q_c that minimises the discontinuity of the pseudopotential, even though these two Q_c are usually close. We regard the quality of scattering being optimised by the Q_c as being more significant than the existence of the discontinuity.

The harmlessness of a small discontinuity is further confirmed by our experience that good agreement is obtained between the results of super-cell calculations using both k-space and r-space versions of the same pseudopotential expressed in Kleinman-Bylander form [9]. To convert the k-space pseudopotential to one in r-space we use the method of King-Smith et al. [10]. It will modify the original pseudopotential in a way that depends on E_{cut} in minimising the aliasing error of the Fast Fourier Transform in planewave supercell calculations. The discontinuity at r_c in the original pseudopotential is smoothed out by the transformation. The fact that both the original and the transformed pseudopotentials gave almost identical results for the relaxation and energy of structures shows that the high q feature at r_c is irrelevant to the super-cell results when a reasonable E_{cut} is used.

3 Generation and Test of Some Pseudopotentials

Although the logarithmic derivative test gives useful indication about the quality of a pseudopotential, there is no precise criterion of how good the agreement should be for a particular physical application. Also the test is evaluated at a given r outside the pseudising radius r_c , which does not give us the information whether the r_c is small enough for the frozen core approximation to be valid for the given application. A solid state calculation is therefore always necessary for a serious test of a pseudopotential.

To test the pseudopotential generated by our current scheme, we have chosen some bulk properties of Cu metal because it is a popular case tested by other authors [1, 11]. We follow the RRKJ paper in using a slightly ionised Cu configuration $3d^{9.00}4s^{0.75}4p^{0.25}$ from which to generate the pseudopotential. After generating the pseudopotential for each l as described in Section 2, it was converted to Kleinman-Bylander form with the s-potential chosen as the local potential. Two Cu pseudopotentials were prepared (Fig. 2), one with smaller d-core and the other a larger d-core, with $r_c(s,p,d) = (2.0, 2.0, 2.0)$ a.u. and $r_c(s,p,d) = (2.0, 2.0, 2,4)$ a.u. respectively. The Q_c for these two potentials are $Q_c(s,p,d) = (3.17, 4.66, 6.47)$ and $Q_c(s,p,d) = (3.17, 4.66, 5.17)$. In most cases, we found it useful to choose q_3 as the initial guess for Q_c from which to start the tuning, so that it is convenient to express the final Q_c in terms of the ratio Q_c/q_3. For the Cu pseudopotentials in this section, this becomes $Q_c/q_3(s,p,d) = (0.8, 1.0, 1.175)$ and $Q_c/q_3(s,p,d) = (0.8, 1.0, 1.2)$.

The Cu pseudopotential with the smaller d-pseudocore ($r_c = 2.0$ a.u.) allows our results to be compared directly with those of other popular schemes in the literature [1, 11], while we shall

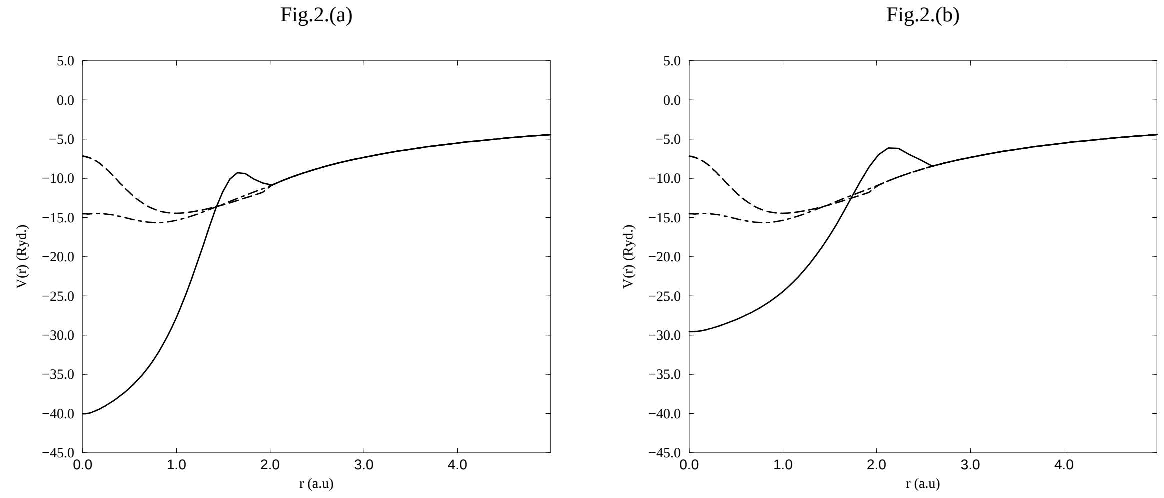

Figure 2: The s, p, d pseudopotentials for Cu. (a) Small r_c =2.0 a.u. for $l = 0, 1, 2$. (b) r_c =2.0 a.u. for $l = 0, 1$ but larger r_c =2.4 a.u. for $l = 2$. (s: dashed line, p: dot-dashed line, d: solid line)

use the one with a big d-pseudocore to demonstrate the flexibility of using Q_c -tuning to generate a pseudopotential with a larger r_c . Although a pseudopotential with larger r_c is always softer, it may not be accurate enough. In our current scheme we can tune the value of Q_c so that we obtain a good logarithmic derivative even for such a large r_c .

For calculating the bulk properties of Cu metal, an $8 \times 8 \times 8$ Monkhorst-Pack k-point grid [14] was used for a simple-cubic unit cell containing four atoms. With such a coarse grid of k-points, a gaussian smearing of the occupation function at the Fermi level of $1eV$ was needed, and the energy was corrected appropriately [15]. In the case of the small d-core pseudopotential, the convergence test was done and the sudden drop of the total energy in a super-cell calculation was found to occur at 650 eV where absolute convergence to about 0.1 eV per atom is reached (Fig. 3). To justify the results obtained at $E_{\text{cut}} = 650\ eV$, a similar calculation was also performed at 1000 eV where the total energy converged to within 0.01 eV per atom, and the results for the bulk properties, as shown in Table 1, were found to be essentially the same. This is consistent with our experience that the E_{cut} that gives the calculated total energy converged to around 0.1 eV per atom is usually high enough for reliable solid state bulk properties. In the case of the pseudopotential with a large d-core, the convergence test was also done (Fig. 3) and we chose $E_{\text{cut}} = 500\ eV$ to run the simple bulk property tests which are shown as the third line in Table 1. Note that the valid comparison is with an exact all-electron calculation because we are testing the pseudising, not the accuracy of LDA, and we give the LAPW [16] results without knowing how closely it approximates to that. As one can see from the table, the overall result is satisfactory in comparison with experiment [17] and other computational methods.

We have already outlined in the Introduction the idea of "projector reduction", i.e. using Q_c tuning to make the pseudopotentials for two angular momenta i and j sufficiently nearly the same that a common potential can be used for both. The latter then becomes the local

FIG.3

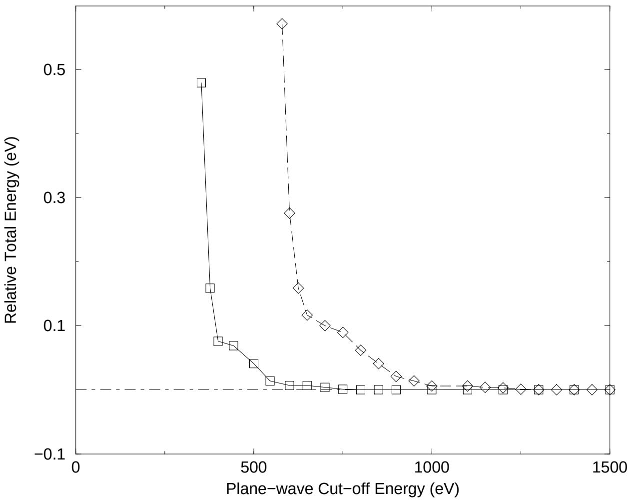

Figure 3: Convergence of total energy per atom of copper metal with respect to the cut-off energy for two pseudopotentials with r_c =2.5 a.u. (solid line) and r_c =2.0 a.u. (dashed line).

component $V_{\mathrm{L}}(r)$ of the atomic pseudopotential, leaving only one set of projection operators for the third angular momentum component. The elements B, C, N, O in the first row of the periodic table have only 1s orbitals in the atomic core and hence both the p ($l = 1$) and d ($l = 2$) pseudopotentials $V_s(r)$, $V_p(r)$ contain no core cancellation in the sense of the cancellation theorem of pseudopotential theory [18], and one may therefore expect them to be similar. With Q_c tuning it has been found that they can be made extremely similar, as shown in Fig. 4 for carbon using the parameters given in Table 2. The $V_{\mathrm{L}}(r)$ is then taken as $V_p(r)$ because the $l = 2$ components in the wave functions are presumed to be very small. This gave a logarithmic derivative for $l = 2$ practically identical to that from the V_d pseudopotential and very close to the all-electron one by the standards of pseudopotentials. Similarly, very good pseudopotentials with only an $l = 0$ projector were also generated for C, N and O with the parameters of Table 2. Extensive tests were carried out on the C and O pseudopotentials for the work of Ref.[8] and on the N pseudopotential with methylamine [19].

Similarly with Q_c tuning a pseudopotential was generated for Al with only the $l = 0$ part non-local, as given in Table 2. It has been well tested in solid state calculations and gives a satisfactory value for the C_{44} elastic constant (correct to 10%) which is notoriously sensitive to the pseudopotential (Ref [19] p.IV-18). For Br with the parameters in Table 2 the local potential

$$V_{\mathrm{L}}(r) = \alpha V_p(r) + (1 - \alpha)V_d(r) \tag{3.1}$$

with $\alpha = 0.7$ gave good logarithmic derivatives for $l = 1$ and 2, again leaving only a projector for $l = 0$. This also avoided some problems in generating the Kleinman-Bylander form of the pseudopotential [9] for calculations, which was in fact the reason for generating it.

Table 1: The solid state bulk test of Cu pseudopotentials, comparing the results of the present calculations (first three rows) with those from another pseudopotential [11] and from an all-electron calculation (LAPW), and with experiment : for lattice constant a, bulk modulus B and B' the pressure derivative of bulk modulus fitted from the equation of state.

Type	$E_{\text{cut}}(eV)$	a(Å)	B(GPa)	B'
$r_c(d) = 2.0$ a.u.	1000	3.60	166	5.0
$r_c(d) = 2.0$ a.u.	650	3.59	163	5.4
$r_c(d) = 2.4$ a.u.	500	3.66	145	4.8
$r_c(d) = 2.3$ a.u.[a]	982	3.60	160	5.1
LAPW [b]		3.61	162	
Experiment [c]		3.61	142	5.28

[a] Ref [11]

[b] Ref [16]

[c] Ref [17]

In the transition elements the V_d pseudopotential is very different from the V_s and V_p ones, and it was found for Fe, Co and Cu the latter two could be well represented by the local potential

$$V_{\mathrm{L}}(r) = \beta V_s(r) + (1 - \beta)V_p(r) \tag{3.2}$$

which leaves only a set of projectors for $V_d(r)$. The parameters are given in Table 2, the pseudopotential for Co having been tested by solid state calculations for the work on CoSi2 in Ref [20]. In Cu the q_3 for $l = 0$ was set equal to q_2 so that (1.1) effectively only contains two terms instead of three.

In Al and Ge, it was possible with Q_c tuning to make the pseudopotentials for $l = 0$, 1 and 2 all quite similar, which would give a local potential if taken as equal. Such a potential is probably

Table 2: Parameters for pseudopotentials with projector reduction. The second column gives the label of the pseudopotential in Ref [19] where more details and tests may also be found. The third column gives the atomic wavefunction used for generating the s and p pseudopotentials, and the second line in the same column for $V_d(r)$. The values of Q_c for $l = 0, 1, 2$ are given in the form of $Q_c/q_3(s, p, d)$. The last two columns give α, β in Eqs. (3.1), (3.2).

Element	(Label)	Configuration V_s, V_p	V_d (if different)	$r_c(s, p, d)$	$Q_c/q_3(s, p, d)$	α	β
B	B001a	$2s^{2.00}2p^{1.00}$	$2s^{1.00}3d^{0.20}$	all 1.4	0.80, 0.80, 1.00	1.0	-
C	C021	$2s^{2.00}2p^{2.00}$	$2s^{0.75}2p^{1.00}3d^{0.25}$	all 1.4	0.80, 1.05, 1.0325	1.0	-
N	N010	$2s^{2.00}2p^{1.00}$	$2s^{0.75}2p^{2.00}3d^{0.25}$	all 1.4	0.80, 1.05, 1.035	1.0	-
O	O051	$2s^{2.00}2p^{4.00}$	$2s^{1.00}2p^{1.75}3d^{0.25}$	all 1.4	0.40, 1.11, 1.0325	1.0	-
Al	Al013a	$3s^{2.00}3p^{1.00}$	no d is used	all 2.4	1.10, 1.10	-	0.8
Br	Br000	$4s^{2.00}4p^{5.00}$	$4s^{1.00}4p^{3.75}4d^{0.25}$	all 1.4	1.00, 1.00, 0.90	0.7	-
Fe	Fe002	$3d^{4.00}4s^{1.00}4p^{0.25}$		all 2.4	0.48, 0.87, 1.18	-	0.3
Co	Co013_v2	$3d^{7.00}4s^{1.00}4p^{0.25}$		2.0, 2.0, 2.4	0.70, 0.965, 1.18	-	0.2
Cu	Cu006g	$3d^{9.00}4s^{0.75}4p^{0.25}$		2.0, 2.0, 2.5	0.80, 0.95, 1.20	-	0.5

FIG.4

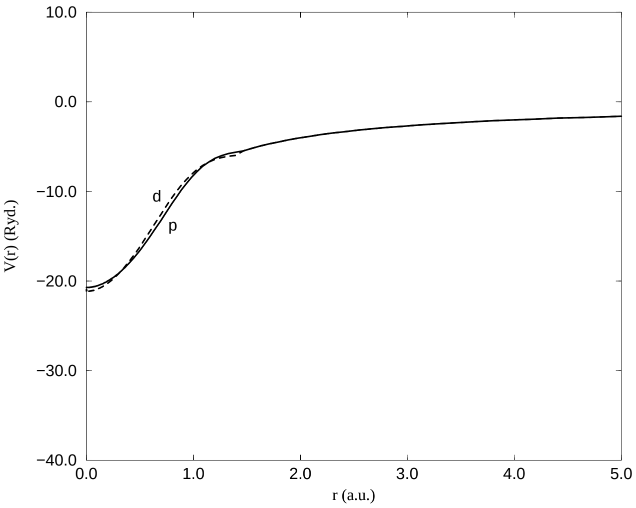

Figure 4: $V_{l=1}(r)$ (solid line) and $V_{l=2}(r)$ (dashed line) for carbon with the parameters of Table 2.

not good enough for modern work, but explains perhaps why empirical local potentials were found to give rather good results through the 1960's and 1970's and even more recently for Al, Ge and As [21, 22].

4 Discussion and Conclusion

In Section 2 we described how Q_c may be varied to obtain the best fit to the logarithmic derivative of the original potential, and we turn now to look at how the variation of Q_c manifests itself in the resultant pseudopotential as is required for projector reduction. Fig. 1 shows that the main effect of varying the Kinetic Energy Filter parameter Q_c is to change the depth of the pseudopotential in r-space. One can interpret qualitatively the effect of the optimisation on the shape of a pseudopotential from an r-space view point, which is useful when using Q_c to regulate the shape of the pseudopotential. If Q_c is set to be relatively small, this pushes $\Psi_l(r)$ in the direction of having lower Fourier components, which means having lower kinetic energy inside r_c. Since the energy eigenvalue is fixed and is equal to the kinetic energy plus potential energy, the low kinetic energy implies a rather shallow (weak) pseudopotential. On the other hand using a higher Q_c results in a deeper pseudopotential as shown in Fig. 1(c). If Q_c is reduced even further, the pseudopotential becomes even shallower (weaker) and a barrier will be raised near r_c as a result of the norm-conserving constraint so that the pseudopotential preserves the correct amount of charge within the pseudo-core region. Such a barrier may look strange but experience shows it does not affect E_{cut} or the accuracy of the pseudopotential in solid state tests provided the logarithmic derivative fits well.

The effect of Q_c-tuning on the shape of a pseudopotential also depends on other factors. In the

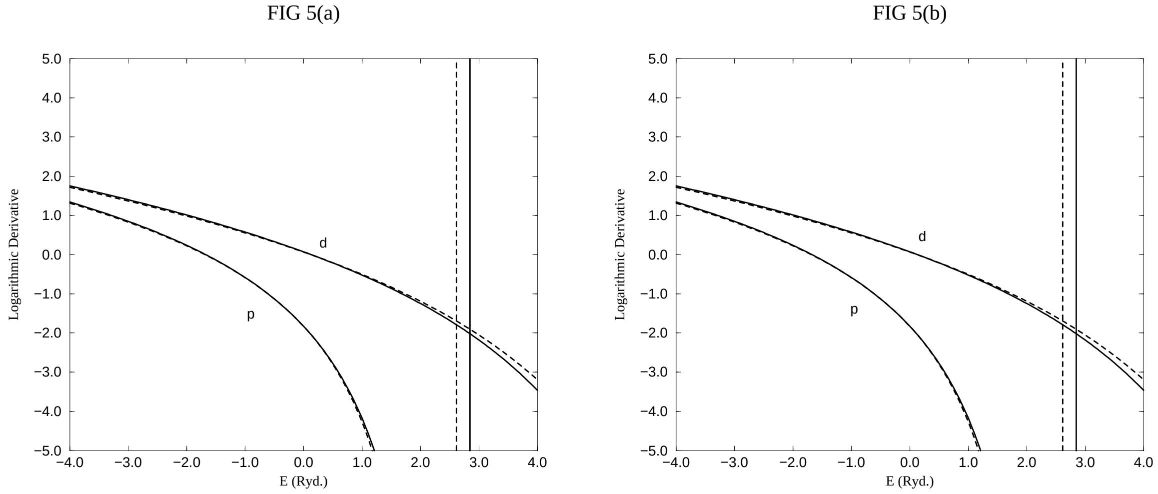

Figure 5: Logarithmic derivative of carbon before (a) and after (b) projector reduction.

case of nodeless orbitals such as $2p$ and $3d$, the pseudopotentials are highly attractive because there is no "Cancellation Effect" from inner shells in the sense of conventional pseudopotential theory [18]. Optimising these pseudopotentials therefore means shifting the electrons outward from the centres of the atoms. On the other hand, in the case of (soft) pseudopotentials that do have a cancellation effect from inner shells, using a smaller Q_c means spreading the charge distribution inwards towards the centres of the atoms, which serves to lower the magnitude of the originally repulsive (or weakly attractive) pseudopotentials at $r = 0$, but has less effect on their shape near r_c. Such a trend can be used to systematically regulate the shape of a pseudopotential by tuning Q_c.

Figure 4 illustrates the use of Q_c tuning to achive projector reduction. It shows $l = 1$ and $l = 2$ pseudopotentials $V_1(r)$ and $V_2(r)$ for C which have been tuned using Q_c to resemble each other as close by as possible while retaining a good fit to the all-electron logarithmic derivative (Fig. 5). Tests showed that the resemblance was sufficiently good to use $V_1(r)$ also for $V_2(r)$ and for all higher l, i.e. to take it as the local component of the pseudopotential. Thus only one projector for $l = 0$ was required. The experience with generating pseudopotentials with reduced number of projectors for the elements listed in Table 2 suggests that this idea can probably be extended to a significant number of other elements.

The current scheme has been used to generate a significant number of pseudopotentials for a wide range of applications. A complete periodic table of pseudopotentials is available commerically from Molecular Simulation Inc. for use with the CASTEP code for solid state applications, though not all have been thoroughly tested. Nearly 300 papers have been published in the academic literature with calculations using pseudopotentials generated by the present method. We reference some of the early ones because they tend to contain more details of the pseudopotentials, namely those for Co [18]; Ge [21]; C, O and Pd [22]; Cu and Cl [23]. The pseudopotentials for C and O were tuned especially for projector reduction in the large dynamic calculation on a zeolite [8] as already mentioned. More details on 38 elements may be found in Ref [19].

The code for generating pseudopotentials by the present method will be available at the website http://www.phys.tku.edu.tw/qc/

In summary, therefore, we have introduced an improved scheme for generating Optimised Pseudopotentials. The Q_c parameter is used in a new way, and is tuned to give as accurate a pseudopotential as possible, meaning a good match to the all-electron logarithmic derivative of the wave function over a suitably wide range of energy. The continuity constraint of $\Psi_l''(r)$ at r_c is dropped and the number of terms in the expansion (1.1) is also reduced to three, to remain equal to the number of constraints in order to give a numerically stable algorithm. The reduction to three terms automatically tends to make the pseudopotential softer because the cut-off E_{cut} in solid state applications is largely controled by the highest qi appearing in (1.1). Dropping the constraint on continuity of the $\Psi_l''(r)$ means the pseudopotential has a discontinuity at r_c, but in practice the Q_c is tuned in our scheme to match the logarithmic derivative which always makes the discontinuity small, so that it does not adversely affect the accuracy or the softness of the pseudopotential. In some sense the dropping of one constraint allows the pseudo wavefunction (and hence pseudopotential) greater freedom for optimisation with regard to accuracy and convergence properties.

A most important point is that the generated pseudopotential and the corresponding logarithmic derivative vary with the chosen Q_c parameter in a systematic way. One therefore has a well controlled situation for generating and improving a pseudopotential for any given physical application, depending on the required balance between E_{cut}, the accuracy of the pseudopotential and the width of the energy range over which it has to be accurate. This is important for many calculations. Moreover we have shown how one can physically understand the connection between Q_c and the shape of the pseudopotential, which helps one to operate the scheme systematically and efficiently. The scheme represents a further significant step toward generating systematically good norm-conserving pseudopotentials for a wide variety of physical systems. We have also demonstrated how to use Q_c tuning method to reduce the number of non-local projectors of pseudopotentials for quite a few elements. These projector reduced pseudopotentials allow one to save significant computing time while remain as accurate as normal unreduced ones.

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