HCM Newsletter

Ψ_k Network

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

Number 11 October 1995

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Editorial

The **Editorial** is followed by the section **News from the Network** where we remind you of the importance of acknowledging the *Network* in your publications, as well as about abstracts.

In the section **News from the Working Groups** readers will find reports on recent collaborative visits supported by the *Network*. These are followed by the report by *Balazs L. Gyorffy*, the conference chairman, on the ERC conference on "*Itinerant Magnetism*" that took place in Lunteren from 9-14th of September 1995. Then readers will find a reflection of *Peter H. Dederichs*, the spokesman of the *Magnetism Working Grop of the Network* on the same conference. Straight after this there is a first announcement of the "*Bond-Order Potentials Workshop*" to be held in Oxford next March. Then there are the announcements of some postdoctoral and Ph. D. positions. These are followed by the **Abstracts** section.

In the section **Presenting Other Networks** Rex Godby writes about the *EPSI Network* and the current issues of interest of this network.

In the **Highlight of the Month** section there are two contributions from Cavendish Laboratory in Cambridge (UK). The first one, by *R. Perez, M.C. Payne, I. Štich and K. Terakura*, is on *'First principles Simulations of Nanoindentation and Atomic Force Microscopy on Silicon Surfaces'*. This project is partially supported by the *Network*. The second contribution is a comment by *Volker Heine and Roger Haydock* on *'Towards a "Quick and Dirty" Fully Variational DFT Calculations'*.

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

http://www.dl.ac.uk/TCSC/HCM/PSIK/main.html

This also contains pointers to several other nodes: *O.K. Andersen (Stuttgart)* which includes information on the **Network Conference**, *M. Gillan (Keele)*, *B.L. Gyorffy (Bristol)*, *J. Nørskov (Lyngby)* with information on CAMP, *M. Scheffler (FHI Berlin)*, and *A. Walker (UEA Norwich)*. If you maintain a home page on your activities we will be happy to include a pointer from the *Network's* home page to your home page.

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

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

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

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

News from the Network

Acknowledgement of the Network

Please note that this is the one before last newsletter of this calendar year. This also means that the time of submitting to Brussels a report on our *Network's* activity is approaching. For this we will need all available information on the publications that acknowledge the *Network* explicitly. Therefore, if any of you published or submitted for publication such papers where the *Network* had been acknowledged, we would like to hear from you. Could you please just send us detailed references of such papers, namely the authors, journal (volume, page, year) and the title of the paper. We would not like to miss any of such publications.

If you are currently preparing a paper for publication and the work has in any way benefited from the collaborations within the *Network*, e.g. by using computer codes distributed within the *Network* or by being financially supported by the *Network* when attending a workshop or making a collaborative visit, then please do acknowledge it in your paper. One can do it e.g. in the following way:

This work has benefited from collaborations within, and has been partially funded by, the Human Capital and Mobility Network on "Ab-initio (from electronic structure) calculation of complex processes in materials" (contract: ERBCHRXCT930369).

If the Network's funds have not actually been used, but the work has benefited from some form of collaboration or a computer code distributed within the Network, then the part of the sentence: *...", and was partially funded by," ...* should be omitted in the above acknowledgement. Please note that if you obtained a computer code at a workshop organised by the *Network* then the *Network's* funds were used and this should be acknowledged.

Abstracts

It is very important for our **Abstracts** section to be successful that you make an effort and send us the abstracts of all papers **recently** submitted for publication. The papers that have already been published are easily accessible to everybody, so there should be no need in readvertising their abstracts in the *Newsletter*. Of course, we would usually consider bringing to attention of others those papers, of direct relevance to the *Network* activities, which have already been published in less widely distributed journals.

News from the Working Groups

Report on the collaborative visit of J.M. Thijssen (Nijmegen) to Cambridge

7-9 August, 1995

From 7 to 9 August, I visited C. Nex and R. Haydock at the TCM (Theory of Condensed Matter) group of the Cavendish Laboratory to discuss possibilities for and difficulties in the calculation of charge densities in discretisation methods via the recursion method. The difficulties are connected with the relatively large number of grid points that is necessary to represent the kinetic energy sufficiently accurately. Possible solutions, such as taking starting states which are smoothly distributed over the grid have been discussed. These approaches will be tested in the near future. Also, R. Haydock suggested using the Harris functional instead of the ordinary DFT approach in which the charge output density resulting from an input density used in constructing the effective potential does not have to be calculated explicitly. This will be pursued further.

The visit to the TCM group has turned out very useful for my research.

(J.M. Thijssen)

Report on the collaborative visit of Alexander Settels (KFA Juelich) to Prof. Hubert Ebert (Ludwig-Maximilian-University Munich)

6-10 August, 1995

From 6 to 10 August I have visited Prof. Hubert Ebert and his group at LMU Munich. There I was introduced to the KKR-Green's function program for many atoms per unit cell, which has been developed by Hubert Ebert and his group. Especially I directed my attention to the part of the program, wherein the KKR structure constants for many atoms per unit cell are set up.

Furthermore Hubert Ebert and I discussed the possibilities of varying parts of the program to use the datas in our impurity program.

Then I took over this program and did some test calculations to get well acquainted with it. The results, in particular the density of states of Si, seem to be very useful. Thus, the program will be used for Green's function calculation for impurities in semiconducters.

In summary, this visit to LMU Munich was very profitable and helpful for me and I would like to thank the HCM-PSIK Network for funding this collaborative visit.

(A. Settels)

Report on

EUROPEAN RESEARCH CONFERENCE

Electronic Structure of Solids: ITINERANT MAGNETISM

The conference took place in Lunteren, a most attractive hide-away in The Netherlands, from 9-14th of September 1995. Its chair and vice-chair were Balazs L. Gyorffy (Bristol) and Peter Blöchl (Zürich), respectively. Most of the organisation was in the competent hands of the European Science Foundation, and in preparing the program we were assisted by Stefan Blügel (Jülich).

As advertised, this was our fourth European Research Conference on the *Electronic Structure of Solids* and its theme was *Itinerant Magnetism.* Hopefully, it is clear from the following conference program that whilst we focused on current topics of interest no interesting contribution, which dealt with magnetism in terms of moving electrons was rejected. There were about 80 participants, 40 or so posters, and long fruitfull disscussions.

In keeping with the tradition of these conferences, on Tuesday (12th September) evening we had a town-meeting to select the theme of the 1998 event and elect its organiser (chair). You may recall that the first ERC meeting (Cambridge 1992), chaired by V. Heine was on "**Computational Leading Edge**", the next two (Porto Carras 1993, chaired by Matthias Scheffler, and Gausdal 1994, chaired by Risto Neminen) emphasised "**Surfaces and Interfaces**" and "**Dynamics and Exitations**", respectively and, except for the launch in Cambridge, each time the organiser was chosen at such town-meetings of the earlier conferences. At the moment we have settled into the routine of deciding two meetings ahead. Thus, as there will be no meeting in 1996, on account of our **big** HCM Network Conference in Schwäbisch Gmünd, and we have earlier selected the program of Peter Blöchl on "*Chemical Processes in Bulk, Surfaces and Molecules*" for 1997 conference last year, we were discussing ideas for 1998. There were three proposals:

- ELECTRONIC AND ATOMIC PROCESSES AT SURFACES by Andrew Fisher (*University College, London*)
- STRUCTURE, GROWTH AND DYNAMICS AT SURFACES AND INTERFACES by Michael Methfessel (*Frankfurt/O*) and Elisa Molinari (*Modena*)

- PHASE STABILITY by Borje Johansson (*Uppsala*) and Peter Mohn (*Vienna*)

Each of them was presented in a 5 minutes contribution by one of the proposers: Fisher, Methfessel and Mohn, respectively, and all three were well received. Nevertheless, after a brief discussion Peter Mohn withdrew his proposal with the view of bringing forward a revised version at a future date. This was followed by a longer, spirited exchange of ideas concerning the precise content of the other two proposals, ending with a secret ballot. The count revealed that the proposal of Andrew Fisher was adopted by a small margin.

Further information about the 1997 conference to be organised by Peter Blöchl, as well as, details of Andrew Fisher's proposal for 1998 will appear in future HCM Network newsletters.

Conference Programme

MAGNETIC MULTILAYERS AND NANOSTRUCTURES

Professor B. Johansson (Uppsala)
"Spin-Polarised Density Functional Theory"
Discussion lead by: Prof. V. Heine (Cambridge)

Professor P.H. Dederichs (Jülich)
"Oscillatory Coupling Between Magnetic Layers Separated By Non-Magnetic Spacers"
Discussion lead by: Professor B.L. Gyorffy (Bristol)

Professor J. Mathon (London)
"Quantum Wells of Magnetic Multilayers"
Discussion lead by: Dr. J. Kudrnovsky (Prague and Wien)

Professor I. Mertig (Dresden)
"Giant Magnetoresistance In Magnetic Multilayers"
Discussion lead by: Prof. J. Mathon (London)

Dr. W.E. Pickett (Washington D.C.)
"Half-Metallic Ferromagnetism in Collosal Magnetoresistance in Manganites"
Discussion lead by: Professor P. H. Dederichs (Jülich)

LSDA AND BEYOND

Professor Peter Fulde (Dresden)
”Electronic Correlations In Cluster Calculations”
Discussion lead by: Professor B. Johansson (Uppsala)

Professor Ferdi Aryasetiawan (Lund)
”The GW Approximation For Transition Metal Oxides”
Discussion lead by: Professor F. Manghi (Modena)

Dr. Walter Temmerman (Daresbury)
”Self Interaction Corrections: Beyond LSDA”
Discussion lead by: Professor A.M. Oleś (Krakow)

Professor Hans Skriver (Lyngby)
”First Principles Calculations Of Magnetism Of Surfaces
And Interfaces”
Discussion lead by: Professor J. Hafner (Wien)

Professor Manfred Fähnle (Stuttgart)
”Magnetism In The Rare Earth Intermetallic Compounds”
Discussion lead by: Dr. M.S.S. Brooks (Karlsruhe)

MAGNETIC ANISOTROPY

Dr. Stefan Blügel (Jülich)
”Spin Density Functional Theory Of Surface Magnetism”
Discussion lead by: Professor H. Skriver (Lyngby)

Professor Hubert Ebert (München)
”X-Ray Circular Dichroism”
Discussion lead by: Dr. P.J. Durham (Daresbury)

Dr. Laszlo Szunyogh (Budapest)
”The Origin Of The Magnetic Surface Anisotropy”
Discussion lead by: Professor P.H. Dederichs (Jülich)

Dr. Leonid H. Sandratskii (Ekaterinburg and Darmstadt)
"Non-Colinear Magnetism In Metals"
Discussion lead by: Professor H. Ebert (München)

Professor P.-A. Lindgård (Risø)
"Nuclear Magnetic Order In Metals"
Discussion lead by: Professor B.N. Harmon (Ames)

MAGNETISM IN DISORDERED SYSTEMS

Dr. J.B. Staunton (Warwick)
"Metallic Magnetism In Random Alloys"
Discussion lead by: Dr. G.M. Stocks (Oak Ridge)

Professor J. Hafner (Wien)
"Non-Colinear Magnetism In Amorphous Metals"
Discussion lead by: Professor J. Kübler (Darmstadt)

Professor P. Entel (Duisburg)
"INVAR: Basic Facts, New Results And Open Questions"
Discussion lead by: Dr. P. Mohn (Wien)

Dr. J. Kudrnovsky (Prague and Wien)
"A Method For Random Surfaces And Interfaces"
Discussion lead by: Dr. S. Blügel (Jülich)

Professor R.A. de Groot (Nijmegen)
"Half-Metallic Magnetism"
Discussion lead by: Professor M. Fähnle (Stuttgart)

MODEL HAMILTONIANS FROM LDA

Prof. Igor Sandalov (Uppsala)
"Orbital Polarisation in f-band Metals"
Discussion lead by: Professor P. Fulde (Dresden)

Professor A.M. Oleś (Krakow)
"Electron Correlations"
Discussion lead by: Dr. W.E. Pickett (Washington D.C.)

Dr. J.F. Annett (Bristol)
"Constrained Density Functional Calculations"
Discussion lead by: Dr. A.I. Liechtenstein (Stuttgart)

(Balazs L. Gyorffy)

Reflection on
ERC 1995 " Itinerant Magnetism" in Lunteren

by Peter H. Dederichs

(Spokesman of the Magnetism Working Group of the Network)

The fourth European Research Conference on the Computational Physics of the Electronic Structure of Solids was held from 9–14 September 1995 in Lunteren, The Netherlands. The '95 focus was on the "Itinerant Magnetism" – the first-principles description of magnetic phenomena in solids. The conference was organized by Balazs Gyorffy (Bristol) assisted by Stefan Blügel (Jülich). About 80 participants from more than 10 different countries joined the conference. While contributions to all subjects which answered to the above broad description were welcomed, special emphasis was given to the following selected topics: (i) Magnetism at surfaces and interfaces, (ii) Magnetic metallic multilayers and nano-structures, (iii) Magnetic anisotropies, (iv) Magnetism in disordered systems, and (v) LSDA, model Hamiltonian from LDA, and beyond LSDA.

The conference was organized so that there were 3 talks in the morning session and two talks in the late afternoon. Evening hours were reserved for poster sessions, discussions and the ballot for the 1998 conference. The talks were scheduled to 40 minutes followed by a discussion of 20 minutes.

B. Johansson's (Uppsala) talk on Sunday morning started the whole conference by summarizing the successes of and the deficiencies of the LSDA by discussing spin and orbital moments in bulk and surfaces, magnetism and the implications on structure of transition metals and rare earths. The rest of the morning session was devoted to description and the origin of the oscillatory exchange coupling in magnetic multilayers. While P.H. Dederichs (Jülich) discussed the oscillatory exchange coupling for a large number of Co/Cu samples using a full *ab–initio* description, J. Mathon (London) approached the same problem from the quantum well point of view. The Sunday afternoon was occupied with talks on the giant magneto-resistance in magnetic multilayers by I. Mertig (Dresden) and the colossal magneto-resistance by W.E. Pickett (Washington D.C.) on the half-metallic ferromagnetic manganites. I. Mertig gave a clear talk on a difficult subject in which she used the Bolzmann equation to describe the giant magneto-resistance. A lot of discussion was generated on the significance and the description of the ballistic transport regime or a different treatment of the transport by the Kubo–Greenwood formula. It became evident that the understanding of the giant magneto-resistance is a very difficult subject. This became even more clear during a round–table discussion in the evening where different opinions have been exchanged.

The morning session of the second day was allocated to LSDA and beyond. P. Fulde (Dresden) discussed recent results on the 6eV satellite for Ni and the correlation in transition metal clusters. F. Aryasetiawan (Lund) discussed the effect of the GW approximation on the bandgap of NiO and the bandwidth and exchange splitting of Ni. W. Temmerman (Daresbury) introduced the self–interaction free LSDA and discussed an impressive amount of results particularly on the α–γ transition of Cerium and a large class of Ce-compounds. The large amount of results he presented suggests that one can now manage to "routinely" apply the self–interaction free LSDA to complicated compounds. During the afternoon session H. Skriver (Lyngby) introduced his implementation of the Green's function TB-LMTO method as an efficient new method to treat ordered and disordered surfaces, interfaces and multilayers. The potential of this method was demonstrated by the many interesting results he presented. M. Fähnle (Stuttgart) discussed some problems in the description of rare earth compounds.

The morning session of the third day started with a summary of the magnetism of ultrathin films with emphasis on the structural stability on ultrathin films given by S. Blügel (Jülich). The talk was followed by H. Ebert (München) on X-Ray Circular Dichroism. He presented calculations for a large amount of systems and compared these with experiments and gave a critical discussion on the so-called sum rules, liked by experimentalists, to deduce magnetic spin and orbital moments from experimental data. L. Szunyogh introduced the important subject of the magnetic surface anisotropy. L.H. Sandratskii (Ekaterinburg and Darmstadt) introduced the non-collinear magnetism, a subject of increasing importance, in connection with and without spin–orbit interaction. P.–A. Lindgård (Risø) led us to the world of the micro-Kelvin physics where nuclear spin systems become model systems for investigation of phase transitions.

On Wednesday we heard a sequence of impressive talks on the magnetism of disordered systems started by J.B. Staunton (Warwick) on the metallic magnetism of random alloys, followed by J. Hafner (Wien) on the non-collinear magnetism in amorphous metals, by P. Entel (Duisburg) on recent results on the longstanding invar problem, and by J. Kudrnovsky (Prague and Wien) on the magnetism of surfaces and interfaces of random alloys. In the last talk of the afternoon session, R.A. de Groot (Nijmegen) returned back to the problem of the half-metallic magnetism and the colossal magnetoresistance. He gave a detailed discussion on the electronic properties of half-metallic magnets and gave convincing arguments that the roughness and the defects are detrimental in order to understand the colossal magneto-resistance.

The speaker of the last morning session, A.M. Oleś (Krakow), Sandalov (Uppsala) and J.F. Annett (Bristol) discussed the derivation of model Hamiltonians from LDA and its implication to understand correlation effects from these models.

All talks enjoyed good attendance and generated a broad discussion. The discussion time of 20 minutes allocated for each talk was in many cases not sufficient. The discussion continued during the lunch break, during the poster sessions and after dinner at the bar till late hours. About 40 posters have been displayed during the entire time of the conference. The poster session had been distributed over two evenings, where many interesting new results had been displayed. It was an important enrichment of the conference. It also encouraged the discussions between students and senior scientists.

The stimulating and creative atmosphere of the conference has benefited from the conference site “De Blije Werelt” (“The Happy World”), which was very convenient and quite adequate for this size of conference. It was placed in an unexpectedly nice location in the center of The Netherlands near Lunteren/Ede, surrounded by a forest inviting many of us to relaxing after–lunch walks or jogging activities. One afternoon, we made an excursion to the “Kröller–Müller” museum located in the “De Hoge Veluwe” Natl. Park, famous for many van Gogh paintings and the sculpture garden.

In summary, this was a well organised, very exciting and stimulating conference on a timely subject, which took place in a good atmosphere and in a pleasant surrounding. Many thanks to Balazs Gyorffy. Well done!

First Announcement

BOND–ORDER POTENTIALS WORKSHOP

University of Oxford, Department of Materials

Materials Modelling Laboratory

18-19 March, 1996

The realistic atomistic simulation of materials requires the development and application of O(N) methods that avoid the crippling N^3 constraint of matrix diagonalisation for finding the electronic structure and hence the energy of a system.

This two-day workshop presents the background theory and concepts behind the novel Bond Order Potentials (BOPs) which allow the Tight Binding (TB) energy to be expressed exactly as a rapidly convergent many-atom expansion. The BOP approach has the advantage over other O(N) density matrix methods in that it is equally applicable to both metals and semiconductors, and it is naturally parallelisable.

The nature of the BOP computer codes will be described and a hands-on afternoon session will give workshop attendees experience in simulating a wide range of materials from hydrocarbon molecules through to bulk semiconducsctors and intermetallics.

For further information please contact:

A.M. Bratkovsky (Alex Bratkovsky)
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email: DGP2@vax.ox.ac.uk

Announcement

Postdoctoral Position in Ab Initio Calculations of Circular Magnetic X-ray Dichroism in Magnetic Multilayers and Thin Films

Daresbury Laboratory, UK

This 3 year position, to work with Drs. G.Y. Guo and W.M. Temmerman, concerns the calculation of magnetic X-ray dichroism in multilayers and thin films. This project also aims to relate the dichroism to the underlying magnetic properties of these materials, such as magnetic anisotropy, exchange coupling, enhanced moments, etc.. This work will support the flourishing experimental programme on the Synchrotron Radiation Source in Daresbury Laboratory.

Candidates should send a curriculum vitae, and a list of three references to:

Dr. W.M. Temmerman,
Daresbury Laboratory,
Daresbury, Warrington, WA4 4AD
Cheshire, UK
tel.: +44-(0)1925-603227
fax: +44-(0)1925-603634
e-mail: w.m.temmerman@daresbury.ac.uk

For further information please contact either Dr. G.Y. Guo (e-mail: g.y.guo@dl.ac.uk, tel.: +44-(0)1925-603153) or Dr. W.M. Temmerman.

Announcement

Postdoctoral Research Associateship in Ab Initio Computational Many-Body Theory

University of York

DEPARTMENT OF PHYSICS

Applications are invited for the above postdoctoral position available from October 1995, or as soon as possible thereafter, to work with Professor R.W. Godby in the development and application of ab initio computational many-body theory for solids. The appointment will be for one year in the first instance, with the possibility of extension for one or two further years.

Salary within the range 14,317 - 18,294 pounds per annum on Grade IA of the scales for research staff.

For further information and details of how to apply, please contact the Personnel Office, University of York, Heslington, York YO1 5DD, U.K. (Tel.: +44 1904 434032, Fax: +44 1904 434035), quoting reference number 6602. The closing date for applications is 18 October 1995.

The University of York - Promoting excellence in teaching and research.

The above advertisement will appear in New Scientist and Physics Today. Some further information about the appointment may be seen on the World Wide Web at http://www.york.ac.uk/ rwg3/postdoc_details.html.

Applicants who require clarification or further details of any point are invited to contact Rex Godby by e-mail.

Rex Godby
E-mail: rwg3@york.ac.uk
WWW home page: http://www.york.ac.uk/ rwg3/

Announcement

Postdoctoral Position in Condensed Matter/Matrials Theory

Department of Physics
and Computational Materials Theory Center
California State University Northridge

Applications are invited for a postdoctoral research position in condensed matter/materials theory beginning October 1996 or shortly thereafter.

Areas of particular interest are first-principles electronic structure theory, and atomistic, mesoscopic or macroscopic simulation and modelling of real materials problems.

Candidates should send a curriculum vitae, statement of research interests, and a list of three references to:

Prof. Nicholas Kioussis,
Department of Physics and Astronomy,
California State University,
Northridge, Northridge, CA 91330-8268

California State University Northridge is an equal opportunity/ affirmative action employer.

The above advertisement will appear in Physics Today (October 1995). Applicants who require clarification or further details of any point are invited to contact Nicholas Kioussis by e-mail.

Announcement

Research Assistantship
and
Postdoctoral Position

Research Group TSM, Department of Physics

University of Antwerpen (RUCA)

Applications are invited for a position as research assistant and a postdoctoral position with the group (TSM) of P.E. Van Camp and V.E. Van Doren to do research on density functional theory in polymers and bio-polymers. The appointments are expected to start on January 1, 1996. The research assistantship is for four years and the postdoctoral position is for one year. The assistantship can lead to a PhD degree. The montly salary is about 40000 BEF for the assistantship and 60000 BEF for the postdoctoral position. The applicants for the assistantship should be citizens of an EU country. The topics of the theoretical research of the TSM-group for these positions are:

1. Research on new truly non-local density functionals, capable of generating more realistic band structures than those obtained from local functionals. At the same time these new functionals should reproduce the ground state and structural properties as the local functionals do.

2. Application of local and non-local functionals in ab-initio calculations of the total ground state energy of materials from which the structural, electronic and optical properties can be derived. For this part of the research these materials are polymers and bio-polymers.

Candidates should have a working knowledge of total energy calculations and of computers (mainly UNIX and FORTRAN).

The TSM-group has currently collaborations with :

1. Dr.J.W. Mintmire, NRL, Washington D.C., USA.
2. Prof.J.M. Martins, INESC, Lisbon, Portugal.
3. Prof.J. Ladik, University of Erlangen, Erlangen, Germany.
4. Dr.G. Straub, Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM, USA.
5. Prof.P.Cavaliere, CNRSM, Brindisi, Italy.

Candidates should send a curriculum vitae to:

P.E. Van Camp or V.E. Van Doren
Research Group TSM
Department of Physics
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Groenenborgerlaan 171
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E-mail : vancamp@ruca.ua.ac.be

Postdoctoral Position in Application of Ab initio Plane Wave Codes to Catalysis by Solid Acids

Max Planck Society

Research Unit "Quantum Chemistry" at the Humboldt University

A postdoctoral position is available IMMEDIATELY in the field of: Application of Ab-initio Plane Wave Codes to Catalysis by Solid Acids. Existing codes based on plane waves and density functional theory should be applied to study the adsorption of small molecules on zeolites. Both energy minimization and molecular dynamics techniques may be required. The applicant should have a Ph. D. in Theoretical Chemistry/Physics as well as experience and skills in implementing and using complex ab-initio programs. A network of modern RISC workstations and a four processor-shared memory computer are available within the group. External resources (CRAY T3D) can also be used. Payment is about 38,000 to 45,000 DM/year as a scholarship depending on experience and marital status.

Applicants should send their resume to:

Prof. Joachim Sauer
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Jaegerstr. 10/11
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E-mail: js@qc.ag-berlin.mpg.de

Announcement

Ph. D. Position

University of Sheffield (UK)

A Ph. D. studentship is available from October 1995 to work with Professor Gillian Gehring (University of Sheffield) and Dr. Walter Temmerman (Daresbury Laboratory) on the total energy and Fermi surface studies of the heavy fermion compounds.

A prospective student will be expected to make a detailed study of UBe_{13}. This is expected to help the interpretation of the planned de Haas van Alphen experiments in Professor Mike Springford's group (University of Bristol). The theoretical study will involve both development or generalisation of computer codes and necessary calculations.

To apply, please send your CV and letter of application to the addresses below either by normal or electronic (only postscript or latex files are acceptable) mail.
Further information can be obtained from:

Dr. W.M. Temmerman,
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Quantum well states in Cu/Co overlayers and sandwiches

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Abstract

We report *ab initio* calculations of quantum well states in Cu/Co(001) and Co/Cu(001) overlayers and in Co/Cu/Co(001) sandwiches. Overlayer states are found which coincide well with those previously identified in photoemission and inverse photoemission experiments. In Cu/Co and at energies overlapping with the substrate continuum, minority spin resonances are clearly identifiable. However in the majority spin channel coupling to the substrate is strong enough to effectively destroy quantum well features. In Co/Cu/Co(001) sandwiches discrete states are found at similar energies to those in overlayers of corresponding Cu thicknesses, but resonance states are absent in both spin channels. There is no longer strongly size-dependent electronic structure at the Fermi energy. We conclude care must be taken in extrapolating from the electronic structure of overlayer systems to that of other modulated structures.

(submitted to Phys. Rev. B)
Revtex manuscripts are available from: peterg@mentor.tvs.kun.nl

This work has benefited from collaborations within the EU Human Capital and Mobility Network on *"Ab initio (from electronic structure) calculation of complex processes in materials"* (contract:
ERBCHRXCT930369).

t_{2g} versus *all 3d* localization in LaMO_3 perovskites (M=Ti-Cu): First Principles Study

Igor Solovyev[1], Noriaki Hamada[1] and Kiyoyuki Terakura[2]
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Abstract

Using the LDA+U method we show that a separate treatment of t_{2g} and e_g electrons on transition metal sites as localized and itinerant respectively gives an appropriate description for the band structure of LaMO_3 perovskites (M=Ti-Cu) and systematically improves results of the local-spin-density approximation (LSDA) for the ground-state and single-electron excited-state properties. The analysis is based on comparison with experimental magnetic, optical and photoemission data. Parameters of the effective Coulomb interaction (U_{eff}) estimated for t_{2g} electrons and a role of e_g-screening are discussed. The present new approach accounts well for the insulating natures of LaTiO$_3$, LaVO$_3$ and LaCoO$_3$ for which the LSDA predicts metallic states. Changes of the LSDA band structure for LaMnO$_3$ and LaNiO$_3$ are almost negligible due to the very efficient screening of on-site t_{2g} interactions by e_g electrons.

(submitted to Phys. Rev. B)
Revtex manuscripts are available from: igor@jrcat.or.jp

A New Theoretical Approach to Electronic Structures of LaMO$_3$ Perovskites (M=Ti-Cu): t$_{2g}$ versus All 3d Localization

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Abstract

A new prescription in the so-called LDA+U method which treats t_{2g} and e_g states on transition-metal sites as being localized and itinerant, respectively, improves the band structures of LaMO$_3$ perovskites (M=Ti-Cu) obtained by the local-spin density approximation. Parameters of effective Coulomb interaction for the t_{2g} orbitals, which include the e_g screening, suggest that the perovskites with M of early transition metal elements may be strongly correlated systems while the electron correlation may be weak for those with M of late transition metal elements.

(submitted to Phys. Rev. Lett.)
Revtex manuscripts are available from: igor@jrcat.or.jp

A comparative study on methods for convergence acceleration of iterative vector sequences

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Abstract

We discuss several methods for accelerating the convergence of the iterative solution of nonlinear equation systems commonly in use and point to interrelations between them. In particular we investigate two of the most sophisticated schemes, namely the Anderson mixing and the Broyden update both generalized to the consideration of arbitrarily many previous iterations. For the Broyden method we give a new derivation which is much simpler as that recently proposed by Vanderbilt and Louie. We show that if the additional parameters invented by these authors in order to increase flexibility are used to optimize the convergence of the iteration process they in fact cancel out. In addition we prove that in this (optimal) case the Anderson mixing and the Broyden update as applied to the inverse Jacobian are fully identical. Thus we come to the conclusion that neither of these schemes is superiour. Moreover we show that Broyden update of the inverse Jacobian is superiour to updating the Jacobian itself. Finally we propose an extension of the Anderson mixing which avoids numerical difficulties all these methods are faced with.

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Ab initio Study of Hydrogen Bonding in Lizardite 1T

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Abstract

Periodic ab initio Hartree-Fock crystal orbital study is performed on 1:1 sheet silicate lizardite, $Mg_3Si_2O_4(OH)_4$. The hydrogen bonding (HB) is characterized in terms of full and difference charge density. The difference density is compared and contrasted with covalent and ionic bonding thus demonstrating the characteristic picture of the HB. Within the region of the hydrogen atom a shift of the charge density towards the oxygen atom represents a dipole. A partial positive charge of the dipole interacts with a partial negative charge of the basal oxygen. According to this picture new definition of the HB is proposed. *An effective hydrogen bond exists when a partial positive charge on the hydrogen, raised by its bonding to an electronegative atom, contacts a partial negative charge accumulated by other electronegative atom.* The area between atoms participating in the HB thus exhibits depletion of the charge density just opposite to its gain which has been looking for in the HB by several authors so far. Two typical examples are demonstarated. Lizardite represents the most common type of the HB exhibiting a dipole-to-ion (partial charge) interaction. The second type of the HB is demonstrated for brucite showing a dipole-to-dipole interaction in the head-to-tail arrangement. The total energy of the hydrogen bonding (including all types of interaction) is 28.121 kJ mol^{-1} and 4.203 – 5.782 kJ mol^{-1} for lizardite and brucite, respectively. The comparison is completed with the disscussion on the role of the HB in dioctahedral mineral kaolinite.

Deformation of the electron density due to the interlayer interactions shows strengthening (weakening) of the O – H bond in the outer (inner) hydroxyl, well comparable with stretching frequences in infrared spectra. Hydrogen bonding thus paradoxically causes increased frequencies just opposite to criteria for hydrogen bonds. The gain of the charge density on the inner hydrogen explains why the ditrigonal cavity behaves as weak Lewis bases. Due to the interlayer interaction all atoms of the layer are polarized in vertical direction. The charge density of the apical oxygen tend to be flattened, contrary to that of the basal oxygen where elongated charge density is characterized.

(submitted to Phys. Chem. Miner.)
Manuscripts available from: uachbenc@savba.savba.sk

Ab-initio calculation of electronic structure, crystal field, and intrinsic magnetic properties of Sm_2Fe_{17}, $Sm_2Fe_{17}N_3$, $Sm_2Fe_{17}C_3$ and Sm_2Co_{17}

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Abstract

In a comparative study we calculated the spin and orbital moments, spin and charge densities, and 4f crystal field (CF) parameters of the rare-earth transition metal intermetallics Sm_2Fe_{17}, $Sm_2Fe_{17}Z_3$ (Z=C,N), and Sm_2Co_{17} using a scalarrelativistic optimized LCAO method. The itinerant valence electron states were treated in the local spin density approximation (LSDA), whereas the localized 4f states were described as open core states within the self-interaction corrected LSDA. The calculations yield magnetic moments in good agreement with experiment. While all local moments of Sm_2Fe_{17} increase upon lattice expansion, the moments of atoms neighboring the interstitial sites decrease and those of more distant Fe atoms increase upon insertion of interstitial N or C. In N interstitial atoms all $2p_\alpha$ orbitals are polarized antiparallel to their respective Fe and Sm neighbor atoms in bond direction, whereas in C all $2p_\alpha$ orbitals are polarized antiparallel to the Fe atoms neighboring the interstitial site. The second order CF parameters A_2^0 dominating the rare-earth magnetocrystalline anisotropy are found to have the same sign and order of magnitude as those derived from magnetization data. In accordance with experiment the calculated negative A_2^0 is larger for the Co compound than for the Fe parent compound and is strongly increased upon insertion of interstitial N or C. The agreement between theory and experiment is improved by taking into account the CF contribution arising from the asphericity of the exchange-correlation potential of the non-4f states.

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Manuscripts available from: lutz@tmps10.mpg.tu-dresden.de

Density functional approach to the valence change in SmS: normal and high pressure phase

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Abstract

The electronic structure of SmS in dependence of the lattice constant is calculated by means of density functional theory. The local density approximation (LDA) to the exchange and correlation potential is employed. The 4f-electrons, however, are treated in three different ways, i.e. (*i*) as localized core states, (*ii*) as extended band states, and (*iii*) as self-interaction corrected (SIC) band states. While the experimentally observed Sm valency of normal state SmS (black phase) cannot be described by methods (*i*) and (*ii*) the SIC calculations are consistent with the measured value. For pressures above 30 kbar, method (*ii*) agrees well with the observed Sm valency, whereas the methods (*i*) and (*iii*) fail. Therefore we conclude that the phase transition in SmS is very similiar to the α-γ transition in Ce metal. The SIC bandstructure shows the splitting between the occupied and empty 4f-states due to the large on-site electron correlation. The Fermi level ϵ_F is situated in the gap between the S 3p-states and the Sm bandstates mainly of 5d character. In the high pressure phase the 4f states become presumably delocalized resulting in vanishing self-interaction corrections. Therefore the uncorrected LDA results are appropriate for the high pressure phase.

(Phys. Rev. B, in press, presumably 15th Sept. issue)
LATEX + postscript files can by obtained from: manuel@tmps06.mpg.tu-dresden.de

First-principles molecular dynamics simulations for neutral and radical anion of p-chloranil

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Abstract

The neutral p-chloranil (2,3,5,6-tetrachloro-p-benzoquinone) and its radical anion are extensively studied by means of the Car-Parrinello projector augmented wave method which is an all-electron electronic structure method, for first-principles molecular dynamics based on the local density approximation of the density functional theory. Frequencies and eigenmodes are derived by fitting a system of harmonic oscillators to the molecular dynamics trajectories. Bond lengths and vibrational frequencies dependence on molecular ionicity are presented. Electron affinity, Coulomb repulsion and the spin-splitting parameter of p-chloranil are also estimated.

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Preprints available from : katan@univ-rennes1.fr, hoerner@univ-rennes1.fr

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STRUCTURAL PHASE TRANSFORMATION AND EQUATION OF STATE OF THE ALKALINE-EARTH OXIDES

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Abstract

The alkaline-earth oxides MgO, CaO and SrO naturally occur in the rocksalt (B1) structure. Under pressure they undergo a structural phase transformation to the cesiumchloride (B2) structure. Ab-initio local density non-local pseudopotential calculations of the total energy of the three compounds are performed in the B1, B2 and in the zincblende (B3) structure. It is found that the B1 structure is stable at normal conditions while the B3 structure is unstable under all conditions. The B1 to B2 phase transformation is found at respectively 1012.9 GPa, 61.0 GPa and 24.1 GPa. Experimental estimates of these transition pressures are 61 GPa and 63 GPa for CaO and 36 GPa for SrO. For MgO no experimental transition has been observed up to 227 GPa. The calculated lattice constants, bulk moduli and their pressure derivatives agree well with the experimental values.

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HIGH PRESSURE PROPERTIES OF THE ALKALINE-EARTH SULPHIDES

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Abstract

The alkaline-earth sulphides MgS, CaS, SrS and BaS naturally occur in the rock-salt (B1) structure. Under pressure they undergo a structural phase transformation to the cesiumchloride (B2) structure. Ab-initio local density non-local pseudopotential calculations of the total energy of the first three compounds are performed in the B1, B2 and in the zincblende (B3) structure. It is found that the B1 structure is stable at normal conditions while the B3 structure is unstable under all conditions. The B1 to B2 phase transformation occurs at respectively 230.7 GPa, 49.8 GPa and 20.9 GPa. Recent experimental estimates of these transition pressures are 256 GPa for MgS and 44 GPa for CaS. Another experimental value for CaS is 37.1 GPa. The calculated lattice constants, bulk moduli and their pressure derivatives agree well with the experimental values.

(in Phys.Sat.Sol. B190 193 (1995))
Manuscripts available from: vancamp@ruca.ua.ac.be

HIGH PRESSURE PHASE TRANSITIONS IN ALUMINUM PHOSHIDE

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Abstract

The electronic structure, the charge density and the total energy of AlP in the zincblende (B3), rocksalt (B1), nickelarsenide (B81), β-Sn (A5) and tungstencarbide (Bh) structures are studied using first-principles self-consistent local- density calculations in a plane wave basis employing soft non-local pseudopotentials. Similar to AlAs upon applying pressure, AlP transforms to the metallic nickelarsenide structure at a calculated pressure of 8.3 GPa, to be compared with a recent experimental value of 9.5 ± 5 GPa. The volume reduction at the transformation is calculated to be 20.5% (experimental value 17%). The equilibrium lattice constant of the nickelarsenide structure is found to be a=3.584 $\AA$ and c=5.74 $\AA$7. From this structure no transformation appears to be possible to the rocksalt or tungstencarbide structures but there is a further transition to the beta-tin structure at 199.8 GPa.

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Manuscripts available from: vancamp@ruca.ua.ac.be

GROUND STATE PROPERTIES OF TITANIUMDIBORIDE

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Abstract

The electronic structure, the charge distribution and the total energy of hexagonal titaniumdiboride are calculated using non-local pseudopotentials in both the local density approximation (LDA) and the generalized gradient expansion approximation (GGA). In the LDA we obtain a=3.023 $\AA$, c=3.166 $\AA$ and B_0=271.0 GPa. For these quantities the GGA values are slightly lower and both compare well with experiment. We also determined selected elastic constants by fitting the total energies to a quadratic surface in the lattice parameters. Using strains that do not break the hexagonal symmetry we obtain $C_{11}+C_{22}$=777.0 GPa, C_{13}=83.0 GPa and C_{33}=568.0 GPa. Again slightly lower values are obtained using the GGA. These values agree well with a recent experiment.

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Full-potential photoemission calculations for $KTaO_3$

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Abstract

In this contribution, we have calculated the electronic structure of cubic $KTaO_3$ using the self-consistent tight-binding linear muffin-tin orbital method (TB-LMTO) as well as the full-potential linear muffin-tin orbital method (FP-LMTO). Due to the generalization of the one-step model of photoemission to the case of several atoms per unit cell and the development of the full-potential photoemission theory, a detailed study of angle-resolved ultraviolet photoemission intensities (ARUPS) is possible now. Therefore, we present calculated photoemission spectra from the (100)-surface of a $KTaO_3$ crystal in the cubic phase by excitation with unpolarized NeI and HeI radiation. The results include a comparison of theoretical data calculated from TB-LMTO and FP-LMTO potentials with recently measured experimental spectra. The overall agreement between theory and experiment turns out to be very satisfactory.

(submitted to Surface Science)
Manuscripts available from: jbraun@dosuni1.rz.Uni-Osnabrueck.de

Magneto-optical properties of transition metal systems in the visible and X-ray regime

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Abstract

The basis of theoretical investigations of the magneto-optical properties of transition metals is outlined. It is shown that an appropriate description of the electronic structure has to account for both the spin-orbit coupling and the magnetic state of the system. Results of corresponding calculations on the magneto-optical Kerr effect in the visible regime of light, as well as of the magnetic dichroism in X-ray absorption are presented, and spectra are found to be in very satisfying agreement with experimental data.

(to be published in IEEE Magn. Transactions - Proceedings if INTERMAG 95)
A postscript file of the manuscript is available upon request from:
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An ab initio investigation of the hyperfine field anisotropy in Fe and Co multilayers

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Abstract

The magnetic hyperfine field in several Fe and Co multilayers have been calculated for both in-plane and perpendicular magnetization by using a relativistic band structure method. The anisotropy in the hyperfine field is pronounced and is connected with the large anisotropy in the orbital and magnetic dipole moments.

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On the origins of the enhanced magneto-optical Kerr effect in ultrathin Fe and Co multilayers

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Abstract

The magneto-optical Kerr effect in several Fe and Co multilayers have been calculated. Three possible origins for the enhanced Kerr rotations found in the ultrathin multilayers, namely, the increased interface Fe and Co magnetic moments, stronger spin-orbit coupling and induced magnetization in the heavy nonmagnetic elements, are investigated.

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Electronic Structure of Cerium in the Self-Interaction Corrected Local Spin Density Approximation

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Abstract

A scheme for performing electronic structure calculations using self-interaction corrections within the local spin density approximation to density functional theory is discussed. A practical implementation based on the tight-binding representation of the linear-muffin-tin orbital method is presented and applied to cerium metal. The two face-centered cubic phases of cerium are well accounted for by this approach. Two competing local minima of the total energy functional are found. In one of these minima the f-electrons are described as itinerant, i. e., they contribute significantly to the bonding, as is appropriate for the low-volume α phase. In the second minimum the f-electrons are localized and non-bonding, as observed for the γ phase. With a simple thermodynamic extension the $\alpha \leftrightarrow \gamma$ phase transition may be discussed, including the occurrence of a critical point in the phase diagram.

(submitted to Phys. Rev. B)
Manuscripts available from: svane@dfi.aau.dk

First-principles calculations of the vibrational properties of H centers in KCl crystals

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Abstract

The atomic and electronic structure of the radiation-induced interstitial halide atoms in KCl crystals (called *H* centers) is calculated using 16-atom supercells and the first-principles full-potential LMTO method. The vibrational properties of the *H* centers are studied for the two orientations of the molecular axis of the *H* centers known to exist in alkali halide crystals - along the (110) axis and (111) axis. Only in the former case (which is known to be energetically more favourable in KCl), the local vibrational frequency is close to that experimentally observed by means of the Raman spectroscopy. A strong coupling is found between the stretching molecular mode of the *H* center and the breating motion of its six nearest K^+ cations. This is predicted to result in another local mode around 257 cm^{-1}.

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Manuscripts available from: svane@dfi.aau.dk

LDA energy bands, low-energy Hamiltonians, t', t'', $t_\perp(\mathbf{k})$, and $J_\perp$

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Abstract

We describe the LDA bandstructure of $YBa_2Cu_3O_7$ in the $\epsilon_F \pm 2$ eV range using orbital projections and compare with $YBa_2Cu_4O_8$. Then, the high-energy and chain-related degrees of freedom are integrated out and we arrive at two, nearest-neighbor, orthogonal, two-center, 8-band Hamiltonians, H_8^+ and H_8^-, for respectively the even and odd bands of the bi-layer. Of the 8 orbitals, $\mathrm{Cu}_{x^2-y^2}$, $\mathrm{O2}_x$, $\mathrm{O3}_y$, and Cu_s have σ character and Cu_{xz}, Cu_{yz}, $\mathrm{O2}_z$, and $\mathrm{O3}_z$ have π character. The roles of the Cu_s orbital, which has some Cu_{3z^2-1} character, and the four π orbitals are as follows: Cu_s provides 2nd- and 3rd-nearest-neighbor (t' and t'') intra-plane hopping, as well as hopping between planes ($t_\perp$). The π-orbitals are responsible for bifurcation of the saddle-points for dimpled planes. The 4-σ-band Hamiltonian is generic for flat CuO_2 planes and we use it for analytical studies. The $\mathbf{k}_{||}$-dependence is expressed as one on $u \equiv (\cos bk_y + \cos ak_x)/2$ and one on $v \equiv (\cos bk_y - \cos ak_x)/2$. The latter arises solely through the influence of Cu_s. The reduction of the σ-Hamiltonian to 3- and 1-band Hamiltonians is explicitly discussed and we point out that, in addition to the hoppings commonly included in many-body calculations, the 3-band Hamiltonian should include hopping between *all* 2nd-nearest-neighbor oxygens and that the 1-band Hamiltonian should include 3rd-nearest-neighbor hoppings. We calculate the single-particle hopping between the planes of a bi-layer and show that it is generically: $t_\perp\left(\mathbf{k}_{||}\right) \approx 0.25\ \mathrm{eV}\cdot v^2 (1-2ut'/t)^{-2}$. The hopping through insulating spacers such as (BaO)Hg(BaO) is an order of magnitude smaller, but seems to have the same $\mathbf{k}_{||}$-dependence. We show that the inclusion of t' is crucial for understanding ARPES for the anti-ferromagnetic insulator $Sr_2CuO_2Cl_2$. Finally, we estimate the value of the inter-plane exchange constant $J_\perp$ for an un-doped bi-layer in mean-field theory using different single-particle Hamiltonians, the LDA for $YBa_2Cu_3O_6$, the eight- and four-band Hamiltonians, as well as an analytical calculation for the latter. We conclude that $J_\perp \sim -20$ meV.

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Quasiparticle bands and superconductivity in bilayer cuprates

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Abstract

We analyze the generic features of the energy spectrum for two coupled CuO_2 layers with a realistic extended Hubbard model. The quasiparticle bands exhibit flat regions near X(Y) points in the Brillouin zone with a large reduction of the bonding-antibonding splitting, and pinning of *extended* van-Hove singularity to the Fermi level, which is more efficient for a bi-layers than for a single layer. In contrast to the results with simpler models, the superconducting temperature for $d_{x^2-y^2}$ pairing is not lowered by the bi-layer hopping.

(submitted to Phys. Rev. Lett.)
Manuscripts available from: liechten@radix6.mpi-stuttgart.mpg.de

New Interpretation of X-ray Absorption Dichroism Experiments

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Abstract

A rule for extracting new information from X-ray magnetic circular dichroism spectra is derived. We show that it is possible to obtain the magnetic moment of the conduction band states probed by dipolar transitions with $j = l - 1/2$ separately from those with $j = l + 1/2$ as a function of energy. This quantity has not been accessible experimentally previously, but is straightforward to determine from the electronic band structure. The new rule is illustrated with an application to pure iron and to the random substitutional alloy $\mathrm{Fe}_{80}\mathrm{Co}_{20}$.

(accepted to Phys. Rev. B (Rapid Communication))
Manuscripts available from: pha05@cc.keele.ac.uk

Influence of gradient corrections to the LDA on the calculation of hyperfine fields in ferromagnetic Fe, Co and Ni

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Abstract

Results of hyperfine field calculations for ferromagnetic bcc-Fe, fcc-Co and fcc-Ni based on the scalar relativistic Korringa-Kohn-Rostoker (KKR) Green's function formalism and using various parametrizations for the exchange-correlation energy and the corresponding potential are presented. Especially the influence of gradient corrections on the electronic structure in the nucleus-near region is investigated. The resulting exchange potentials using these generalized gradient approximations (GGA) lead to the necessity to introduce a finite nucleus model instead of a point nucleus. This procedure removes the divergencies inherent in the general expression for the exchange potential of the GGA's as the radius r approaches 0. However, it has only little impact on the hyperfine fields, although pronounced changes in the charge densities in the nucleus-near region are observed. An explanation for this finding is given.

(submitted to Phys. Rev. B)
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Relativistic Influences on the Hyperfine Fields of Magnetic Metals

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Abstract

It is demonstrated that by application of the spin-polarized relativistic multiple scattering formalism all relativistic influences on the hyperfine interaction in magnetic solids are accounted for in a rigorous way. A decomposition of the corresponding hyperfine Hamiltonian into the familiar Fermi-contact, spin dipolar and orbital contributions is presented. This allows a detailed discussion of the resulting hyperfine fields. First applications are presented for the transition metal alloy systems $\mathrm{Fe}_x\mathrm{Ni}_{1-x}$ and $\mathrm{Co}_x\mathrm{Pt}_{1-x}$ showing that for non-s-electrons the orbital contribution due to the d-electrons is indeed dominating, as expected.

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Manipulation of the spin-orbit coupling using the Dirac equation for spin-dependent potentials

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Abstract

A scheme is presented that allows to manipulate the spin-orbit coupling in calculations based on the Dirac equation for spin-dependent potentials. To demonstrate its application the spin and orbital magnetic moments for the disordered alloy $\mathrm{Fe}_{0.20}\mathrm{Ni}_{0.80}$ as well as the Kerr rotation angle θ_K of pure Ni have been calculated as a function of the spin-orbit coupling strength. While the spin moment changes only slightly, the orbital moment as well as the Kerr rotation angle θ_K increase almost linearly with the spin-orbit coupling strength.

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Manuscripts available from: hf@nike.phys.chemie.uni-muenchen.de

Complex ion formation in liquid Ag-Se alloys

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Abstract

Ab initio molecular dynamics (AIMD) simulations are used to investigate the structure and electronic properties of liquid Ag-Se at three compositions. The difficulties of performing AIMD on a post-transition metal system are overcome by the use of massively parallel computing. The realism of the simulations is shown by comparing with diffraction data for ℓ-Ag_2Se. As the Se content is increased beyond the stoichiometric value, short-lived Se_n complexes are formed. The concentration of complexes and the associated changes of electronic structure can be explained using a simple ionic model.

(submitted to Phys. Rev. Lett.)
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Composition Dependence of the Structure and Electronic Properties of Liquid Ga-Se Alloys Studied by Ab initio Molecular Dynamics Simulation

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Abstract

Ab initio molecular dynamics simulation is used to study the structure and electronic properties of the liquid Ga-Se system at the three compositions Ga_2Se, GaSe and Ga_2Se_3, and of the GaSe and Ga_2Se_3 crystals. The calculated equilibrium structure of GaSe crystal agrees well with available experimental data. The neutron-weighted liquid structure factors calculated from the simulations are in reasonable agreement with recent neutron diffraction measurements. Simulation results for the partial radial distribution functions show that the liquid structure is closely related to that of the crystals. A close similarity between solid and liquid is also found for the electronic density of states and charge density. The calculated electronic conductivity decreases strongly with increasing Se content, in accord with experimental measurements.

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Ab-initio simulation of high-temperature liquid selenium

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Abstract

Ab initio molecular dynamics simulation is used to investigate the structure and dynamics of liquid Se at temperatures of 870 and 1370 K. The calculated static structure factor is in excellent agreement with experimental data. The calculated radial distribution function gives a mean coordination number close to 2, but we find a significant fraction of one-fold and three-fold atoms, particularly at 1370 K, so that the chain structure is considerably disrupted. The self-diffusion coefficient has values ($\sim 1 \times 10^{-8}$ m s^{-1}) typical of liquid metals.

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Towards a Linear-Scaling DFT Technique: The Density Matrix Approach

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Abstract

A recently proposed linear-scaling scheme for density-functional pseudopotential calculations is described in detail. The method is based on a formulation of density functional theory in which the ground state energy is determined by minimization with respect to the density matrix, subject to the condition that the eigenvalues of the latter lie in the range [0,1]. Linear-scaling behavior is achieved by requiring that the density matrix should vanish when the separation of its arguments exceeds a chosen cutoff. The limitation on the eigenvalue range is imposed by the method of Li, Nunes and Vanderbilt. The scheme is implemented by calculating all terms in the energy on a uniform real-space grid, and minimization is performed using the conjugate-gradient method. Tests on a 512-atom Si system show that the total energy converges rapidly as the range of the density matrix is increased. A discussion of the relation between the present method and other linear-scaling methods is given, and some problems that still require solution are indicated.

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The Influence of Gradient Corrections on Bulk and Surface Properties of TiO_2 and SnO_2

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Abstract

First-principles calculations based on density functional theory and the pseudopotential method have been used to investigate the influence of gradient corrections to the standard LDA technique on the equilibrium structure and energetics of rutile TiO_2 and SnO_2 perfect crystals and their (110) surfaces. We find that gradient corrections increase the calculated lattice parameters by roughly 3 %, as has been found for other types of material. Gradient corrections give only very minor changes to the equilibrium surface structure, but reduce the surface energies by about 30 %.

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The Adsorption of H_2O on TiO_2 and SnO_2 (110) Studied by First-Principles Calculations

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Abstract

First-principles calculations based on density functional theory and the pseudopotential method have been used to investigate the energetics of H_2O adsorption on the (110) surface of TiO_2 and SnO_2. Full relaxation of all atomic positions is performed on slab systems with periodic boundary conditions, and the cases of full and half coverage are studied. Both molecular and dissociative ($H_2O \rightarrow OH^- + H^+$) adsorption are treated, and allowance is made for relaxation of the adsorbed species to unsymmetrical configurations. It is found that for both TiO_2 and SnO_2 an unsymmetrical dissociated configuration is the most stable. The symmetrical molecularly adsorbed configuration is unstable with respect to lowering of symmetry, and is separated from the fully dissociated configuration by at most a very small energy barrier. The calculated dissociative adsorption energies for TiO_2 and SnO_2 are in reasonable agreement with the results of thermal desorption experiments. Calculated total and local electronic densities of states for dissociatively and molecularly adsorbed configurations are presented and their relation with experimental UPS spectra is discussed.

(submitted to Surface Science)
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Correlation entropy of the H_2 molecule

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Abstract

Non-interacting systems have idempotent one-particle density matrices (1PDM). The same is true for interacting systems within the Hartree-Fock approximation. Non-idempotency appears when the particle-particle interaction is switched on or correlation is taken into account. In terms of 1PDM eigenvalues (= natural occupation numbers), idempotency means that these occupation numbers equal exactly 0 or 1, whereas non-idempotency allows values between 0 and 1. This observation can be used to define (in terms of these occupation numbers) a q-order non-idempotency $c(q)$ or a Tsallis-type correlation entropy $s(q) = c(q)/(q-1)$ and a Shannon-type correlation entropy $s = s(1)$ as quantum-kinematic measures of the correlation strength. Here it is shown how this general idea must be adapted for finite (especially two-electron) systems in view of conservation laws which mix Slater determinants even in the non-interacting limit. (For example, the total spin of a finite system is conserved.) Results are presented for the correlation entropy s of H_2 as a function of the nucleus-nucleus separation R. In the ground state the entropy of the spatial factor of the wave function maximizes 1.7 bohr beyond the Coulson-Fischer separation. The role of the correlation entropy in density functional theory is also discussed.

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Temperature dependence of the transition metal magnetic susceptibilities

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Abstract

We present a method for calculating accurate Brillouin zone integrals of the Lindhard function at temperatures other than absolute zero. Within the linear tetrahedron method our expression is exact for the imaginary part and accurate to any arbitrary precision for the real part. We apply our method to calculate the temperature dependent contribution to the bulk susceptibility for a range of transition metals as a function of temperature using LMTO bands. For paramagnets our results follow the expected T^2 dependence. However our results for ferromagnets deviate qualitatively from the quadratic law. The different behaviour is attributed to interband and matrix element effects. Our results for Fe exhibit two distinct behaviours. We discuss the implications for calculation of anomalies arising from spin fluctuations.

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Presenting Other HCM Networks

The EPSI Network: Electronic Properties of Semiconductors and Insulators

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The EPSI Network is a network of ten research groups in theoretical condensed-matter physics in Europe, working on common projects in the area of the electronic and optical properties of semiconductors and insulators. The network has been funded by the European Union under the Human Capital and Mobility Scheme since 1 November 1993. The work of the Network focuses on the use of *ab initio* calculations to study the excited-state electronic and optical properties of materials. This is mainly directed towards calculations of the one-electron Green's function using many-body perturbation theory and a self-energy approach, typically the GW approximation, but also includes *ab initio* studies of the dielectric properties of materials and some fundamental problems in density-functional theory. In this article I aim to describe the Network and some of its major projects. The article will conclude by describing the location of further information, including a list of EPSI publications. The shorter list of references given in this article is only intended to be representative of EPSI activity.

Network Nodes (with node administrator shown in brackets)

- Physics Department, University of **Rome** "Tor Vergata" (Rodolfo Del Sole - Network Coordinator)
- Dept. of Physics, University of **Antwerp** (Jozef Devreese)
- Cavendish Laboratory, University of **Cambridge**; and Dept. of Physics, University of **York** (Rex Godby)
- Dept. of Applied Physics, **Eindhoven** University of Technology (Wim van Haeringen)

- Institut für Festkörpertheorie und Theoretische Optik, Friedrich-Schiller-Universität, **Jena** (Friedhelm Bechstedt)
- Department of Thoretical Physics, University of **Lund** (Ulf von Barth)
- Dept. of Physics, UNAM, **Madrid** (Felix Yndurain)
- Istituto di Struttura della Materia, Universita' di **Messina** (Raffaello Girlanda)
- Laboratoire des Solides Irradiés, Ecole Polytechnique, **Paris** (Lucia Reining)
- Max-Planck Institut, **Stuttgart** (Olle Gunnarsson)

Network Projects

The collaborative projects of the Network fall under the following headings:

1. GW Calculations

The usual procedure for *ab initio* calculations of the self-energy operator of solids is Hedin's GW approximation. This is the leading term in an iterative expansion of the self-energy in powers of the screened Coulomb interaction W between electrons, and is therefore successful in materials in which the screening is relatively strong, such as semiconductors, insulators, and simple metals. Calculations have been performed for bulk materials including the wide-gap semiconductor GaN [1] and NiO [2], and for more complex structures including a small sodium cluster [3]. In [3] the GW quasiparticle calculations were followed by *ab initio* calculations of the excitonic excitation spectrum. Other GW-related methods have been used for surfaces [4, 5, 6]. New *ab initio* technical developments include the elimination of sums over unoccupied states in self-energy calculations [3], the use of a cut-off Coulomb interaction to greatly expedite calculations [3], and the development of a real-space-imaginary-time method for self-energy and Green's-function calculations [7].

2. Beyond GW

The GW approximation is not expected to be adequate for materials in which the electronic correlation is strong. A theme of several collaborative EPSI projects is to investigate the limits of GW and the appropriate method of extending the theory beyond that level [8, 9, 10].

3. Dielectric and Optical Properties

Projects include a range of *ab initio* and model-based techniques for calculating the dielectric properties of various bulk and surface systems, including the dynamic structure factor for inelastic X-ray scattering [11], the screened Coulomb interaction for self-energy calculations [12], an investigation of the plasmon contributions to screening [13], and the optical properties of semiconductor surfaces [14].

4. Fundamentals of Density-Functional Theory

Some EPSI projects are aimed at obtaining an understanding of properties of the exact exchange-correlation energy functional, particularly those that are absent from the usual approximations. Recently completed work includes an investigation of exact DFT for a model semiconducting wire using Monte Carlo methods [15] and a study of exact DFT in the presence of a macroscopic electric field [16].

The EXCAM Network

A new Network on self-energy and related calculations, consisting of most of the EPSI members and one new nodes (Valladolid), is known as EXCAM (electronic exchange and correlation in advanced materials). It is hoped that funding will be granted by the EU under the new Training and Mobility of Researchers programme.

Further Information

A starting point for information about the Network's activities is the EPSI World Wide Web home page, http://www.york.ac.uk/~rwg3/epsi.html. This contains links to a list of EPSI publications, and addresses of EPSI members, who may be contacted for further information about particular work.

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HIGHLIGHT OF THE MONTH

First Principles Simulations of Nanoindentation and Atomic Force Microscopy on Silicon Surfaces

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Introduction

One of the most exciting trends in Solid State Physics in the last two decades is the fabrication of structures where several of the characteristic dimensions approach the atomic limit. Characterization techniques have evolved in the same direction, probing the properties of matter on progressively shorter scales. This is the case of indentation experiments, where the use of an atomic force microscope with a sharp indenter has made it possible to reduce the depth of the indentation from the several microns achieved in the 70's to just one nanometer[1]. At the same time, new techniques like the Scanning Tunneling Microscope (STM)[2] and the Atomic Force Microscope (AFM)[3] have been specifically devised to operate in the atomic scale. The development of these techniques and, especially, the interpretation of the images obtained with the tip–based microscopes should rely on a detailed knowledge of the interaction between the tip and the surface. The purpose of this paper is to show what we can learn about that interaction by the quantum mechanical simulation of the problem. The methods used, Total–Energy Pseudopotential calculations, were well established in the mid 80's, but their application have received a great impulse by the use of iterative minimization techniques, a work pioneered by Car and Parrinello[4], and the development of massively parallel computing. Nowadays, we are able to handle systems with hundreds of atoms, and tackle problems which are relevant to Material Science. In particular, we will show the ability of the technique in describing two extreme regimes in the tip–surface interaction problem: The nanoindentation regime, where tip and sample are in close mechanical contact, and the operation of the AFM in the attractive non-contact regime.

Atomic scale simulations using simplified interatomic potentials have already been applied to the problem of tip–surface interaction[5, 6, 7]. These studies have provided significant information about the process, but we consider that the explicit consideration of the electronic degrees of freedom provided by *ab initio* methods[8] is crucial to describe the breaking and remaking of bonds involved in the plastic response, and the weak interaction between the dangling bonds of the adatoms and the apex atom in the tip which provides the contrast mechanism in the non–contact AFM experiments.

Nanoindentation

In indentation experiments, an indenter –made out of a hard material– is pressed against the surface of a sample. From the deformation of the surface we can learn about the mechanical properties of the sample. For small indentations, there is a perfect elastic recovery of the surface, but in general plastic deformations are induced during the loading process, and they remain after the indenter is removed from the surface.

The typical output of these experiments is a relation between the load applied and the indentation depth. While the elastic contribution to these load–indentation depth curves can be handled in an exact way, using the classical solutions of Hertz, very little is known about the plastic deformation, and empirical relations for the yield strength of the material are used in their modelling. As we have mentioned before, the technique has moved in the direction of smaller indentations, and indentation depths of the order of nanometers are now feasible. Due to the higher loads per atom reached in these nanoindentations, plasticity effects are expected to become particularly important. Our simulations will describe the mechanical response of the system for these nanometer–size indentation and explore the microscopic mechanisms involved in the onset and development of plasticity and the active role of the bonding sites of the tip in this process. These results are relevant to the description of this particular regime, as well as to the modelling of the indentation tests used in materials characterization.

The system that we have considered is a supercell containing a hard metallic indenter, a Si (111) slab and a vacuum region. The indenter is a sharp tetrahedral tip built up of twenty Al atoms stacked in four (111)-FCC planes. The relative positions of the atoms in the indenter are held fixed during the whole indentation process. This model retains the most important characteristics of a hard metallic tip, providing an accurate description of the bonding between the atoms in the surface and those on the tip. The Si slab contains 240 atoms and is built up of eight (111) planes in an almost square two-dimensional $5\times3\ \overline{3}$ unit cell each containing thirty atoms. The upper surface of the slab in contact with the tip has a 2×1 Pandey reconstruction[9]. The bottom surface is kept unreconstructed by saturating each dangling bond with an H atom. The total dimensions of the supercell, including the vacuum region of 6.26 Å, are $19.2 \times 19.9 \times 28.15$ Å. Initially the indenter is placed on top of the uppermost buckled atom in one of the π–bonded chains. The orientation of the tip is symmetric with respect to the (110) planes of the slab.

The indentation process was simulated in a stepwise, quasi–static manner by making small movements of the tip normal to the slab. At each step the atoms in the slab were allowed to relax to their equilibrium positions (zero forces) for that particular position of the tip[10]. Optimized non–local pseudopotentials[11, 12] including only s and p components were used to describe the Al and Si ion cores[13]. The pseudopotentials were applied in the Kleinman–Bylander form [14] using the real space projection technique [15]. The electronic states were expanded at the Γ point of the Brillouin zone. A cutoff for the plane wave basis set of 7 Ry was used[16].

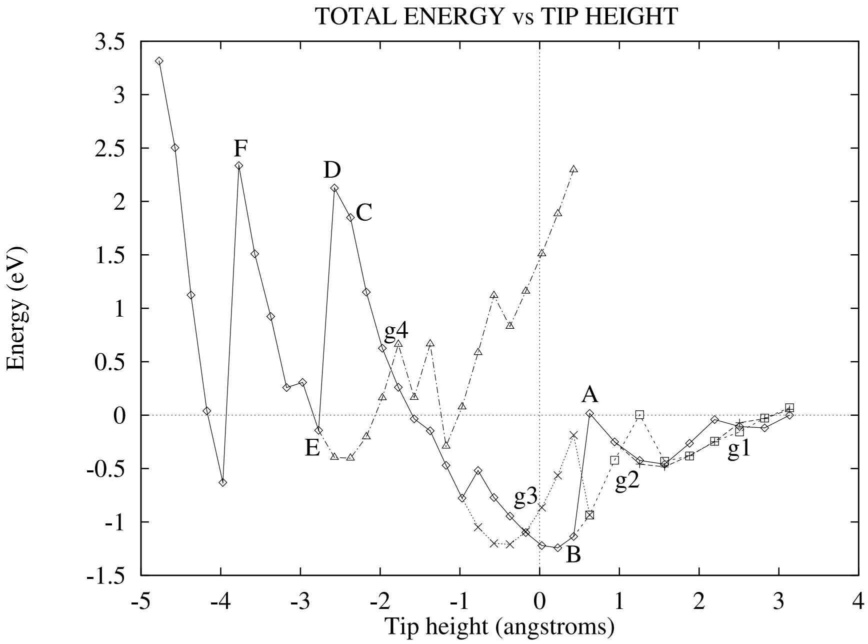

Figure 1: Total–energy of the system as a function of the the tip height. The continuous line corresponds to the indentation process while the different dashed lines refer to the retraction of the tip from different stages of the indentation process. The tip height is referred to the position of the last Si layer in an ideal Si (111) surface.

The total energy of the system for the different positions of the tip during the indentation process (black continuous line) and the retraction of the tip from different stages of the indentation (dashed lines) is shown in Fig. 1. We will consider first the indentation process. The results show a pattern of elastic deformations followed by plastic deformations seen as discontinuous jumps in the energy. These plastic deformations are associated with the breaking of few bonds where the stress has acumulated during the elastic regime. A few atoms in the structure undergo large displacements (of the order of 1 Å) to form a new stable bonding configuration in which the stress has been released. This new structure is elastically deformed upon further loading. The other remarkable feature in the total–energy curve is that it shows work hardening of the material: the stress necessary to produce those plastic deformations increases with the deformation.

As concerned the simulations pulling the tip back from different stages of the indentation process, the total–energy (dashed lines in Fig. 1) shows hysteresis, with several different stable structures for a given value of the tip height, and the system following different paths in the different backward displacements. This hysteric behaviour is related to the breaking of the bonds already formed between the tip and the sample during the loading process. More importantly, the plot shows a transition from perfect recovery of the original structure of the Si slab for small indentations to permanent damage when we unload from a point beyond the step where plastic flow in the second double layer has taken place.

A detailed account of the atomistic processes involved in plastic flow for the different stages of the indentation will be published elsewhere[17]. Let us just mention that two different regimes can be identified. The first one (A–C, in Fig. 1) is characterized by an increasing coordination of the atoms in the first Si surface double layer with atoms in the walls of the tip, and by elastic deformations induced in the Si second double layer. The competition between the bonds formed with the atoms in the tip and the elastic deformation induced in the Si tetrahedral network determines that, upon further indentation, those atoms undergo a stick–slip motion along the walls of the tip, recovering positions in the direction of indentation which are very close to the ones in the original undeformed structure. This stick–slip motion is responsible for the friction, and hence the dissipation observed in earlier simulations[7].

After step C the system can no longer resist the induced stress with a pure elastic deformation, and plastic flow in the second double layer is induced. The transition to this new regime is mediated by the *spontaneous* breaking of the symmetry of the displacement pattern in the [110] direction. The mechanisms which dominate the plastic response are the plastic flow to the interstitials, inside the slab, and the shear flow around the indenter in the surface. As indentation proceeds (E–F), the plastically deformed areas in the surface and below the indenter make contact and we reach the full plastic flow regime, with plastic deformation inside the slab becoming easier because of the upward displacements of atoms in the planes above[17]. The evolution of plastic flow observed in the simulation supports the model used in some continuum elastic theories of the indentation contact to include plasticity effects[18].

Finite temperature and strain rate effects, not considered in our quasi-static, T= 0 simulations are known to influence the indentation process. An estimate of their effect can be obtained by calculating the energy barriers at the crossing points between the different stable structures found in the total–energy diagram. These barriers have been determined for four different crossings (labelled g1–g4 in Fig. 1). In the first three cases (g1–g3), the barriers are quite low: 0.10, 0.12 and 0.30 eV. These processes can be thermally activated easily and the system would follow the lowest energy structure available, avoiding states of high stress like A. On the contrary, the last transformation (g4) has a high barrier of 1.20 eV. A more detailed account of the influence of temperature and strain rate will be given elsewhere[17].

In conclusion, we have presented the first quantum mechanical simulation of a nanoindentation process. The atomic mechanisms for plastic deformation in this regime have been determined: plastic flow of atoms towards interstitial positions inside the slab, and extrusion of material towards the tip at the surface, induced by the non–uniform volume strain and stabilized by the adhesive interactions with the tip. These adhesive interactions, disregarded in many continuum approaches to the problem, are also shown to be responsible for the friction through the induced stick–slip motion of Si atoms along the walls of the tip, the hysteric behaviour observed in the simulations pulling the tip out from different stages of the indentation process, and the recovery of plastic strains during unloading. The plastic deformations are triggered by the delocalization of the charge density induced by the stress in the elastically compressed structure. Finally, the onset of plastic irreversible deformation of the sample is related to the plastic deformation of the second double layer of the slab.

Atomic resolution in non–contact AFM

The Atomic Force Microscope (AFM) was developed as a tool capable of resolving surface structures of both conductors and insulators on the atomic scale, extending to a new whole class of materials the capabilities of the Scanning Tunneling Microscope (STM). The AFM probes the interatomic forces between a tip and a surface and their spatial variations. In the usual operational mode, the so–called constant force mode, the structure of the surface is determined by measuring the tip height which leads to a constant preset force between the surface and the tip as it scans the surface.

In principle, AFM images should be much simpler to interpret than the STM images since atomic forces reflect the total charge density (not the local density of states at the Fermi level), and so they are free of band-structure effects which prevent a direct interpretation of the STM images in terms of atomic structure. However, progress in force microscopy towards true atomic resolution has been slower, and there is a long–standing debate about the possibility of achieving true atomic resolution with the AFM. Many atomic-scale AFM images of crystalline solids have been published, but those images are taken in the contact regime, where the strong repulsive interaction between the tip and the sample provides the constrast mechanism. In this regime, local deformations of the sample and friction effects due to the adhesive interaction between tip and sample are known to affect the recorded topography. Most of the reported data show either perfectly ordered atomic structures or defects much larger than atomic–scale defects. On the other hand, images with point defects are routinely obtained with STM. These facts have raised the question whether the AFM is really a microscope like STM with true lateral resolution.

In the last two years several authors[19, 20] have claimed that it is possible to operate the AFM with atomic resolution, provided you work in the non–contact regime where the attractive Van der Waals forces acting between tip and sample are detected. Those forces are considerably weaker than the forces used in the contact mode, and, therefore, difficult to measure.

Recently Giessibl[20] has shown that atomic resolution is feasible in non–contact UHV conditions using a Si tip scanning a reactive surface, the reconstructed Si(111) 7×7 surface, and a novel force detection scheme that senses the force gradient, instead of the force itself, through frequency modulation[21]. In few words, the tip is subject to a positive feedback, so it oscillates at its eigenfrequency. As the sample approaches the tip, the force gradient of the tip–surface interaction alters the effective force constant and the frequency changes. A scan of the surface at a constant frequency shift creates a map of a constant average force gradient. The lower part of Giessibl's experimental image shows a multitip image of the surface, then the quality deteriorates, and suddenly, for the width of a unit cell, the characteristic protrusions associated with the 12 adatoms on the top layer of the reconstruction according to the DAS model [22] can be clearly seen. After this, the resolution deteriorates again, and no image is obtained for the rest of the scan. It should be notice that the motion of the tip during imaging is very complicated, with the tip mean position much further away from the surface than the expected range of the interaction. According to ref. [20] the distance between the tip and the surface at the closest point is 5 Å and the estimated attractive force, at that point, is -0.14 nN.

The work presented here involves the understanding of the mechanisms of image formation in non–contact AFM. In particular, the possibility of achieving atomic resolution with the Van der Waals interactions, which are not dominated by the interaction between the two closest atoms, and the changes in the tip structure which are related to the true atomic resolution observed in a small area of the experimental image.

We have studied these questions in two menbers of the series of Takayanagi reconstructions [22], the 3×3 and the 5×5, which contain the same features present in the 7×7, particularly the presence of adatoms. The system that we have considered is a supercell containing a Si(111) slab, two tips (one on each side of the Si slab) and a vacuum region. Inversion symmetry has been impossed on the supercell. The Si slab is built up of eight (111) planes with 68 (200) atoms in the 3×3 (5×5) case, in which the central two layers are kept fixed to simulate the bulk crystal termination of the surface. The lenght of the unit cell normal to the surface is 11 times the the double layer spacing in the [111] direction of the bulk crystal. The tips used in the experiment are etched out of single-crystalline Si. As the natural cleavage planes of Si are (111) planes is reasonable to consider that the very end of the tip is bounded by those planes. According to that, we have considered sharp tetrahedral tips with 4 and 10 Si atoms stacked in two (three) (111)-Silicon planes. We have saturated the dangling bonds of the atoms in the base of these tips with Hydrogen atoms, except in one case for reasons to be discussed below. The Si atoms in the base of the tip and the H atoms attached to them are held fixed during the scanning process.

The operation of the microscope was simulated in a stepwise, quasi–static manner by making small movements of the tip parallel to the slab at a constant height above the surface. At each step the atoms in the slab were allowed to relax to their equilibrium positions (zero forces) for that particular position of the tip. In the electronic structure part of the calculation we used the Generalized Gradient Approximation (GGA)[23] of density functional theory, following the prescription of White and Bird[24]. The technical details of the calculation are the same that in the nanoindentation simulations.

We want to explore other contrast mechanisms apart from the Van der Waals interaction. One of the likely candidates to provide a "bonding" attraction, bridging the distance between the tip and the surface, is the interaction between the dangling bonds in the adatoms and a dangling bond pointing out of the apex atom of the tip. In order to analyze this effect, scans in the 3×3 reconstruction have been performed using two different tips. They both have four Si atoms arranged in the same tetrahedral structure, the only difference being the presence or not of H atoms saturating the dangling bonds of the atoms in the base. This saturation changes the hybridization of the Si atoms in the base to a state close to the sp^3 of the bulk, and charge flows from the centre of the tetrahedra to the bonds with the hydrogen atoms and the Si-Si bonds, and the apex atom is left with three strong bonds with the other Si atoms and a dangling bond pointing out in the [111] direction.

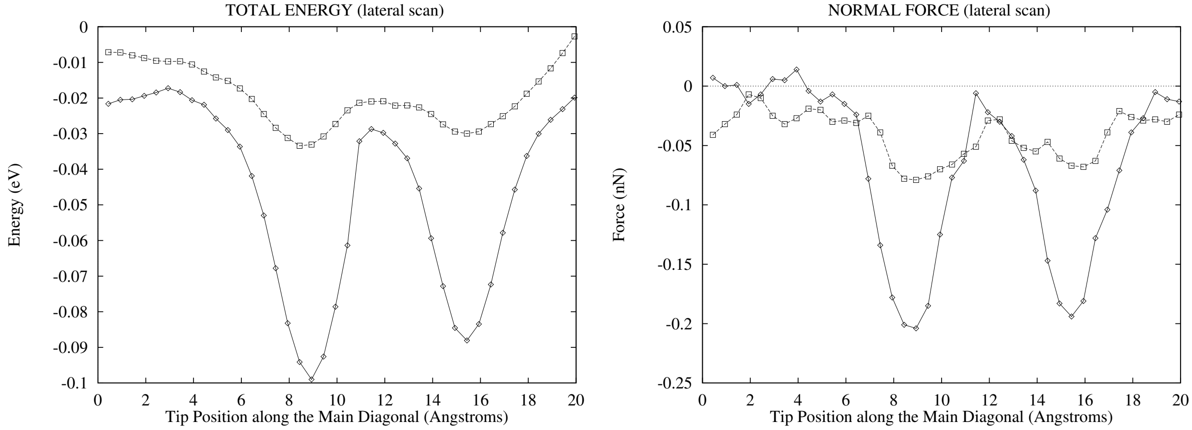

Figure 2: Total energy (in eV) and normal force (in nN) for the scan along the main diagonal of the 3×3 reconstruction at a constant height of 5 Å above the adatoms. The continuous (dashed) line corresponds to the tip with (without) a dangling bond. Both tips show minima at the position of the two adatoms in this reconstruction.

The total energy of the system and the normal force for the different positions of the two tips scanning along the main diagonal of the 3×3 reconstruction at a constant height of 5 Å above the adatoms are shown in Fig. 2. We will consider first the total energy. In each case, the zero of the energy corresponds to the sum of the total energy calculated independently for the slab and the tip using the same unit cell. Both tips show minima at the position of the two adatoms, the one in the stacking–faulted half being deeper, but there is a clear enhancement of the binding energy and, specially, of the contrast between the adatoms and other positions on the surface, when the scan is performed with the tip with the dangling bond pointing out from the apex atom towards the surface. Similar results are obtained in the case of the normal force, where the tip with the dangling bond shows a larger contrast between the position of the adatoms and those in between them or in the corner hole (left side of the figure). It should be noticed that the value of -0.2

nN obtained for the normal force when the tip is on top of one of the adatoms is close to the estimated experimental value.

It is interesting to compare those results with an estimation of the Van der Waals interaction of those tips with a Si surface[25]. Considering just the attractive part of the potential, a typical value for the interaction constant (the same for both Si and H), and a normal distance of 5 Å we obtain values of -0.03 eV and -0.07 eV for the two tips. While the first value is quite close to the value determined for the position on top of the adatom, the second one is clearly smaller than the value obtained in the first–principles calculation, suggesting that there is another contribution, apart from the Van der Waals interaction, to the binding energy of the system. In fact, the results are showing the onset of the bonding between the dangling bonds in the adatoms and the one of the apex atom in the tip. Clear evidence of this process comes from the comparison of the charge densities for the two positions in which the tip is on top of one of the adatoms: Charge accumulates in the region between the adatom and the apex of the tip, depleted from the backbond and from the dangling bond of the other adatom. The normal displacements of the adatoms during the tip scan are also consistent with this picture, with the adatom closer to the tip moving upwards, up to 0.05 Å and taking charge, while the other adatom moves downwards, and charge is removed from its dangling bond. The results for the constant–height scans on the 5×5 reconstruction, using a tip with ten Si atoms, where the dangling bonds of the atoms in the base have been saturated, confirm the picture obtained in the 3×3 case. Constant–force scans are currently being performed[26].

These results suggest an explanation for the sudden switch of the tip to atomic resolution observed in the experiments in terms of changes in the structure of the tip. If the tip picks up an atom from the surface, or it loses a contaminant, a dangling bond pointing towards the surface appears and the contrast is dramatically increased until that dangling bond is saturated again.

In summary, our simulations provide a clear understanding of the imaging process, showing that the range of operation, the values of the force, and the images determined experimentally, can be understood as a result of the interaction of the tip with the adatoms in the surface. Atomic resolution contrast is clearly enhanced by the interaction between the dangling bonds of the adatoms and the apex atom in the tip. The atomic resolution of the tip should be adscribed to the presence of a dangling bond in the apex of the tip, an esentially unstable situation. The contrast mechanism is related to the coupling between the tip and the charge transfer modes among the different dangling bonds in the surface, which have been observed in other experiments involving tip–surface interaction[27].

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Towards a "Quick and Dirty" Fully Variational Density Functional Theory Calculations

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This is to publicise some ideas floating around, perhaps to stimulate some discussion: actually three ideas.

The first is a comment by Eric Wimmer at a workshop (by Mike Finnis as a *Network* precursor) discussing 'order-N' methods for large systems. He said *"You know, it isn't larger system that is our main problem. There is plenty of good science that can be done with systems of the present size. The killer is more usually the size of the parameter space to be explored, and to do that requires faster codes".*
Consider an atom coming down on a surface. Two parameters are needed to specify where in the unit cell it hits, and three more for the direction and the magnitude of the incident velocity: and of course more parameters if it is an incident molecule. The same applies if one thinks about sliding at grain boundaries or crystal growth, in fact, the same is true of most applications to real problems in materials science, surface reactions, etc.. And of course one would really like to do them dynamically at finite temperature.

The second item is that there exists a further generalisation of the Harris-Foulkes functional which treats also the Kohn-Sham potential V_{KS} as an adjustible variable. One expands the wave function Ψ (to be precise the one-electron orbitals ϕ_i) in terms of some chosen set of functions, one puts into the generalised functional $G(\Psi, \rho, V_{KS})$ some suitably <u>*chosen*</u> charge density ρ, and solves the Kohn-Sham equations with a suitably <u>*chosen*</u> V_{KS}, where Ψ, ρ and V_{KS} are not made self-consistent. If everything is self-consistent, then G gives the usual density functional theory (DFT) energy; but if Ψ, ρ, V_{KS} are not self-consistent, then the error is second order in $\delta\Psi$, $\delta\rho$, δV_{KS}. It is no longer an absolute minimum. In fact it is a maximum under variation of V_{KS} alone, and minimal under $\delta\Psi$, $\delta\rho$, so that the situation is controllable if one wants to adjust V_{KS} etc. (which on the whole I think one does not want to do). This was shown by Michael Methfessel who derived the precise form of the second order error terms. We will give and prove the functional below. The point is that G gives an honest evaluation of our usual functional, with only second order errors.

The third question is whether one can now achieve what one may call the Foulkes objective (see his Ph. D. thesis, 1988), namely to develop tight-binding into a quantitatively useable tool, approximate but based on the variational property of the functional without arbitrary fudges. It would be a quick 'one-shot' calculation without self-consistency. This search caused him to rediscover the Harris functional and the present generalisation was already implicit in his work. Let us look at the three ingredients of the generalised functional. The basic purpose of writing down a wave function and solving the Kohn-Sham equation is to evaluate the kinetic energy. Here a minimal tight-binding basis set is known to give a good account of 'conformational' energy differences, i.e. depending on bond angles, as evidenced by the success of Hückel etc. theory and the critique of 'chemical pseudopotentials' by P.W. Anderson and Dave Bullett (see e.g. the discussion by Heine 1980). From chemistry one knows that 'contracted orbitals' are good, i.e. atomic orbitals pulled slightly inwards due to the energy lowering from the bonding. Similarly the charge density is to a good approximation a sum of slightly contracted atomic densities (see e.g. Robertson et al. 1991). Finally a good approximation to V_{KS} seems to be the Wigner-Seitz trick: when in atomic cell n, the electron sees the potential of a singly ionised ion. Namely, one assumes the exchange and correlation hole (containing correctly one electron) extends over the atomic cell n. Perhaps this is a bit too crude in highly ionic situations, but even there it is not bad: the more ionic one takes, say, the metal ion, the more attractive that potential becomes, but the more repulsive the Madelung addition to that potential from the surrounding negative ions. There is scope here for using variational power of the functional.

Otto Sankey (Demkov et al. 1995) already does something like this, though not quite, for various calculations involving SiO_2. Jose Ortega has used it to explore the migration of a Si ion from out of its tetrahedral cage of oxygens, and Sandro De Vita carried out full DFT calculations for several selected configurations. The two sets of energies tracked each other very well, with a consistent 30% difference in energy differences (as yet unpublished). The Sankey code ran 100 times faster than CASTEP (the Cambridge Serial Total Energy Package), a useful factor. Andrew Gibson (Gibson et al. 1993) has done calculation on a vacancy in MgO using the generalised functional and the above prescription for the basis set, ρ, and V_{KS}. Note that having chosen the basis, ρ, and V_{KS}, one must evaluate the functional accurately without further uncontrolled approximations which would destroy the variational nature. In particular, it seems all three-centre integrals in the tight-binding formulation have to be evaluated properly. I have heard this disputed, but Matthew Foulkes found (Ph. D. thesis 1988) that one could choose local orbitals such that three-centre contributions became small at some particular interatomic spacing, but that they did not remain small as one varied the spacing. The biggest problem lies in the representation of the V_{KS}. The straight application of the Wigner-Seitz Ansatz, as done by Gibson, results in very complicated shapes for the atomic cells and hence difficulties in handling the various integrals. Even in a perfect crystal the Ansatz is a mess, with each spherically symmetric ionic potential chopped off to zero at the planar faces of the Wigner-Seitz cell. What is to be done? The strict Wigner-Seitz Ansatz is a good approximation but one should be able to modify it to make it better for calculations without making the approximation worse.

Finally it remains to specify and prove the generalised functional. It is

$$G(\Psi, \rho, V_{KS}) = V_{ion-ion} + < \Psi | T + V_{ext} + V_{KS} | \Psi > - \int V_{KS} \rho d^3\mathbf{r} + E_e(\rho) \tag{1}$$

where $E_e(\rho)$ is the sum of the Hartree, exchange and correlation energies, as is V_{KS} in its way. Variation of G with respect to Ψ, or rather with respect to one-electron orbitals ϕ_i, and subject to the usual normalisation, gives the usual Kohn-Sham equation

$$(T + V_{ext} + V_{KS})\, \phi_i = \epsilon_i \phi_i, \tag{2}$$

where T is the kinetic energy. Variation with respect to ρ gives

$$V_{KS} = \partial E_e(\rho) / \partial \rho \tag{3}$$

as the usual definition of V_{KS}, and variation with respect to V_{KS} gives

$$\rho = |\Psi|^2 = \sum_i |\phi_i(\mathbf{r})|^2. \tag{4}$$

Thus we have proved that G is stationary with respect to variations of Ψ, ρ and V_{KS}, and we see from Eq. (1) that the correct DFT energy is obtained if the self-consistency equations (3), (4) are satisfied. That's it.

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