Ψ_k Newsletter

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

Number 74 April 2006

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1 Editorial

One of the most noteworthy entries in the current newsletter is the announcement in the **General News** section of this year's Agilent Technologies-Europhysics Prize, awarded to the inventors and developers of the Dynamical Mean Field Theory (DMFT), A. Georges, G. Kotliar, W. Metzner and D. Vollhardt, who are members of our Psi-k community. In particular, Antoine Georges was a plenary speaker, while Gabi Kotliar an invited speaker, at our Psi-k2005 Conference, presenting both the method and its applications to realistic systems. Both of them are also active in the RTN "f-electrons". Dieter Vollhardt was one of the contributors of a very useful scientific highlight on DMFT that was published in the Psi-k Newsletter No 56 (April 2003). Here we take the opportunity and congratulate all the winners on the occasion of this fantastic achievement.

The above announcement is followed by a number of conference/workshop/school announcements, as well as the available position announcements. The only report of this newsletter is in the **ESF Programme** section and refers to the recent EPSRC/ESF Workshop on "Water". It concentrates on problems discussed and seems rather useful. Abstracts of newly submitted or recent papers are in their usual section, followed by computer package and new journal announcements. The newsletter is finished with the scientific highlight of the month on **"Core-Level Shifts in Complex Metallic Systems from First Principles"** by W. Olovsson (Kyoto, Japan), C. Göransson, T. Marten, and I.A. Abrikosov (Linköping, Sweden). Please check the table of contents for further detail.

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

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

The above contains information on the Psi-k 2006 workshops and hands-on courses (subject to funding).

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

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

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

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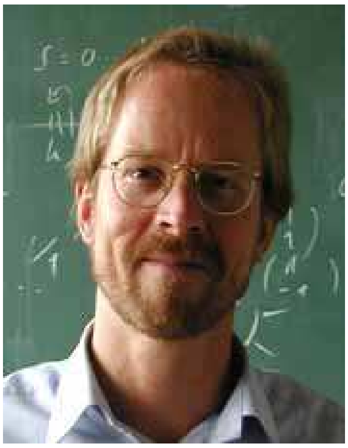
2 General News

2.1 2006 Agilent Technologies-Europhysics Prize

We are very happy to announce that **A. Georges** (*Ecole Polytechnique, Paris, France*), **G. Kotliar** (*Rutgers University, USA*), **W. Metzner** (*MPI Stuttgart, Germany*) and **D. Vollhardt** (*Augsburg University, Germany*)


A. Georges


G. Kotliar


W. Metzner


D. Vollhardt

have been awarded the 2006 Agilent Technologies-Europhysics Prize for **"The development and application of dynamical mean-field theory (DMFT)"**

(see also **http://www.agilent.com/contributions/europhysics.shtml**

and

http://www.eps.org/prizes/agitech.html).

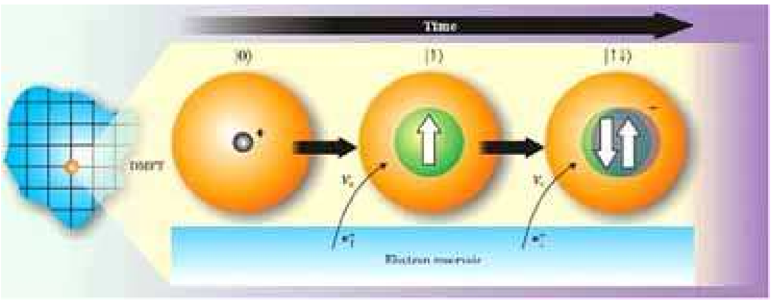


Figure 1: The Dynamical Mean-Field Theory treats the properties of solid materials as electrons fluctuate within it. This figure shows an atom successively capturing two electrons. Reprinted from Physics Today, March 2004, page 54.

" ... The fundamental physical principles that describe materials are well known, but the application of these principles is extremely complex... Dynamical Mean-Field Theory, in combination with other techniques, is able to describe the whole range of materials, encompassing weakly interacting and strongly localized models within one framework that can also handle the intermediate cases. One of the exciting theoretical steps is to imagine the material in a space of higher dimension and then make the approximation that the number of dimensions is infinite. This radical assumption greatly simplifies the equations and leads to remarkably accurate predictions.

The winners of the prize have applied their new theory to many materials, explaining phenomena that had previously been poorly understood, and making predictions that were subsequently verified by experiment. A rich new field of condensed matter physics has been created that will surely result in many important insights and discoveries in the years to come. Some of these discoveries will have direct application to the development of technology, making this an outstanding choice for the Agilent Technologies Europhysics Prize."

(Extracted from the Agilent Technologies Web Pages).

On the occasion of this important prize, let us remind you that in the Psi-k Newsletter No 56 (April, 2003), we had a very nice scientific highlight on the **"Realistic investigations of correlated electron systems with LDA+DMFT"** by K. Held (*Stuttgart*), I. A. Nekrasov (*Yekaterinburg*), G. Keller (*Augsburg*), V. Eyert (*Augsburg*), N. Blümer (*Mainz*), A. K. McMahan (*LLNL*), R. T. Scalettar (*Davis*), Th. Pruschke (*Augsburg*), V. I. Anisimov (*Yekaterinburg*), and D. Vollhardt (*Augsburg*), involving one of the winners of this year's prize.

3 News from the RTN on "f-electrons" (RTN2)

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

3.1 Workshop Announcements of RTN on "f-electrons"

Final Announcement

3.1.1 5th Workshop 'Hands-on FPLO' and FPLO Users and Developers Meeting

IFW Dresden, May 21-24, 2006

Registration deadline May: 10, 2006

Contact: m.richter@ifw-dresden.de

Supported by
IFW Dresden e.V.
RTN on "f-electron"

Organizers:

Helmut Eschrig, Klaus Koepernik, Ulrike Nitzsche, and Manuel Richter
(IFW Dresden, Germany)
Helge Rosner (MPI Chemical Physics of Solids, Dresden, Germany)

http://www.fplo.de/

The full-potential local-orbital (FPLO) code is an efficient and accurate tool to solve the Kohn-Sham equations of density functional theory. FPLO-6 is a completely re-shaped version of the previous FPLO code, with enhanced performance and stability. Features of FPLO-6 include:

no shape restriction to potential and spin density,
scalar/fully relativistic (4-component),
fixed spin moment method,
LSDA+U,
periodic systems with up to about 100 atoms per unit cell on single- processor machines,
clusters/molecules on the same footing as periodic systems.

The workshop will include:

Exposition of the method, introduction into the algorithms, handling of the FPLO electronic

structure calculation package ("Hands-on").
Exchange of experience amongst the users.
Presentation of recent applications and developments in electronic structure theory.

For capacity reasons (available terminals and tutors in the practical sessions) we will have to restrict the number of participants. The workshop will enable the newcomers to use FPLO-6, to interpret its output quantities, and to cope with simple handling problems. Experienced users and developers will meet to discuss recent or forthcoming implementations and interesting applications.

Registration:

The registration fee amounts to 100 EUR (banking information is found below), including meals and snacks but not the accommodation. It is refunded upon purchase of an FPLO-6 license. There is no registration fee for license holders of FPLO-5 and for members of RTN "f-electrons".

Please, send an email to Manuel Richter (m.richter@ifw-dresden.de) with the following information:

```
Name:
Email:
Address:
Arrival:
Departure:
I am interested in the hand's-on sessions: yes/no/details (specify)
I wish to contribute to the users session: poster/talk (specify)
I have payed the registration fee of 100 EUR: yes/no (give reasons)
```

Banking information for the payment of registration fee:

Name of bank: Dresdner Bank Dresden
Bank code: 850 800 00
Account: 410440701
Swift-Code(BIC): DRESDEFF850
IBAN DE73850800000410440701
reason 76 012 52 1 [please add your name]

Accommodation:

It should be organized by the participants.
Recommendation: http://www.city-herberge.de/

`Preliminary Program`

Sunday, May 21

19:00 Registration and get-together reception

Monday, May 22

Morning session: Getting started

09:00 Opening (Helmut Eschrig)
09:10 Getting started with FPLO-6 (Manuel Richter)
10:00 Installation and modifcation of the code (Ulrike Nitzsche)
10:45 Coffee
11:00 Task I: Convergence of k-summation
      Task II: Equilibrium lattice constant / bond length
      Task III: Code modifcation and installation
13:15 Lunch

Afternoon session: FPLO-6, new concept overview and recent add-ons

14:30 FPLO-6, a newly designed all-purpose DFT code (Klaus Koepernik)
15:30 Coffee
15:45 FPLO-6, a newly ... (continued, Klaus Koepernik)
16:30 Orbital polarization corrections (Mahdi Sargolzaei)
17:15 Implementation of PBE-GGA (Alim Hakan Ormeci)
17:30 de Haas-van Alphen module (Vivian Petzold)
18:00 Supper
22:00 Terminal access closed

Tuesday, May 23

Morning session: FPLO-6, features I

09:00 Fixed spin moment method (Michael Kuzmin)
09:45 Task IV: Fixed spin moment calculation
10:45 Coffee
11:00 LSDA+U method (Klaus Koepernik)
11:45 Task V: LSDA+U calculation
12:30 Four-component relativistic version (Ingo Opahle)
13:15 Lunch

Afternoon session: Users meeting I

14:30 Katrin Koch: The intrinsic defect structure of Al1x B2
14:45 Malgorzata Sznajder: Elementary energy bands
15:00 Werner Obermayr: On LCAO positron wave functions in crystals
15:15 Daniela Koudela: Lifshitz transitions in Osmium
15:30 Coffee
16:00 Klaus Koepernik: The story of CoN
16:15 Kwan-Woo Lee: Prediction of LDA+U method in layered transition metal oxides.
16:30 Helmut Eschrig: Overlayer Phase Diagrams at T=0.
18:00 Reception
22:00 Terminal access closed

Wednesday, May 24

Morning session: FPLO-6, features II

09:00 Strategies for complex problems (Helge Rosner)
09:30 Application of FPLO-6 to molecules (Klaus Koepernik)
09:45 Task VI: Molecules
10:45 Coffee
11:00 Evaluation of model parameters (Helge Rosner)
11:30 Task VII: Model parameters
12:30 Coherent potential approximation (Klaus Koepernik)
13;15 Lunch

Afternoon session: Users meeting II

14:30 Kemal Ozdogan: First-principles study of ferrimagnetism in Mn2VGa full Heusler alloy
14:45 three slots for contributions
15:30 Coffee
16:00 four slots for contributions
17:00 Closing (Helmut Eschrig)

4 News from the ESF Programme

"Towards Atomistic Materials Design"

4.1 ESF Workshop/School/Conference Announcements

4.1.1 Psi-k/NANOQUANTA SCHOOL and WORKSHOP

SECOND: Psi-k/NANOQUANTA SCHOOL + WORKSHOP PROPOSAL

"Time-Dependent Density-Functional Theory: Prospects and Applications"

August 27th to September 11th 2006
Benasque Center for Physics, Spain
http://benasque.ecm.ub.es/2006tddft/2006tddft.htm

Organizers:

E. K. U. Gross
Institut fuer Theoretische Physik,
Freie Universitaet Berlin
Arnimallee 14, D-14195 Berlin, Germany

Miguel A. L. Marques and Fernando Nogueira
Dep. de Física, Faculdade de Ciências e Tecnologia,
Universidade de Coimbra and Centro de Física Computacional
Rua Larga, 3004-516 Coimbra, Portugal

Angel Rubio
Dpto. Fisica de Materiales, Facultad de Quimicas U. Pais Vasco,
20018 San Sebastian/Donostia, Spain

History and Scientific motivation:

The first School and workshop was hosted by the Benasque Center for Science, Spain from August 28th to September 12th, 2004. The aim of the school was to introduce theoretical, practical, and numerical aspects of time-dependent density-functional theory (TDDFT) to young graduate students, post-docs and even older scientists that are envisaging a project for which TDDFT would be the tool of choice.

The use of TDDFT is increasing, and it is fast becoming one of the tools of choice to get accurate and reliable predictions for excited-state properties in solid state physics, chemistry and biophysics, both in the linear and non-linear regimes. This interest has been motivated by the recent developments of TDDFT (and time-dependent current functional theory) and include the description of photo-absorption cross section of molecules and nanostructures, electron-ion dynamics in the excited state triggered by either a small or high intense laser fields, van der Waals interactions, development of new functionals coping with memory and non-locality effects, applications to biological systems (chromophores), transport phenomena, optical spectra of solids and low-dimensional structures (as nanotubes, polymers, surfaces...).

Following our previous experience, the most efficient scheme for training of young researchers in these techniques is to have a school where the basic theory is taught followed by a workshop that introduces them to the forefront research in the field. The school should have an equal share of theoretical and practical classes. This would ease the learning of the techniques and would provide the students with the practical knowledge of the numerical aspects and difficulties, while also introducing them to well-established open source numerical codes. At the end of the school, students should have sufficient working knowledge to pursue their projects at their home institution.

The school will be followed by an international workshop, where the new developments of TDDFT and Many-Body Techniques for the calculation of excitations will be discussed. Students attending the school will be encouraged to attend the workshop, so they can get in contact with state of the art research in the field. The purpose of the workshop is to bring together leading experts in all these fields with different backgrounds, like density functional, many-body, nuclear physics and quantum chemists. This will allow the exchange of ideas between the different fields and the creation of links between the traditionally separated communities. We believe that the intense and informal discussion which is possible in this kind of workshops can contribute to the formation of a strong community in the field of TDDFT.

Location/Timing

We plan to organize this event at the “Benasque Center for Science”, Benasque, Spain, from August 27, 2006 to September 10, 2006. Benasque is a beautiful town in the heart of the Pyrenees. The school will take place from August 27 (Day 0 - arrival of students for the school) to September 6, and the workshop will start September 6 (arrival of participants to the workshop) and finish on September 11 (departure of all participants).
See http://benasque.ecm.ub.es/.

Participants

The call for participation will be mainly directed to students and scientists specialized on computational physics, quantum chemistry and biophysics. We will limit the number of students to the school to 35 and participants to the workshop to less than 100, in order to ensure a maximum interaction between all the scientists participating. Attendance of graduate students and postdocs will be strongly encouraged through the inclusion of short contributed talks and a poster session. Furthermore, we will award to PhD students who present an outstanding poster short oral presentations.

Applications/Support:

School/Workshop:

All persons who wish to participate should fill out the application form at

http://benasque.ecm.ub.es/2006tddft/2006tddft.htm

In the comments section, please indicate if you wish to participate in the Summer School or in the Workshop (or in both).

School only:

As we have a very limited number of places for the school (35), students will be selected from among an open pool of applicants who have demonstrated a strong interest in computational sciences, applied to chemistry, physics, materials science and biology. Therefore, in order that we can make a reasonable selection, we ask that *all* candidates include in the comments section the following information:

Date of birth
Sex
Motivation/Why they want to come (just a couple of lines is enough)
What is their current and previous positions (if PhD or Post- doc state your supervisor).

We will *not* accept applications that do not include this information. Furthermore, we will give priority to students willing to participate in both the Summer School and the Workshop.

We also have a certain number of grants available that cover traveling and part of the stay in Benasque. If you want to apply for a grant, please indicate explicitly that you wish to be supported in the comments section, and explain why (just a couple of lines is enough).

For participants coming from the USA, please check the following address for support:

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

4.1.2 Summer School on Electronic Structure Calculations and Correlated Materials

Les Houches, France

August 27th to September 8th 2006

Sponsored by:
Ecole Predoctorale des Houches, and Psi-k Network

Organized by:
Silke Biermann, CPHT, Ecole Polytechnique, France

and Bernard Amadon, CEA, Bruyeres-le-Chatel, France

Email: leshouches@cpht.polytechnique.fr

http://www.cpht.polytechnique.fr/LesHouches.html

In recent years, electronic structure calculations for materials with strong electronic Coulomb correlations have developed into a new research field at the border between band structure theory and quantum many-body problems. The summer school will give an introduction to different aspects of the field ranging from density functional theory and dynamical mean field concepts to the physics of the Mott transition.

Registration is now open at

http://www.cpht.polytechnique.fr/LesHouches.html

4.1.3 Tutorial on "Simulating matter at the nano-scale using density-functional theory, pseudopotentials and plane waves"

CECAM, Lyon

November 6-10, 2006

Sponsors: CECAM, MolSimu, Psi-k

Organizers:
Paolo Giannozzi, SNS Pisa and Democritos Trieste
Xavier Blase, Université Lyon 1 and CNRS
Ralph Gebauer, ICTP and Democritos Trieste

http://www.cecam.fr

This tutorial is aimed at students and young researchers who need an introduction to the field of electronic structure computations. It is also directed to non-specialists (e.g. experimentalists) who need to use the results of computer simulations for their work.

The tutorial will consist in morning lectures, followed by afternoon practical hand-on sessions. In the lectures, emphasis will be put on the fundamental concepts, illustrated by a variety of examples showing the merits, but also the limitations, of the various DFT implementations. In addition to standard ground state properties (equilibrium structure, cohesive energy, etc.) and Kohn-Sham orbitals analysis, an introduction to modern linear response theories (dielectric response, vibrational properties) will be provided. Finally, the concepts and tools of molecular dynamics (Verlet algorithm, thermostats, etc.) will be presented. In the hands-on sessions, examples of practical applications will be shown, using the Quantum-ESPRESSO distribution as computational tool.

The number of participants is limited to 30. Some background in condensed-matter physics or theoretical chemistry, and a basic knowledge of Unix (Linux), are required. Cecam and MolSimu will provide funding covering travel and living expenses for eligible participants. Interested people should apply via the web site `http://www.cecam.fr` (select *Tutorials* in the *Activities* menu; to apply please require a user and a password if you do not have any, and check that your application is "submitted", not just "open"). Notifications of acceptance will be sent starting in July. It will still be possible to apply until all slots are filled.

4.2 Reports on ESF Workshops/Conferences

4.2.1 Report on Workshop on Water, water everywhere; nor any drop to drink

4th-6th January 2006, Sheffield, UK

Funded by

Engineering and Physical Sciences Research Council (UK)
ESF Psi-k Network

Summary

The workshop was held at Sheffield 4th-6th January 2006 and comprised 29 delegates (list not attached). The meeting was partly funded by the European Science Foundation (through the Psi-k Network). The balance of the funding came from EPSRC (through a grant GR/S80103/01 ”Structural Modelling of the Biological Interface with Materials” headed by one of the organisers (John Harding)). The format of the workshop was deliberately informal. The programme was divided into eight sessions, each led by a chairman. The chairmen were invited to give a brief introduction to the session and then guide the discussion. The intention of the meeting was that there should not be formal conference presentations. Instead, participants brought powerpoint slides to illustrate the issues they wished to discuss. In the detailed report, those who gave a contribution of this kind are indicated at the end of each session.

The workshop brought together a wide range of people working on water (and problems that involve water) to discuss what the real problems are and what needs to be done to solve them with specific emphasis on the role of modelling. A major benefit of the meeting was this bringing together of a wide range of people, both theoreticians and experimentalists, to discuss a range of problems with a common theme. A synopsis of the discussions and conclusions for each session can be found in the detailed report below. A number of specific scientific challenges were identified:

- Simulation of the phase diagram of water
- Structure of water at interfaces and surfaces
- Structure of ice surfaces (and reactions at such surfaces)
- Importance of quantum effects (i.e. failure of the classical equations for nuclear motion) for water properties
- Full inclusion of water in biological simulations.

These were discussed in depth and as a result of the discussions, it is likely that a number of individual collaborations will be set up. It was agreed that the effect of the meeting had been

to constitute a network that should continue to meet. Plans were discussed to enable this (see below). Also, it was agreed that a topical review on water simulation should be written. Prof. Pat Unwin has suggested that we raise the matter with the managing editor of Physical Chemistry Chemical Physics (whom he knows personally) and this is currently in progress.

Detailed report

Session 1: Ab initio methods (leader: Mike Gillan)

The session began with an overview of the successes and failures of density functional theory (DFT) for bulk water; in particular the phase equilibrium and the critical point (essential for experimental comparison at the same reduced state point). The early DFT dynamical simulations [1] (but not in [2]) found that both structure and diffusion coefficients depended strongly on the exchange-correlation functional, a result confirmed by more recent work [3]. The BLYP functional appeared to agree well with experiment (radial distribution functions look respectable, as does the self diffusion coefficient: 1.3 x 10^{-9} m^2 s^{-1} (BLYP), 2.4 x 10^{-9} m^2 s^{-1} (expt). Early simulations were too short (few ps compared with 20-30ps used in more recent work). Later work [4] also showed that the fictitious mass used in [1] was too large. Even with much smaller masses however, some coupling between the classical motion of the electronic and ionic degrees of freedom remains. Grossman et al. [4a] recently reported that diffusion coefficients calculated by the Car-Parinello method differ from those calculated strictly on the Born-Oppenheimer surface by a factor of two. However, Kuo et al. [4b] did not observe such a difference between Car-Parrinello and Born-Oppenherimer dynamics and found no dependence of the diffusion constant on the fictitious mass (using values of 100, 200, and 300 a.u.). Gibbs ensemble MC calculations [5] show that the vapour-liquid coexistence curve depends strongly on the functional and the basis set. Also very large cutoffs (1200 Ry) were needed to get convergence. Results obtained using the SIESTA code (Emilio Artacho) show that a 20% temperature rescaling is needed to reconcile calculations with experiment. The RPBE functional appears to perform better [6] but this is likely to be due to cancellation of errors. Alfredsson's work shows strong basis-set dependence for water dimer calculations.

The main problem is that various functionals give different answers and it is not known why this is so. Careful calculations on sets of water clusters may help resolve this. Quantum Monte Carlo calculations are needed to investigate the adequacy of the functionals. It is unlikely that failure of the classical equations for atomic motion is relevant. Dispersion terms are not often considered and may be important. We need a hierarchy of modelling techniques, within which parameterized models and ab initio methods act in concert.

Main contributers: Ilja Siepmann, Philip Lindan, Emilio Artacho, Maria Alfredsson.

Session 2: Classical simulations and potentials (leader: Mark Rodger)

Parameterized interaction models for water go back many years. Well-known models include: SPC, TIPnP (n = 3, 4, 5..), AMOEBA, GCPM (Gaussian Charge Polarizable Model). There are over 50 such models [8]. Simple models use unpolarizable point charges on fixed sites in molecule; more sophisticated models are polarizable (dipole moment of H_2O molecule is 50%

greater in bulk than in gas). Shell models are sometimes used to include polarizability. All models are valid only over a limited range of thermodynamic states. The problem is finding suitable functional forms to parametrize. Many models have large numbers of parameters. The AMOEBA potential has 304 parameters, all of which might require re-fitting for a mixed system. Complex models are expensive to run; multiple timestep or perturbation methods can be used to speed them up. Models are fitted either to an empirical data set or (increasingly) to a combination where the charge distribution and multipole moments are fitted to quantum calculations and Lennard-Jones parameters to experiment. Gibbs-Duhem methods can be used to optimize and test potentials. We need to find a reasonable compromise between accuracy, transferability and expense. CONDOR pools offer an attractive tool for searching parameter space. A further problem for complex systems is the validity of mixing rules in obtaining potentials and what to do when they fail.

Main contributers: Jamshed Anwar, John Finney, Steve Parker, Ilja Siepmann, Dewi Lewis.

Session 3: Ions in solution (leader: Dave Sherman)

Understanding is needed for geological simulations, in particular the properties of metal complexes in solution as a function of temperature and pressure. Major questions surround the mechanisms of formation of hydrothermal ore deposits and the behaviour of metal complexation in high ionic strengths (60 wt% of NaCl) Often geologists use simple Born models of solvation and hope. The lifetime of water molecules in the first hydration shell ranges from 10^{10} sec (Ir^{3+}) to about 10^{-10} sec (Cs^+, Cu^{2+}). Potential-based calculations obtain good local geometries for the first hydration shell. Short residence times can be calculated directly from integrating over correlation functions; long residence times are obtained using transition state theory. A combination of MIES (Metastable Impact Electron Spectroscopy), photoelectron spectroscopy can be used to probe the behaviour of ions and metallic atoms in contact with amorphous ice and compared with classical MD simulations. Above about 120K, ice behaves rather like liquid water FOR solvation of alkali halide ions.

Main contributers: Steve Parker, Volker Kempter, Dewi Lewis.

Session 4: Ionisable water molecules (leader: Steve Parker)

Many problems involving water are pH dependent. An apparently simple solution is to use fixed concentrations of H_3O^+ and OH^-. This is not satisfactory, firstly because any absorption of these species at a surface changes the solution pH, secondly, the usual size of system used in simulations (a few thousand ions) means that the most important pH conditions cannot be modelled (for example in biological systems, pH is often around six). There are serious difficulties in obtaining reactive water molecules. If partial charges are used, what should the charges of the ions be? If fully charged models are used, the electrostatics needs to be damped. Charge equilibration models need clear rules for the adjustment of the charge. Combined MD/MC calculations (constant pH MD) can be used to obtain sensible structures for the system, but gives up the possibility of understanding the detailed dynamics. Rustad [11] has developed a potential based on the Stillinger-David model; Garafolini [12] has used a damped electrostatic model. Massimo Mella described quantum chemistry calculations to test models. Potentials of the Stillinger type agree with MP2 calculations up to $H^+(H_2O)_6$. Improved semi-empirical methods like PM3 may be a way forward. Also, can cluster calculations of this type be used as a "training set" for deriving new potentials. An allied problem is the simulation of the condensation (and ultimately self-assembly of zeolites (Lewis)). Basic reactions include $Si(OH)_4 + OH^- \rightarrow SiO(OH)_3{}^- + H_2O$. Reasonable results are obtained for these reactions and the water autolysis reaction $H_3O^+(H_2O)_3 + OH^-(H_2O)_4 \rightarrow (H_2O)_4 + (H_2O)_5$ provided that both a first coordination shell of water and a dielectric representation of the water (COSMO) are used.

Main contributers: Massimo Mella, Dewi Lewis.

Session 5: Mineral Interfaces (leader: Neal Skipper)

Questions that arise in the simulation of mineral/aqeous interfaces include (i) What are the interfacial ionic species? (ii) How do ions adsorb/desorb? (iii) What is the interfacial water structure? (iv) What is the extent of the aqueous interface? (v) What are the interfacial dynamics/kinetics? (vi)What are the effects of temperature and pressure? (vii) What is the effect of pH? Clay minerals (starting around 1990) have been the subject of a plethora of Monte Carlo and MD simulations using all known brands of water potentials. The water and surface oxygens usually assumed to have the same short-range parameters. Overall, excellent agreement with experiment obtained. Simple models have been used to investigate double layer effects and DFT calculations of speciation are available. Calculations combining these methods are, however, rare. Water on MgO has been studied by a huge range of ab initio methods [7] (Hartree-Fock, correlation-corrected Hartree-Fock, DFT, quantum chemistry). RPBE seems to be the functional of choice for water on TiO_2 (Lindan). Alfredsson's MD calculations show strong reconstructions for water absorbed on La_2O_3 (001) surfaces. Can static lattice calculations be of use in these problems or is MD essential?

Main contributors: Maria Alfredsson, Steve Parker, Mike Gillan, Philip Lindan.

Session 6: Biological systems (leader: Marie-Claire Bellissent-Funel)

Hydration water is found in living cells where it fills cavities and is bound at the surface of protein and membranes. It plays a major role in the stability and function of biological macromolecules. We must consider both the effects of proteins on the structure and dynamics of water and the effects of hydration on the structure, dynamics and function of proteins. At physiological temperatures, internal motions are partly vibrational, partly diffusive, some of which are required for function of proteins. The diffusive motions is of particular interest in the context of the dynamical or "glass transition", which is observed experimentally at $\sim$ 180-220 K. The characterisation of internal diffusion in proteins is complicated by the variety of the motions present, involving groups of atoms undergoing a plethora of continuous or jump-like diffusive dynamics. Dynamic neutron scattering is the most direct probe of diffusive protein dynamics on the ps-ns time scale. However, this technique provide us only with some average information. It is possible to attack this problem and get some detailed information on motions of various parts of protein as well as of hydration water by combining MD simulations (CHARMM force field, TIP3P model potential for water) with neutron results [15]. Other techniques such as NMR, IR, Raman spectroscopies can be associated. MD simulation in native protein environments seem to be the most promising way to achieve progress in this field, in particular to reach the structure and dynamics of water near biological macromolecules. A major problem, particularly with protein folding is that of looking for small differences between a set of large terms. $\Delta G_{\text{folding}} \sim 20$ kcal/mole (Finney); the various contributing terms involved can be well over ten times as great. Hydration cannot be neglected. Experimental neutron scattering measurements on a range of amphiphilic molecules that might serve as simple models for self-assembling systems suggest that popular 'standard' potential functions may often lead to structures that are qualitatively different from those found experimentally, perhaps suggesting problems in handling the balance between different competing interactions (e.g. solute- solute c.f. solute-water. The Solvent-Accessed Surface (SAS) can be obtained [16].

Water is also important for protein-substrate interactions. Walsh discussed the selective adsorption of hexapeptides on titania under aqueous conditions. No model of hydroxylated amorphous titania is currently available so the fully hydroxylated TiO_2 (110) rutile surface as a model surface. A potential due to Predota et al. [17] was used. Very few tests have been published for AMOEBA (bulk water simulations, small molecule interaction energies). Walsh tested AMOEBA for interactions of the COO^- group in water.

Main contributors: Tiffany Walsh, John Finney, Ilja Siepmann, Carmen Domene, Alex de Vries.

Session 7: Ice (leader: Alain Allouche)

In the interstellar medium, temperatures between 10K and 100K, ice is amorphous. This is however metastable with respect to ice XI, the thermodynamically preferred state. If ordered ice is cooled below 80K, proton order sets in. Amorphous ice is medium-range ordered and can be reasonably well simulated using a proton ordered model. The main reactive sites on its surface are the dangling OH bond (very sensitive infrared mode), the lone-pair dangling oxygen and the four-coordinate oxygen [18]. The dangling OH is indicative to any perturbation on the surface, this can be observed through its vibrational frequency shift. It has been shown that this frequency shift is quadratically related to the electric field variation along the OH bond. It has been shown that the strong ice surface electric field ($7 \text{x} 10^9$ Vm^{-1}) polarises layers of absorbed molecules that, in turn, induces a vibrational Stark effect in the OH bond [19]. The electric fields into the ice bulk are also partly responsible for electron trapping. This has been shown by combining MIES/UPS experiments with quantum DFT calculations on metallic sodium ionization in ice [20]. Quantum DFT calculations on dissociation on water ice surface have also been described for some small acids of interstellar or atmospheric interest [21], various DFT and mixed DFT methods were compared. It was shown (V.K.) how spectra [22], obtained with MIES, can be related to the DOS obtained from DFT calculations. The comparison of MIES spectra and the DOS was presented in detail for the interaction of Na atoms with a surfaces of amorphous solid water. The comparison suggests that the Na - induced dissociation of water molecules is initiated by the water - induced delocalization (solvation) of the 3s Na electron.

The complex phase diagram of ice is built from two ideas: each water molecule has two bonds and two hydrogen bonds so the coordination of the oxygens is always tetrahedral; the different possible arrangements of hydrogen bonds mean that structures can be disordered. The calculation of the ice phase diagram is a major challenge for models; calculations [9] using the TIP4P and SCP/E models show that the former is clearly better, but still far from reproducing the topology, let alone the phase boundary positions. Models should also be able to predict the metastable phases and the disordering. Maria Alfredsson presented some calculations on ice VIII using various hybrid functionals. The results show that functionals need to contain significantly more Hartree-Fock character than B3LYP to reproduce the ice structure. Still worse, different properties seem to require different amounts of exact exchange in their functionals. The AMOEBA potential and others can be shown to reproduce most of the water/ice phase diagram remarkably well. However, the ice XI is problematic because proton ordering is not well described by the pair potentials. Ben Slater showed that the deficiency is due to inadequate description of electrostatic multipoles - when terms up to the hexadecapole are included, proton ordering energetics can be reproduced accurately.

Main contributors: Maria Alfredsson, John Finney, Volker Kempter, Ben Slater.

Session 8: Common challenges; new perspectives (leader: Philip Lindan)

The workshop has underlined the problems that DFT functionals have in describing water. Calculations on simple systems (dimers?) desirable to find out exactly where the functionals are going wrong. The introduction of Quantum Monte Carlo methods is clearly desirable and is under way. We need a better potential for water, preferably incorporating dissociation. The basic problem is that of functional form. Comparison with DFT is not adequate because of the enduring DFT problems; training sets of clusters obtained at MP2-MP4 accuracy are needed. More effort is needed to make quantum and classical calculations work together through embedding strategies. Simulations at interfaces particularly have problems with length and timescales. A number of specific scientific challenges were identified:

- The phase diagram of water
- Structure of water at interfaces and surfaces
- Structures of aqueous solutions of ions and molecules
- Structure of ice surfaces (and reactions at such surfaces)
- Importance of quantum effects (i.e. failure of the classical equations for nuclear motion) for water properties
- Full inclusion of water in biological simulations.

In all these, the necessity of making explicit connections with experiment was emphasised.

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Results of the meeting and future plans

It was agreed that the meeting had been a highly successful review of the current state of modelling water. The format of the meeting worked well and there was a wide range of contributions from participants as noted above. In particular, the informal nature of the discussion encouraged contributions from younger research workers and also discussion both within and outside the individual sessions. The combination of a wide range of scientific interests with a focus on water enabled participants to identify problems that are common to several areas. A number of collaborations are likely to result from discussions at the meeting.

Particular areas where progress is needed clearly include:

- **The problem of the current choice of functional.** We need to understand why well-known functionals give different answers for water and how this can be put right. Careful calculations on sets of water clusters may help resolve this. Quantum Monte Carlo calculations are also needed to calibrate systems and work is already in progress to look into this.
- **Methods for fitting suitable classical potentials.** The basic problem remains of finding a reasonable compromise between accuracy, transferability and expense. The use of CONDOR pools as a tool for searching parameter space (particularly for complex potentials of the AMOEBA type) was emphasised.
- **The application of models for ions in solution to geological problems** was emphasised. Speakers pointed out the crudity of current methods of considering solutions at high concentration in the geological literature and the opportunities that this gave to more accurate simulations.
- **The need for an accurate model for ionisable water** was discussed. Many problems in interface chemistry in a wide range of fields are pH dependent and therefore require such a model if progress is to be made. The possibility of using improved PM3 models was canvassed. These issues were also raised in the discussion on mineral interfaces.
- **The proper inclusion of "hydration water" effects, particularly in proteins.** Moreover, there remains the computational difficulty of small effects that are the result of the subtraction of large individual terms. This is a particular issue for protein folding.
- **The simulation of the full phase diagram of water (the various ice phases)** is both a major challenge in itself and a test-bed for both ab initio and potential-based water calculations. The importance for proton ordering of calculating the correct electrostatics was demonstrated.

It was agreed that the meeting formed the basis of a possible network and that action should be taken to ensure that this network should continue to meet. Moreover, a number of possible collaborations emerged during the meeting, and a means of lubricating these should be looked for. Another meeting will be held in about a year's time and possible funding for this meeting has been identified. The organisers of this workshop (Harding and Lindan) have agreed to plan this. Second, it was agreed that an application should be made for a Marie-Curie Research Training Network under Framework 7 when the rules for the new organisation has been announced. In the meantime, the possibility of obtaining funding for a network from the UK Science Research Council (EPSRC) will be investigated.

Professor Pat Unwin (one of the participants) invited the meeting to submit a review article to Physical Chemistry Chemical Physics on the subject of water simulations. We intend to pursue this option. (There is an obvious problem with assigning authorship since such a review (implicitly or explicitly) would consist of contributions from most if not all of the participants. We have discussed this issue in detail with Professor Unwin and the problem is not insuperable.
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PROGRAMME

4th January

12:00-13:30 Lunch

13:30-15:00 SESSION 1: Developments in Ab initio calculations
Leader: MIKE GILLAN

15:00-15:30 Tea

15:30-17:45 SESSION 2: The state of water potentials:
classical simulations
Leader: MARK RODGER

18:00 Dinner

5th January

07:30-08:45 Breakfast

09:00-10.30 SESSION 3: Solutions: ions and molecules
Leader: DAVE SHERMAN

10.30-11.00 Tea

11.00-12.00 SESSION 4: Solutions: pH and ionisable water models
Leader: STEVE PARKER

12:00-13:30 Lunch

13:30-15:00 SESSION 5: Aqueous mineral interfaces
Leader: NEAL SKIPPER

15:00-15:30 Tea

15:30-17:45 SESSION 6: Biological systems and water
Leader: MARIE-CLAIRE BELLISSENT-FUNEL

18:00 Dinner

6th January

07:30-08:45 Breakfast

09:00-10.30 SESSION 7 Ice
Leader: ALAIN ALLOUCHE

10.30-11.00 Tea

11.00-12.00 SESSION 8: Common challenges and new perspectives
Leader: PHILIP LINDAN

12:00-13:30 Lunch

5 General Workshop/Conference Announcements

5.1 Materials Computation Center 2006 Summer School

2006 SUMMER SCHOOL ON COMPUTATIONAL MATERIALS SCIENCE

"Ab Initio Molecular Dynamics Simulation Methods in Chemistry"

July 31 - August 11, 2006

The Material Computation Center
University of Illinois at Urbana-Champaign

OVERVIEW

Our Summer School 2006 will focus on Ab Initio Molecular Dynamics (AIMD) Simulations and provide the background to understand and use AIMD techniques. An overview advanced electronic-structure and molecular dynamics methods and their interplay will be given. Both theory and practical applications of density functional theory and wavefunction based methods will be included, as will classical and quantum molecular dynamics.

The summer school will include focused sessions on use of high-performance computing techniques, and a hands-on introduction to the Quantum-ESPRESSO code for electronic-structure calculations, structural optimization, and AIMD.

Participants should have some familiarity with either electronic-structure theory or molecular dynamics techniques.

INVITED LECTURERS

S. Baroni, SISSA & DEMOCRITOS, Trieste
R. Car, Princeton University
T. Dunning, UIUC
M. Elstner, University of Heidelberg, Germany
M. Gordon, Iowa State University
S. Iyengar, Indiana University
G. Martyna, IBM Yorktown Heights
L. Mitas, North Carolina State University
T. van Voorhis, MIT

SCHOOL ORGANIZERS and LECTURERS

AIMD: T. Martínez, D. Ceperley, R. Martin, and D.D. Johnson (UIUC)
Quantum-ESPRESSO : N. Marzari (MIT) and P. Giannozzi (Scuola Normale Superiore, Pisa, and DEMOCRITOS, Trieste)
High-Performance Computing: J. Kim (UIUC)

APPLICATION and INFORMATION

Web: http://www.mcc.uiuc.edu/summerschool/2006

Email: summerschool@mcc.uiuc.edu

Application deadline: April 28, 2006

SPONSORS

The 2006 School is sponsored at UIUC in part by:

Materials Computation Center and National Science Foundation
National Center for Supercomputing Applications
Frederick Seitz Materials Research Laboratory
Computational Science and Engineering Program

The Summer School on Computational Materials Science is one of the education and training activities of the Materials Computation Center

http://www.mcc.uiuc.edu

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W. Green Street, Urbana, IL 61801
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MSE: http://www.mse.uiuc.edu

5.2 ACCMS Meeting in Japan

The Asian Consortium on Computational Materials Science

Sendai, Japan
7-9 September, 2006

We would like to bring to your attention that the ACCMS meeting (The Asian Consortium on Computational Materials Science) which will be held in Sendai, Japan.

Asian Consortium for Computational Materials Science (ACCMS) has entered into 5th year of its existence and we have successfully organized three conferences involving various active research groups in the Asian region. In order to optimally utilize our resources and manpower, it is widely felt that we should have a few working group meetings on the emerging areas of materials science. In view of the phenomenal growth in experimental as well as computational research in the field of clusters and nanomaterials all over the world, it is worthwhile to mobilize the community of people working in this area in different Asian countries and regions. We propose to have the first Working Group Meeting on Clusters and Nanomaterials organized under the banner of ACCMS and the Cluster Science initiative in Japan. The scope of this meeting will encompass fundamentals as well as application aspects of all nano-scale materials and phenomena. The deliberations will include theoretical as well as experimental research in this field.

The topics covered will include

Metallic and Semiconducting Clusters
Fullerenes and Nanotubes
Cluster Assembled Materials
Nano-spintronics Materials
Transport in Nanoscale and Molecular Electronics
Quantum Dots
Biological Materials
Methodologies for Size-dependent Properties

The venue, dates and expected number of participants and deadlines are :

Venue : Institute for Materials Research, Tohoku University, Sendai, Japan
Dates : 7-9 September, 2006
Expected number of participants : 100
Deadline for submission of Abstracts : 7 June, 2006

Programme Advisory and Execution Committee (Tentative):

Y. Kawazoe (Japan) : Convener
T. Kondow (Toyota), K. Ohno (Japan), G.P. Das (India)
J. Ihm (Korea), Q Sun (China/USA), V. Kumar (Japan/India)
K. Esfarjani (Iran), V. Belosludov (Russia

Local Organizing Committee

H. Mizuseki : General Secretary
M. Takahashi, T. Nishimatsu, R. Sahara, R. Belosludov
`http://www-lab.imr.edu/~accms/`

Contact : accmsgm1@imr.edu

Additional information about the conference can be found at

`http://www-lab.imr.edu/~accms/`

Please forward information on this conference to individuals who might benefit from participation.

Dr. Hiroshi Mizuseki
Institute for Materials Research
Tohoku University
URL: `http://www-lab.imr.edu/~mizuseki/contactus.html`

5.3 Amsterdam Conference

"Multi-scale modelling: Electrons, Molecules and (Bio)Materials"

3-5 April 2006

The detailed information on the conference can be found on the website

`http://www.knaw.nl/cfdata/events/events_detail.cfm?agenda__id=757`.

The conference has an impressive list of confirmed invited speakers.

First principle approaches to simulations of complex systems with lectures from K. Reuter (Berlin), M. Parrinello (Switzerland), R. Needs (Cambridge), B. Lester (Berkeley).

From inter-atomic potentials to macroscopic properties with lectures from F.F. Abraham (Almaden), D.N. Theodorou (Athens).

Mechanical properties with lectures from J. Yeomans (Oxford), E. van der Giessen (Groningen), E.A. Carter (Princeton), U. Landman (Atlanta).

Development of methods for multi-scale simulations and electronic structure calculations for large systems with lectures from K. Binder (Mainz), C. Dellago (Vienna), D. Bowler (London), G. Brocks (Enschede).

Macromolecules and biosystems with lectures from A. Louis (Cambridge), U. Röthlisberger (Lausanne), A. Chakraborty (Cambridge), W. Thiel (Mülheim).

Prof. dr. M. I. Katsnelson
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5.4 The 8th Prague Colloquium on f-Electron Systems & General Workshop Prague of the COST Action P16

September 8-11, 2006

We have the pleasure to announce that following the long tradition (since 1992), the 8th Prague Colloquium on f-Electron Systems will be again organized this year as a joint meeting with the General Workshop Prague of the COST Action P16.

The meeting covering various aspects of physics of lanthanides, actinides and genrally all materials with strongly correlated electrons will be organized as a satellite of:

44TH EUROPEAN HIGH-PRESSURE CONFERENCE,
SEPTEMBER 4-8, PRAGUE
http://kfes-80.karlov.mff.cuni.cz/EHPRG/

We are strongly determined to preserve the academic character of the Colloquium, relying on oral contributions with ample time for discussions in stress-free atmosphere of our University building, Ke Karlovu 5, Prague 2

http://www.mff.cuni.cz/toISO-8859-2.en/fakulta/budovy/kampus/karlov.htm .

There will be no proceedings, but contributors are encouraged to submit a short abstract.

The on-line registration and abstract submission is opened already - please visit:

http://kfes-80.karlov.mff.cuni.cz/PCFES8/registration/

As you may have noticed, there will be one day (September 8) overlap with the 44th European High-Pressure Conference, when relevant aspects of high-pressure research will be discussed.

The conference fee will be

80 Euro for regular participants
0 Euro (voluntary contributions possible) for students and retirees without any contract.

The free registration will be offered also to those, who paid the full registration fee for the 44th European High-Pressure Conference (unfortunately it will not work the other way around).

The fee will allow attending all technical sessions and will essentially cover the refreshments during coffee breaks, on-site parties and the rent for using the university premises.

For COST P-16 Participants the Colloquium has the status of the official COST workshop.

Official e-mail address of the Colloquium: pcfes8@mag.mff.cuni.cz

For the organizers:

Vladimir Sechovsky
sech@mag.mff.cuni.cz

Ladislav Havela
havela@mag.mff.cuni.cz

5.5 ICSFS-13 Conference

International Conference on Solid Films and Surfaces

http://www.cab.cnea.gov.ar/icsfs-13

6-10 November, 2006, Bariloche, Argentina

This is the first announcement of the ICSFS-13 Conference. Please forward this information to anyone you consider could be interested in attending this Conference. This is the premier ICSFS Conference to be held in Latin-America.

CALL FOR PAPERS:

The ICSFS-13 conference will focus on the advanced and novel physical and chemical properties of films and surfaces. This international meeting will feature the state "of the art" scientific achievements in the emerging fields of supramolecular objects, nanostructured materials and spintronic among others.

IMPORTANT DATES:

Open abstract submission and registration: May 1, 2006
Abstract deadline: July 20, 2006
Deadline for early registration: September 19, 2006
Deadline for manuscript submission: October 20, 2006

For further information, please visit

http://www.cab.cnea.gov.ar/icsfs-13 .

VENUE:

Bariloche is a tourist town located in the heart of the Nahuel Huapi National Park, in the Patagonia lake region. The host institution will be the Centro Atómico Bariloche one of the most prestigious research centers in Argentina.

H. Ascolani and M. Asensio

5.6 ICM2006 Conference

International Conference on Magnetism 2006

20-25 August, 2006, Kyoto, Japan

The registrations for ICM2006 have begun. Applicants can also book for accommodation and excursion programs during the Conference.

Please check the URLs shown below.

URL for registration to the Conference:

http://icm2006.com/regi.html

URL for booking accommodation:

http://www.jtb.co.jp/society/institution/icm2006/

URL for booking excursion programs:

http://www.jtb.co.jp/society/institution/icm2006/

Those who apply for registration in advance through the on line facility above by June 1 will be offered discount rates for early registration.

The Notice of Acceptance for selected Abstracts will be sent out via email around mid-April.

The organizers very much hope that the Conference hosts as many participants as possible from all over the world.

We look forward to receiving as many registrations as possible.

ICM2006 Conference Secretariat
FAX: +81-6-6456-4105
E-mail: icm2006@jtbcom.co.jp

6 General Job Announcements

Lecturer in Theoretical Physics

University of Bristol, Bristol, UK

Based within the Department of Physics, you will have an outstanding record of research, or outstanding research potential, in an area of theoretical physics that complements and enhances our current research activities. These include condensed matter theory, statistical physics, quantum information and geometric aspects of waves. Strong candidates in an existing area of research or those who bring new expertise to the Department for example theorists in the areas of nanoscience, biophysics and quantum optics, are encouraged to apply.

This post is part of a major strategic investment in the Physics Department which includes a several tens of million pounds development of the Departments teaching and research facilities.

In addition to the basic salary, this vacancy may attract a golden hello payment of 9k over three years (or a pro-rata payment for an appointment of less than three years or a part-time appointment) for a candidate who is working towards an Institute for Learning and Teaching in Higher Education recognised teaching award or equivalent and has not previously taught on a regular basis (at lecturer level) at a UK funded Higher Education Institution. Further details can be found at

http://www.bris.ac.uk/personnel/recruitment/goldenhellos.html

Grade : Lecturer Grade B Salary : £28,829 - £36,959

Professor J.F. Annett
E-mail: james.annett@bristol.ac.uk Tel: 0117 928 8752

Alternative Contact: (Department of Physics)
Professor R. Evans
E-mail: bob.evans@bristol.ac.uk
Tel: 0117 928 8703

Closing Date : 20 April 2006
Interview Date : not set
Timescale of Appointment(s) - Contract : Permanent

Further details and an application form can be found at

`https://www.bris.ac.uk/boris/jobs/ads?ID=47016`

Alternatively you can telephone (0117) 954 6947, minicom (0117) 928 8894 or E-Mail Recruitment@bris.ac.uk (stating postal address ONLY), quoting reference number 11933.

The closing date for applications is 9.00am, 20 April 2006
An Equal Opportunities Employer.

Post-Doc/Research Associate Position

Catalysis on Complex Oxide Surfaces

Center for Theoretical Chemistry, University of Bochum, Germany

Applications are invited for a research associate position that is expected to become available in July 2006.

The ideal candidate would have significant experience in plane-wave-based density functional calculations. A PhD in theoretical physics, chemistry, or related field is required. He or she will be involved in a number of challenging research projects in the realms of heterogeneous catalysis and nanostructured surfaces (see e.g. PRL 95, 266104 (2005); PRL 95, 136101 (2005); PRL 95, 096102 (2005); Angew. Chem. Int. Ed. 44, 2790 (2005); Angew. Chem. Int. Ed. 43, 6641 (2004) for recent work). The project will strongly benefit from collaborations with other theory groups as well as experimental groups within our Collaborative Research Center SFB 558 "Metal-substrate interactions in heterogeneous catalysis". Information on the techniques used and developed at CTC are accessible via www.theochem.rub.de/go/cprev.html.

The Center for Theoretical Chemistry at RUB offers an exciting interdisciplinary research environment and excellent facilities including several high-performance parallel platforms in house, see

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

Candidates should send a detailed resume including an outline of their research achievements and interests as well as contact information for academic references to

Dr. Bernd Meyer or Professor Dominik Marx
Lehrstuhl fuer Theoretische Chemie
Ruhr-Universitaet Bochum
44780 Bochum, Germany
Email: office@theochem.rub.de

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

Ph. D. Studentship

"Quantum Simulations of Complex Molecular Systems"

Center for Theoretical Chemistry, University of Bochum, Germany

Applications are invited for a Ph. D. position embedded in our international doctorate study program, www.rub.de/gscb, which promotes international postgraduate education. The preferred starting date would be in spring or summer 2006.

You will learn about state–of–the–art quantum simulation techniques (such as ab initio path integral MD and MC) and apply them to challenging problems in order to understand complex molecular processes in collaboration with experimental groups. Candiates should have, or be about to receive, an honors degree in Physics or Chemistry with a solid background in theory.

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

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

The Center for Theoretical Chemistry at RUB offers an exciting interdisciplinary research environment and excellent facilities including several high-performance parallel platforms in house, see

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

Candidates should send a detailed resume including an outline of their achievements and interests as well as contact information for academic references to

Professor Dominik Marx
Lehrstuhl fuer Theoretische Chemie
Ruhr-Universitaet Bochum
44780 Bochum, Germany
Email: office@theochem.rub.de

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

Postdoctoral Positions
in Computational Condensed Matter Physics
College of William and Mary, Williamsburg, Virginia

Two postdoctoral positions are available at the College of William and Mary in computational condensed matter physics, in the areas of (1) electronic structure of materials and (2) ultra-cold atoms. In (1), the focus is on the application and development of quantum Monte Carlo (QMC) methods to study electron correlations in model and realistic systems. In (2), the focus is on simulation studies of strongly interacting ultra-cold atoms, including trapped atomic gases and optical lattice systems. More information about the group can be found at

`http://www.wm.edu/physics/condensed-matter-theory.php`

and

`http://physics.wm.edu/~shiwei`

Candidates with interests and background in either area are encouraged to apply. Experience in computational approaches (e.g., QMC, or mean-field calculations for cold atoms, or density-functional or quantum chemistry methods for electronic structure) is desirable. Candidates should send a CV and arrange to have three letters of recommendation sent to

Prof. Shiwei Zhang (shiwei@physics.wm.edu).

Consideration of candidates will begin immediately and will continue until the positions are filled.

The College of William and Mary (W&M) is located in Williamsburg, Virginia, about 150 miles from Washington D.C.

W&M is an EO/AA employer.

Available Postdoc Position

in Electronic-Structure Theory and Applications to Materials Properties

Theoretical Division of Los Alamos National Laboratory

I am looking for a postdoc to work with me on first-principles and tight-binding electronic-structure calculations, including extensions to DMFT and electronic correlation effects. Applications to phonons, thermodynamic, and other materials properties will also be involved. Most of the materials will involve d- and f-electron metals. The position is open immediately; however, some allowance can be made for the candidate to finish a degree or current postdoc position. All positions are initially for one year, and could be renewed up to a possible maximum of 3 years.

If you are interested, please send a Curriculum Vitae and 3 letters of recommendation to

Robert C. Albers, Group Leader
Condensed Matter & Statistical Physics Group
Theoretical Division, Group T-11, MS B262
Los Alamos National Laboratory
Los Alamos, NM 87545
E-mail: rca@lanl.gov
Phone: (505)665-0417, Fax: (505)665-4063

Postdoctoral Position

Institute of Mineralogy and Physics of Condensed Matter (IMPMC)

University of Paris VI, Paris, France

A postdoctoral position is available at the Institute of Mineralogy and Physics of Condensed Matter (IMPMC, University of Paris VI) on the fall 2006. Our group is active in both developement and application of the density functional perturbation theory (DFPT) methods to compute the spectroscopic and structural properties of materials. Special attention is paid to infrared and Raman spectroscopy. The goal of the project is to describe the vibrational properties of transition metal oxides with open d electron shells, studying the impact of the magnetic and electronic structure of the metal ion. To this purpose, we plan to use DFPT and to extend it beyond DFT using approaches as DFT+U and dynamic mean field theory. This work is done in close collaboration with experimentalists and is part of an interdisciplinary project focusing on the vibrational properties of Earth materials. It will provide new constrains on the evolution and transformation of natural systems.

Selected publications:

Balan E., Mauri F., Lemaire C., Brouder C., Guyot F., Saitta A.M., Devouard B., (2002), Multiple ionic plasmon resonances in naturally-occurring multiwall nanotubes: infrared spectra of chrysotile asbestos, Physical Review Letters, 89, 177401.

Balan, E., Saitta, A.M., Mauri, F., and Calas, G., (2001), First-principles modeling of the infra-red spectrum of kaolinite, American Mineralogist, 86, 1321-1330.

Lazzeri, M. and Mauri, F., (2003), First principles calculation of vibrational Raman spectra in large systems: signature of small rings in crystalline SiO2, Physical Review Letters, 90, 036401.

Pickard, C. and Mauri, F., (2002), First-Principles Theory of the EPR g Tensor in Solids: Defects in Quartz, Physical Review Letters, 88, 086403.

Contacts: etienne.balan@impmc.jussieu.fr, michele.lazzeri@impmc.jussieu.fr,
francesco.mauri@impmc.jussieu.fr

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tel : 01.44.27.74.52
fax : 01.44.27.37.85
Web: `http://www.lmcp.jussieu.fr/~balan`

Postdoctoral Position
CRISMAT Laboratory, Caen Cedex, France

A post-doc position will be shortly opened for a theoretician in the CRISMAT laboratory under the ANR contract in order to work with Marie-Bernadette LEPETIT.

Research project

The research project is the electronic structure of "multiferroic" oxides with magneto-electric properties. It aims at understanding the microscopic mechanisms underlying the coupling between the magnetic and ferroelectric layers, using ab-initio calculations.

Practical aspects

The initial contract will be for one year, possibly renewed for an additional year. It could start anytime between April and September 2006. Candidate should be aware that there is not any nationality requirements in the ANR contacts.

Candidate

The candidates should be Physics or Chemistry Ph. D. holders with a good experience of ab-initio calculations. A knowledge of DFT methods and/or the CI methods will be particularly appreciated.

Applications

Applications including a Curriculum Vitae, copies of the best papers of the applicant and recommandation letters, should be send to

Marie-Bernadette LEPETIT
CRISMAT - ENSICAEN
6 bd du maréchal Juin
14050 Caen Cedex
FRANCE
Phone : (+33) 2 31 45 29 13
E-mail : lepetit@ensicaen.fr

Ph. D. Studentship

"Theory of Functionalized Nanostructures on Surfaces"

Surface Science Research Centre/Department of Chemistry
University of Liverpool, UK

A University-supported postgraduate research studentship is available from October 1, 2006 to work on a project supervised by Prof. Mats Persson (`http://www.liv.ac.uk/~mpersson`) in the Surface Science Research Centre (http://www.ssci.liv.ac.uk) with high international research profile.

The project concerns computer simulations and modelling in the field of atomic scale manipulation and characterization of nanostructures with desired functions on surfaces. The simulations and modelling will primarily be based on density functional theory. The proposed work will be carried out in close collaboration with leading experimental groups. Candidates should (be about to) receive a Masters degree or equivalent in physics or chemistry and should be highly qualified. Experience of computational physics/chemistry is essential. The studentship is not available to citizens of non-EU countries.

Enquiries to Professor Mats Persson on email: mpersson@liv.ac.uk or by phone +44-151-794-3872.

Closing Date: April 15, 2006 and continues until post is filled.

Applicants should send their CV with a few references by e-mail (mpersson@liv.ac.uk) to Mats Persson.

Ph.D and Postdoctoral positions in Computational Materials Physics

University of Twente, Enschede, The Netherlands

2 PhD/**5 Postdoc** positions in Theoretical Condensed Matter Physics/Computational Materials Science are available for *graduates*/PhDs with a top grade in theoretical physics or chemistry to carry out research on

- Quantum Transport: Spin and Molecular Electronics
- Materials-specific studies of the physical properties of novel Nano-Electronic Materials

The research is funded by the Dutch NanoNed program and the Chemical Science (CW) Foundation's Echo program. Two of the projects will be carried out in collaboration with Prof. J. van den Brink at Leiden University. Common to all the projects is the use of ab-initio electronic structure calculations to study the physical properties (magnetic, optical and electrical) of condensed matter and to relate them to their chemical composition and atomic structure. Candidates will be expected

- to *acquire*/**have** a broad knowledge of theoretical condensed matter physics,
- to study in detail modern methods of electronic structure theory,
- to develop new theoretical methods in a form suitable for numerical implementation and
- to apply them to the relevant problems.

Experience with modern methods of electronic structure calculation is *desirable*/**necessary**. Successful candidates will get a contract for *4*/**1+** years. The gross salary for a *PhD student* in the first year is *1,877.-* per month which will increase to *2,407.-* in the fourth year. For **postdocs**, salaries are in the range **2,639. - 3,472.-** per month depending upon experience.

Candidates *(PhD candidates should not be older than 26 years of age)* are invited to submit applications including a CV, list of university courses followed and grades obtained, **a list of publications** as well as the names and full contact details of 2 referees to:

Prof. P.J. Kelly,
Faculty of Science and Technology,
University of Twente,
P.O. Box 217,
7500 AE Enschede,
The Netherlands

E-mail: P.J.Kelly@utwente.nl
Tel.: +31-53-4893166
Homepage: http://cms.tnw.utwente.nl/

from whom particulars about each of the positions can be obtained.

Postdoctoral Position
University Duisburg-Essen, Duisburg, Germany

The newly formed theory group ”First-Principles and Statistical Methods in Materials Physics” (Prof. P. Kratzer) invites applications for a post-doc position in the field of

***ab initio* simulations of processes at surfaces**

The project requires a strong background in surface physics and in the methods of first-principles electronic structure theory. The successful candidate should preferentially have expertise in one of the following areas

- adsorption dynamcis on surfaces
- electronic excitations and time-dependent density functional theory
- theory of epitaxial crystal growth

The project forms part of the collaborative research efforts at the Physics Department in the Center SFB616 (”Energy Dissipation at Surfaces”) funded by Germany's National Science Foundation DFG.

Information about our research can be found at

http://www.physik.uni-duisburg-essen.de/fbphysik/AGWEB/Kratzer/

The University of Duisburg-Essen aims at enhancing the proportion of females in science. Therefore, applications from women are particularly welcome, and preference will be given to female candidates with equal skills, abilities and professional qualifications. Applications from persons with disabilities are welcome. Preference will be given to disabled candidates with equal skills.

Further inquiries and applications with a complete CV and list of publications should be sent to:

University Duisburg-Essen, Dekanat Fachbereich Physik, Lotharstr. 1, 47048 Duisburg, Germany

PhD Position
Institute for Crystal Growth (IKZ), Berlin, Germany

The scope of the position is the investigation of the growth kinetics during MOCVD of oxide layers by means of ab-initio and kinetic Monte-Carlo simulations.

The investigation of the growth of oxide layers with piezo- and ferroelectric properties is an interdisciplinary research topic at the IKZ. Both experiments (Group ,,Oxide Layers“) and numerical calculations (Group ,,Numerical Modelling”) are performed at the IKZ.

The ab-initio calculations should give information about diffusion pathes and barriers and can be performed in close co-operation with the Independent Junior Research Group (PD Dr. Karsten Reuter) at the Fritz-Haber-Institute of the Max-Planck-Society. The results of these calculations should be used for the further development of the kinetic Monte-Carlo program. The results of calculations with various process parameters should be compared with experiments. A close collaboration with the group ,,Oxide Layers“ is expected.

Requirements:

Candidates should have good knowledge in solid state physics and in programming (C,C++). Knowledge in crystallography and density functional theory would be of advantage.

Payment is accoording to TVÖD (Treaty for German public service). The appointment is for three years.

The Institute for Crystal Growth is an equal opportunity employer. Female candidates are encouraged to apply. Among equally qualified applicants preference will be given to disabled candidates.

Applications with reference to the job number K153 including curriculum vitae, photo copies of certificates and publication list should be submitted as conventional post by 21.04.2006 to

J. Warneke, Institute for Crystal Growth, Max-Born-Str. 2, D-12489 Berlin, Germany

For further information contact

Dr. Wolfram Miller, Tel. 63923074, miller@ikz-berlin.de

Or have a look on http://www.ikz-berlin.de

Post-Doctoral Positions

COMPUTATIONAL MATERIALS SCIENCE CENTER

NATIONAL INSTITUTE FOR MATERIALS SCIENCE, TSUKUBA, JAPAN

Applications are invited for one or two post-doctoral positions at the Computational Materials Science Center, National Institute for Materials Science (CMSC-NIMS) in Tsukuba, Japan. The initial appointment will be for one year, but can be renewed every year for up to three years.

NIMS is one of the world's largest materials research centers, and CMSC is a major grouping of researchers within the Institute, having a strong focus on materials modeling using first-principles methods. The successful candidate(s) will work in the FPS1 group (First-Principles Simulation Group 1) within CMSC-NIMS, together with Dr. T. Miyazaki as well as the group leader, Dr. T. Ohno. The FPS1 group currently has five permanent members of staff and seven post-docs. For further details of the group, see http://www.nims.go.jp/cmsc/.

The aim of the research project supporting the post-doctoral positions is to apply large-scale first-principles simulations to investigate the structure and physical properties of nano-structured materials and bio-materials. The work of the post-doc(s) will include the development and application of the linear-scaling first-principles code CONQUEST for the study of such materials. CMSC has access to exceptional computational resources, and the successful candidate(s) will use supercomputers such as the Hitachi SR11K at NIMS and the Earth Simulator in Yokohama for large-scale simulations. The project will be performed in close collaboration with Prof. M. J. Gillan and Dr. D. R. Bowler at the London Centre for Nanotechnology, a joint research centre hosted by UCL and Imperial College.

Applicants must have, or expect to obtain before the start of the work, a Ph.D. in a relevant discipline. A strong background in theoretical condensed matter science and experience with electronic structure methods are essential, and a knowledge of bio-materials or biophysics is desirable.

The appointment will initially be for one year, but the available funding provides for renewal of the appointment every year for up to three years. The salary will depend on age and experience, but will not be less than 5.2 million yen per year. The initial deadline for applications is April 30, 2006, but the search for candidates will continue until the positions are filled.

Candidates should send the following by e-mail in Word, pdf or html format:

1. CV
2. List of publications

3. Reprints of three selected papers
4. Summary of past accomplishments
5. Names and e-mail addresses of two referees.

Contact Information:

Dr. Takahisa Ohno,
Computational Materials Science Center,
National Institute for Materials Science (NIMS),
1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, JAPAN
e-mail: OHNO.Takahisa@nims.go.jp
e-mail: MIYAZAKI.Tsuyoshi@nims.go.jp
phone: +81-29-859-2622
fax : +81-29-859-2601

For candidates in Europe, informal enquiries to Prof. Mike Gillan (m.gillan@ucl.ac.uk) or Dr. David Bowler (david.bowler@ucl.ac.uk) are strongly encouraged.

7 Abstracts

Oxidation and aging in U and Pu probed by spin-orbit sum rule analysis: Indications for covalent metal-oxide bonds

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M. A. Wall
Lawrence Livermore National Laboratory, Livermore, California 94550, USA
A. J. Schwartz
Lawrence Livermore National Laboratory, Livermore, California 94550, USA

Abstract

Transmission electron microscopy is used to acquire electron energy-loss spectra from phase-specific regions of Pu and U metal, PuO_2 and UO_2, and aged, self-irradiated Pu metal. The $N_{4,5}$ ($4d \rightarrow 5f$) spectra are analyzed using the spin-orbit sum rule. Our results show that the technique is sensitive enough to detect changes in the branching ratio of the white-line peaks between the metal and dioxide of both U and Pu. There is a small change in the branching ratio between different Pu metals, and the data trends as would be expected for varying f electron localization, i.e., δ-Pu, δ-Pu, and aged δ-Pu. Moreover, our results suggest that the metal-oxide bonds in UO_2 and PuO_2 are strongly covalent in nature and do not exhibit an integer valence change as would be expected from purely ionic bonding.

Accepted for publication in Physical Review B **73**, 033109 (2006).
Manuscript available from g.vanderlaan@dl.ac.uk

Are the Structures of Twist Grain Boundaries in Silicon Ordered at 0 K?

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[2]*TCM Group, Cavendish Laboratory, University of Cambridge,*
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[3]*Department of Physics, Imperial College London,*
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Abstract

Contrary to previous simulation results on the existence of amorphous intergranular films at high-angle twist grain boundaries (GBs) in elemental solids such as silicon, recent experimental results imply structural order in some high-angle boundaries. With a novel protocol for simulating twist GBs, which allows the number of atoms at the boundary to vary, we have found new low-energy ordered structures.We give a detailed exposition of the results for the simplest boundary. The validity of our results is confirmed by first-principles calculations.

(Physical Review Letters **96**, 055505 (2006))
Contact person: Sebastian von Alfthan (galfthan@lce.hut.fi)

All-electron GW approximation in the augmented-plane-wave basis-set limit

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52425 Jülich, Germany
Takao Kotani
Department of Chemical and Materials Engineering, Arizona State University,
Tempe, AZ 85287-6006, USA

Abstract

This paper investigates the so far unresolved influence of the basis set on the GW self-energy correction in the full-potential linearized augmented-plane-wave (LAPW) approach and similar linearized all-electron methods. A systematic improvement is achieved by including local orbitals that are defined as second and higher energy derivatives of solutions to the radial scalar-relativistic Dirac equation and thus constitute a natural extension of the LAPW basis set. Within this approach linearization errors can be eliminated, and the augmented-plane-wave basis-set limit can be reached. While the exchange contribution to the self-energy is little affected by the increased basis-set flexibility, the correlation contribution benefits from the better description of the unoccupied states, as do the quasiparticle energies. The resulting band gaps remain relatively unaffected, however; for Si we find an increase of 0.03 eV.

(Submitted to Physical Review B)

Contact person: C.Friedrich@fz-juelich.de

Probing the population of the spin-orbit split levels in the actinide $5f$ states

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Magnetic Spectroscopy Group, Daresbury Laboratory, Warrington, WA4 4AD, UK
J.G. Tobin, B.W. Chung, M.A. Wall and A.J. Schwartz
Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

Abstract

Spin-orbit interaction in the $5f$ states is believed to strongly influence exotic behaviors observed in actinide metals and compounds. Understanding these interactions and how they relate to the actinide series is of considerable importance. To address this issue, the branching ratio of the white-line peaks of the $N_{4,5}$ edge for the light actinide metals, α-Th, α-U, and α-Pu were recorded using electron energy-loss spectroscopy (EELS) in a transmission electron microscope (TEM) and synchrotron-radiation-based X-ray absorption spectroscopy (XAS). Using the spin-orbit sum rule and the branching ratios from both experimental spectra and many-electron atomic spectral calculations, accurate values of the spin-orbit interaction, and thus the relative occupation of the $j = 5/2$ and $7/2$ levels, are determined for the actinide $5f$ states. Results show that the spin-orbit sum rule works very well with both EELS and XAS spectra, needing little or no correction. This is important, since the high spatial resolution of a TEM can be used to overcome the problems of single-crystal growth often encountered with actinide metals, allowing acquisition of EELS spectra, and subsequent spin-orbit analysis, from nm-sized regions. The relative occupation numbers obtained by our method have been compared with recent theoretical results and they show a good agreement in their trend.

Published in Ultramicroscopy **106**, 261–268 (2006).
Manuscript available from g.vanderlaan@dl.ac.uk

Embedded–atom potential for Fe and its application to self–diffusion on Fe(100)

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Washington, DC 20375–5345, USA

Abstract

We have constructed an embedded–atom potential for Fe by fitting to both experimental and first–principles results. The potential reproduces with satisfactory accuracy the lattice properties, surface energies and point defect energies for both BCC and the high temperature FCC phases of the metal. The potential was used in tandem with molecular–dynamics simulations to calculate the thermal expansion of both BCC–Fe and FCC–Fe, the phonon dispersion curves, mean–square displacements and surface relaxations of the element. In addition, we have studied self–diffusion of single adatoms on the BCC–Fe(100) surface at several temperatures. The migration energies and pre–exponential factors for three main diffusion mechanisms were determined and compared with available experimental data. We have found that the diagonal exchange diffusion process is energetically favored over the direct hopping mechanism and that its migration energy is close to the experimental value. Furthermore, the diffusion coefficient associated with the diagonal exchange diffusion process is about an order of magnitude higher than those of the hopping and the non–diagonal exchange mechanisms.

(Surface Science, accepted)

Contact person: nikpap@cc.uoi.gr

Lattice Distortion and Magnetism of $3d$-t_{2g} Perovskite Oxides

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Computational Materials Science Center (CMSC),
National Institute for Materials Science (NIMS),
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Abstract

Several puzzling aspects of interplay of the experimental lattice distortion and the the magnetic properties of four narrow t_{2g}-band perovskite oxides ($YTiO_3$, $LaTiO_3$, YVO_3, and $LaVO_3$) are clarified using results of first-principles electronic structure calculations. First, we derive parameters of the effective Hubbard-type Hamiltonian for the isolated t_{2g} bands using newly developed downfolding method for the kinetic-energy part and a hybrid approach, based on the combination of the random-phase approximation and the constraint local-density approximation, for the screened Coulomb interaction part. Apart form the above-mentioned approximation, the procedure of constructing the model Hamiltonian is totally parameter-free. The results are discussed in terms of the Wannier functions localized around transition-metal sites. The obtained Hamiltonian was solved using a number of techniques, including the mean-field Hartree-Fock (HF) approximation, the second-order perturbation theory for the correlation energy, and a variational superexchange theory, which takes into account the multiplet structure of the atomic states. We argue that the crystal distortion has a profound effect not only on the values of the crystal-field (CF) splitting, but also on the behavior of transfer integrals and even the screened Coulomb interactions. Even though the CF splitting is not particularly large to quench the orbital degrees of freedom, the crystal distortion imposes a severe constraint on the form of the possible orbital states, which favor the formation of the experimentally observed magnetic structures in $YTiO_3$, YVO_3, and $LaVO_3$ even at the level of mean-field HF approximation. It is remarkable that for all three compounds, the main results of all-electron calculations can be successfully reproduced in our minimal model derived for the isolated t_{2g} bands. We confirm that such an agreement is only possible when the nonsphericity of the Madelung potential is explicitly included into the model. Beyond the HF approximation, the correlations effects systematically improve the agreement with the experimental data. Using the same type of approximations we could not reproduce the correct magnetic ground state of $LaTiO_3$. However, we expect that the situation may change by systematically improving the level of approximations for dealing with the correlation effects.

(Submitted to Phys. Rev. B, cond-mat/0602035)
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Angle-dependent x-ray magnetic circular dichroism from (Ga,Mn)As: Anisotropy and identification of hybridized states

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E. Arenholz
Advanced Light Source, Lawrence Berkeley National Laboratory,
Berkeley, California 94720, US

Abstract

Remarkably anisotropic Mn $L_{2,3}$ x-ray magnetic circular dichroism spectra from the ferromagnetic semiconductor (Ga,Mn)As are reported. States with cubic and uniaxial symmetry are distinguished by careful analysis of the angle-dependence of the spectra. The multiplet structures with cubic symmetry are qualitatively reproduced by calculations for an atomic-like d^5 configuration in tetrahedral environment, and show zero anisotropy in the orbital and spin moments within the experimental uncertainty. However, hybridization with the host valence bands is reflected by the presence of a pre-edge feature with a uniaxial anisotropy and a marked dependence on the hole density.

Published in Physical Review Letters **96**, 117207 (2006).
Contact person: g.vanderlaan@dl.ac.uk

Electronic structure, magnetism, and spin-dependent transport of CeMnNi$_4$

E. N. Voloshina[1], Yu. S. Dedkov[2], M. Richter[3], and P. Zahn[4]
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[2] *Institut für Festkörperphysik, Technische Universität Dresden,*
01062 Dresden, Germany
[3] *IFW Dresden e.V., P.O. Box 270 116, 01171 Dresden, Germany*
[4] *Fachbereich Physik, Martin-Luther-Universität Halle-Wittenberg,*
06099 Halle/Saale, Germany

Abstract

Theoretical investigations of the electronic band structure and ferromagnetism of CeMnNi$_4$ have been performed by means of an LSDA approach. The calculated magnetic moment of $4.88\,\mu_B$ per formula unit is in good agreement with the value determined experimentally. Recent point contact Andreev reflection experiments show that this compound has a relatively large transport spin polarization. The calculations reveal a much smaller polarization of the density of states and transport coefficients at the Fermi level. A small shift of the Fermi level by about 0.1 eV raises the polarization values close to the experimental ones.

(Accepted for Phys. Rev. B)

Contact persons: dedkov@physik.phy.tu-dresden.de,
peter.zahn@physik.uni-halle.de,
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All-electron first-principles investigations of the energetics of vicinal Cu surfaces

Juarez L. F. Da Silva,[1] Cyrille Barreteau,[2] Kurt Schroeder,[1] and Stefan Blügel[1]
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Abstract

Using first-principles calculations we studied the energetics (surface energy, step energy, stability with respect to faceting) of the low- and high-Miller-index (vicinal) Cu surfaces, namely, the (111), (100), (110), (311), (331), (210), (211), (511), (221), (711), (320), (553), (410), (911), and (332) surfaces. Our calculations are based on density-functional theory employing the all-electron full-potential linearized augmented plane-wave (FLAPW) method. We found that the unrelaxed vicinal Cu surfaces between (100) and (111) are unstable relative to faceting at 0 K, while fully relaxed vicinal surfaces between (100) and (111) are stable relative to faceting, which is in agreement with the observed stability of vicinal Cu surfaces at room temperature. Thus atomic relaxations play an important role in the stability of the vicinal Cu surfaces. Using the surface energies of Cu(111), Cu(100), and Cu(110) and employing the effective pair-potential model, which takes into account only the changes in the coordination of the surface atoms, the surface energies of the vicinal Cu surfaces can be calculated with errors smaller than 1.0is due to the almost perfect linear scaling of the surface energies of the Cu(hkl) surfaces as a function of the total number of broken nearest-neighbor bonds. Furthermore, we calculate step-step interactions as a function of terrace widths and step energies of isolated steps.

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Linear scaling of the interlayer relaxations of the vicinal Cu$(p, p, p-2)$ surfaces with the number of atom-rows in the terraces

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Abstract

We investigate the multilayer relaxation trends in the vicinal Cu$(p, p, p-2)$ surfaces employing the all-electron full-potential linearized augmented plane-wave method. Calculations are performed for the (331), (221), (553), (332), (775), and (443) surfaces, which have 3, 4, 5, 6, 7, and 8 atom-rows in the terrace, respectively. The following trends are identified: (i) The interlayer relaxations perpendicular to the surface scale almost linearly with the number of atom-rows in the terraces. (ii) The nearest-neighbor distances do not depend on the surface termination, but only on the local coordination. (iii) For Cu$(p, p, p-2)$ in which the topmost n surface layers have nearest-neighbor coordination smaller than the bulk Cu (calculated for the unrelaxed surfaces), the topmost $(n-1)$ interlayer spacings (d_{12}, $\cdots$, $d_{n-1,n}$) contract compared with the unrelaxed spacing, while the nth interlayer spacing ($d_{n,n+1}$) expands. The next $(n-2)$ interlayer spacings ($d_{n+1,n+2}$, $\cdots$, $d_{2n-2,2n-1}$) contract, while the interlayer spacing indicated by $d_{2n-1,2n}$ expands. A similar rule was found for the relaxations parallel to the surfaces. These trends provide a better understanding of the atomic structure of vicinal Cu surfaces.

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“Textbook”adsorption at “non-textbook” adsorption site: halogen atoms on alkali halide surfaces

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Abstract

Density-functional theory (DFT) and second order Møller-Plesset perturbation theory (MP2) calculations indicate that halogen atoms bond preferentially to halide substrate atoms on a series of alkali halide surfaces, rather than to the alkali atoms as might be anticipated. Analysis of the electronic structure in each system reveals that this novel adsorption mode is stabilized by the formation of textbook two-center three-electron covalent bonds. The implications of these findings to, for example, nanostructure crystal growth are briefly discussed.

(submitted to: Physcial Review Letters)
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Adsorption Geometry and Carbon K-edge NEXAFS Spectra of Three Phenylpropene Isomers on Cu(111)

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Abstract

Theoretical C 1*s* NEXAFS spectra for the C_9H_{10} isomers trans-methylstyrene, α-methylstyrene, and allylbenzene in gas phase and adsorbed at Cu(111) surfaces have been obtained from DFT calculations where adsorbate geometries were determined by corresponding total energy optimizations. The three species show characteristic differences in widths and peak shapes of the lowest C 1s $\rightarrow \pi^*$ transitions which are explained by different coupling of the π-electron system of the C_6 ring with that of the side chain in the molecules as well as by the existence of non-equivalent carbon centers. The adsorbed molecules bind only weakly with the substrate which makes the use of theoretical NEXAFS spectra of the oriented free molecules meaningful for an interpretation of experimental angle-resolved NEXAFS spectra of the adsorbate systems obtained in this work. However, a detailed quantitative account of relative peak intensities requires theoretical angle-resolved NEXAFS spectra of the complete adsorbate systems which have been evaluated within the surface cluster approach. The comparison with experiment yields almost perfect agreement and confirms the reliability of the calculated equilibrium geometries of the adsorbates. This can help to explain observed differences in the catalytic epoxidation of the three molecules on Cu(111) based on purely geometric considerations.

(submitted to: Journal of Chemical Physics)

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Quasiparticle Corrections to the Electronic Properties of Anion Vacancies at GaAs(110) and InP(110)

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Abstract

We propose a new method for calculating optical defect levels and thermodynamic charge-transition levels of point defects in semiconductors. The approach evaluates quasiparticle corrections to the Kohn-Sham eigenvalues of density-functional theory. Its applicability is demonstrated for anion vacancies at the (110) surfaces of III-V semiconductors. We find the (+/0) charge-transition level to be 0.49 eV above the surface valence-band maximum for GaAs(110) and 0.82 eV for InP(110). The results show a clear improvement over the local-density approximation and are in close agreement with experiment.

(submitted to: Phys. Rev. Lett.)

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Electronic structure of rare-earth impurities in GaAs and GaN

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Abstract

The electronic structures of substitutional rare-earth (RE) impurities in GaAs and cubic GaN are calculated. The total energy is evaluated with the self-interaction corrected local spin density approximation, by which several configurations of the open 4f shell of the rare-earth ion may be investigated. The defects are modelled by supercells of type $\mathrm{REGa}_{n-1}\mathrm{As}_n$, for $n = 4$, 8 and 16. The preferred defect is the rare-earth substituting Ga, for which case the rare-earth valency in intrinsic material is found to be trivalent in all cases except Ce and Pr in GaN. The $3+ \rightarrow 2+$ f-level is found above the theoretical conduction band edge in all cases and within the experimental gap only for Eu, Tm and Yb in GaAs and for Eu in GaN. The exchange interaction of the rare-earth impurity with the states at both the valence band maximum and the conduction band minimum is weak, one to two orders of magnitude smaller than that of Mn impurities. Hence the coupling strength is insufficient to allow for ferromagnetic ordering of dilute impurities, except at very low temperatures.

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Disordered magnetic multilayers: Electron transport within the coherent potential approximation

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Abstract

We develop an efficient technique for *ab initio* calculations of the current-perpendicular-to-plane (CPP) electron transport in disordered magnetic multilayers. The method is based on the tight-binding linear muffin-tin orbital (TB-LMTO) theory and the coherent potential approximation (CPA) to treat the substitutional randomness in an effective-medium approach. A formulation of the CPA vertex corrections, giving rise to an incoherent part of the CPP conductance, is described in detail and the numerical implementation is discussed. The developed approach is illustrated on several disordered systems derived from fcc Co|Cu|Co trilayers and its results are compared to those of a supercell technique simulating the randomness in terms of two-dimensional lateral supercells. The overall good agreement of the two techniques proves reliability of the CPA for a number of specific features encountered in disordered multilayers. As another example, results for layered diluted ferromagnetic (Ga,Mn)As semiconductors are reported, including a brief discussion of spin-resolved and incoherent CPP conductances and a comparison to bulk residual resistivities.

To be published in: Physical Review B
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8 Presenting Other Initiatives

8.1 Special Issue on Silicon Clusters

"Computing Letters" (COLE)

Papers are invited for a special issue of the new magazine on scientific computing, "Computing Letters" (COLE). This special issue with the general title "Silicon clusters: Problems, challenges and perspectives" with guest editors Professors George Maroulis and Aristides Zdetsis.

The special issue will be published promptly (in electronic and hard copy form) well before the end of 2006, after peer review. It could also be published as a separate volume by Brill Academic publishers, Netherlands. For a few selected papers there will be also the possibility of further oral presentation in a special symposium of the forthcoming International Conference on Computational Methods in Science and Engineering, ICCMSE 2006, to be held between October 27 and November 1, 2006 in Chania Crete, Greece.

If you are interested you can send your manuscript or your inquires for further information directly to one of the co-editors, Aristides Zdetsis or Maroulis (e-mails: zdetsis@upatras.gr or Maroulis@upatras.gr, respectively).

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8.2 Announcement of a Computer Package

BAND Program: Part of the Amsterdam Density Functional (ADF) Package

http://www.scm.com

BAND, which is part of the Amsterdam Density Functional (ADF) package, is a full-potential LCAO DFT code for general periodicity: molecules, linear chains, surfaces, and solids. BAND uses Slater and numerical orbital basis sets, which can be all-electron.

Relativistic effects are included through the accurate ZORA method (scalar and spin-orbit effects). BAND is an accurate code that can reliably deal with systems in the whole periodic table. BAND can calculate optical spectra using Time-Dependent DFT. Academic pricing information is available on http://www.scm.com.

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9 SCIENTIFIC HIGHLIGHT OF THE MONTH: "Core-Level Shifts in Complex Metallic Systems from First Principles"

Core-Level Shifts in Complex Metallic Systems from First Principles

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Abstract

We show that core-level binding energy shifts (CLS) can be reliably calculated within Density-functional theory. The scheme includes both the initial (electron energy eigenvalue) as well as final state (relaxation due to core-hole screening) effects in the same framework. The results include CLS as a function of composition in substitutional random bulk and surface alloys. Sensitivity of the CLS to the local chemical environment in the bulk and at the surface is demonstrated. A possibility to use the CLS for structural determination is discussed. Finally, an extension of the model is made for Auger kinetic energy shift calculations.

1 Introduction

Electrons that occupy the orbitals closer to the atomic nucleus are tightly bound. These have experimentally well resolved binding energies, and are often referred to as *core-electrons.* The binding energy E_B of a core-electron in an atom is typically sensitive to the atoms specific *chemical environment.* This fact can be used to gain a deeper understanding of the underlying physical properties related to the electronic structure and bonding in the systems under study. One very useful aspect is that due to its sensitivity to the chemical environment, E_B can be used as a tool for structural determination. Another interesting aspect is that while the binding energy of a core-level i in a substitutional random alloy can be studied as a function of the *global composition* of the alloy, the specific *local environment* around each and every atom at a particular composition will lead to some differences in E_B, leading to the effect of disorder broadening of the core spectral lines.

It is a common practice to analyze core-level binding energies in terms of a difference, a core-level binding energy shift (CLS), against some reference energy E_B^{ref}, which in principle can be chosen arbitrarily,

$$E_{CLS}^{exp} = E_B - E_B^{ref}. \tag{1}$$

In the case of solids the reference is most often the corresponding core-level binding energy in the pure bulk metal. In experiments the sign of the shift is determined from a convention that the binding energies of the core electrons are positive, $E_B > 0$. Thus, if $E_{CLS} < 0$ the electrons are less tightly bound compared to the reference system. Also note that shifts are especially helpful in comparison with theory, due to that differences in energy are typically more trustworthy than directly calculated ionization energies, as errors may cancel. CLSs have been shown to be related to various material properties, such as the cohesive energy [1], the heat of mixing [2, 3], segregation energy [4] and charge transfer [5, 6, 7]. Over the years, different kinds of binding energy shifts have been studied, including the CLS between free atoms and atoms in a metal, as well as CLS between atoms at the surface and in the bulk , the so-called surface core-level shift (SCLS). Shifts are also obtained for molecules, where they can be significantly larger than in solids.

Experimentally it is relatively easy to measure binding energies using x-ray photoelectron spectroscopy (XPS). In XPS the input is a monochromatic (fixed energy) beam of photons with an energy $\hbar\omega > 1000$ eV, directed towards the surface of a sample. The output is in the form of photoionized electrons whose kinetic energies E_{KIN} are measured, and the result is collected in an energy distribution curve, or spectra, showing the intensity of the photoemitted electrons vs their binding energies, defined by

$$E_B = \hbar\omega - E_{KIN} - \phi. \tag{2}$$

In Eq.(2) ϕ is the work function, the lowest energy an electron must overcome to escape from the surface to the vacuum level, E_{vac}. In the case of atoms and molecules the binding energy zero is set to E_{vac}, but for solids the Fermi level, E_F, is typically used as the zero.

A way to model the electron photoemission process is to divide it into two separate steps, first an unperturbed *initial state* before the excitation of a core-electron at the core-level i, and secondly a *final state* describing the system, but now with a core-hole in i:th level. While the orbital energy ε_i can be readily calculated for a core-electron in the unperturbed system, the experimentally measured binding energy depends in general on the relaxation effects, both in the core-region and for the valence charge, because of the core-hole present in the final state. The observed binding energy is better described as a many-body effect, rather than as a one electron property. Consequently, one can think of possible complications in theoretical calculations of the CLS within DFT.

There are a number of effects which contribute to the CLS. Following Weinert and Watson [8] one must for instance consider: interatomic charge transfer, changes in the screening of the final state of the core-hole, changes in the Fermi-level relative to the center of gravity of bands, intra-atomic charge transfer, and redistribution of charge due to bonding and hybridization. This implies that a universally accurate model needs to take all these contributions into account. It is also important to point out that if an experimental shift is near zero, this does not necessarily mean that the environment for the examined and reference atoms are the same. On the contrary it must be taken into account that different effects mentioned above may cancel each other. For more information on experimental technique and binding energy shifts, see for instance the book by Hüfner [9], and a review by Egelhoff [10].

The theoretical models for the calculations of the core-level binding energy shifts within density functional theory (DFT) can be classified in three major groups, based on the complete screening picture, the transition state model and the initial state approximation, respectively. We will focus on the complete screening picture, used in most of our calculations and analysis. Observe that the complete screening picture and the transition state model both include initial and final state effects, though total energies of systems are used in the complete screening scheme and energy eigenvalues in the transition state model. Results from the transition state model have been compared with those from complete screening calculations, while initial state shifts ($-\Delta\varepsilon_i$) have been used mostly to illuminate the final state effects. Also notice that in principle it is the *shift* that is considered in the theoretical models, the calculational methods are generally more accurate for differences in energies, as mentioned above. The overall shape of the spectra from many-body interactions is not considered here. The continued development of photoelectron spectroscopy towards increased resolution encourages a direct comparison between experiment and theory.

All calculations were performed within the density functional theory [11, 12]. In most cases the Green's function technique in the atomic sphere approximation, combined with the computationally efficient coherent potential approximation (CPA), was used [13, 14, 15]. To study local environment effects on the disorder broadening of the spectral core-lines, supercell calculations were done using the locally self-consistent Green's function method, LSGF [16, 17], and the Vienna *ab initio* simulation package, `VASP` [18, 19, 20, 21]. For further details the reader is refered to the above papers concerning the methods and the specific papers with the results in Refs. [22, 23, 24, 28, 29, 30, 31, 32, 33, 34].

The paper is organized as follows, a background of the complete screening picture and the transition state model is introduced in Sec. 2 and 3, respectively. A comparison between different theoretical models is presented in Sec. 4. Sec. 5 discusses CLSs as a function of the global composition in disordered alloys. In Sec. 6 the disorder broadening of the spectral core-lines is investigated in connection with the local environment effects in random substitutional alloys. The CLS for atoms at interfaces are compared with disordered bulk systems in Sec. 7. Examples of the application of SCLS for structural determination are given in Sec. 8, and an extension of the complete screening picture for the calculations of Auger kinetic energy shifts is presented in Sec 9.

2 Complete screening picture

In the complete screening picture for calculating the binding energy shift in Eq. (1), only *total energies*, or thermodynamic properties, are needed. In more details the CLS is obtained from considering the total energies of a system, first in its unperturbed initial state, and second in its relaxed final state with a core-hole at a single core-ionized atom. The most important assumption here is that the final state is fully relaxed in the sense that the core-hole is completely screened by the valence electrons in metallic systems. The initial and final states of the core-ionization can be connected through a *Born-Haber cycle* in a thermodynamical model approach. The core-ionized atom Z* (atomic number Z) is replaced by the next element in the periodic table, Z+1, hence the method is often refered to as the (Z+1)- or equivalent core approximation. The core-hole is assumed to effectively act as an extra proton in the atom, such that the screening by the valence charge of Z* is essentially the same as the valence charge in the Z+1 atom. Born-Haber cycles provide a more intuitive perspective to the calculation and makes it possible to obtain CLSs and thermodynamical properties from other experimental measurements. In particular, the complete screening picture in connection with the Born-Haber cycle was used by Johansson and Mårtensson [1] to calculate the CLS between a free atom and an atom in a metal.

However, it is also possible to calculate the complete screening picture CLS from *first principles*, taking into account the internal relaxation of the core-electrons (e.g. without the equivalent core approximation) as well as the total screening by the valence electrons, according to

$$E_{CLS}^{cs} = \mu_i - \mu_i^{ref}. \tag{3}$$

The shift is here given by the difference in generalized thermodynamic chemical potentials, $\Delta\mu_i$, for the ionization of a specific core-level i at atom A in a system of interest (e.g. a random binary alloy $A_{1-x}B_x$) related to the ionization energy in a reference system (e.g. pure bulk metal A). Notice the correspondence to the experimental sign convention in Eq. (1). The first principles approach has been employed before, for instance to calculate surface core-level shifts (SCLS) [35, 36]. One other advantage of Eq. (3), in view of our particular implementation is that it is a proper way to calculate chemical potentials using the CPA formalism [37].

In Fig. 1 an atom A is shown in its (a) initial state, and (b) final state A^* after the ejection of a core-electron from state i. The resulting core-hole is assumed to be completely screened, as indicated by the extra charge in the local valence band DOS at the atom, effectively corresponding to one extra electron in the valence band. This is modeled in the calculations by promotion of an electron to the lowest unoccupied valence state, preserving the charge-neutrality of the system. The core-levels i, j and k will also shift their positions due to the presence of a core-hole in the atom, Fig 1 (b). We would like to point out that within a psedupotential approach the equivalent core approximation can still be used, and it gives results in good agreement with calculations which do not use the $Z+1$ approximation.

In Fig. 2 a comparison is made between the valence band DOS of core-ionized Cu atoms, Cu*, to the valence state of Zn atoms used to model Cu* within the (Z+1)-approximation. For the `VASP` calculations in Ref. [34] the (Z+1)-approximation was used. An alternative route in `VASP` is to create a specific potential for the core-ionized atom [38].

Here we recall that as a first approximation to CLS in metallic systems one often uses the difference in core-electron energy eigenvalues, which are readily available as side product in conventional computations. All energy eigenvalues ε below are calculated with respect to the Fermi-level, and the co-called initial state CLS is defined as

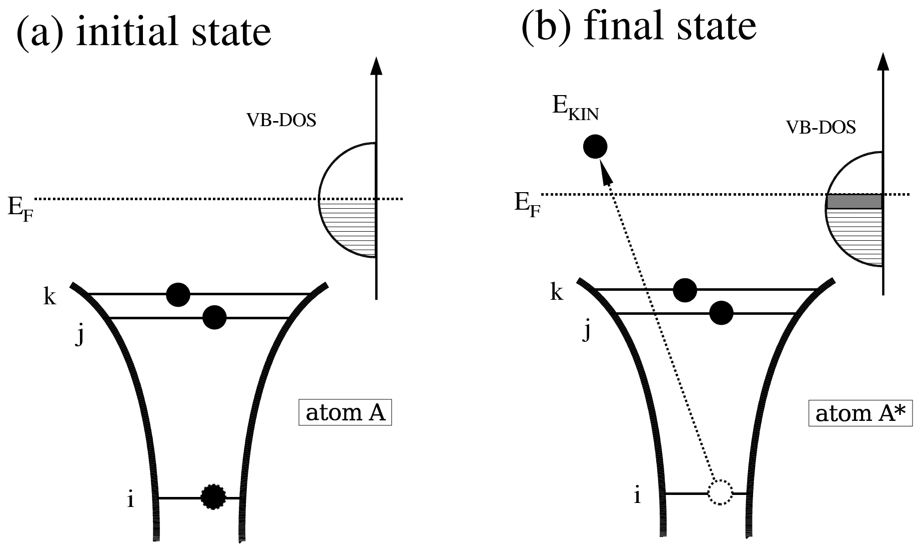

Figure 1: (a) Initial and (b) final states of the photoemission process. An ejection of the core-electron from level i results in a core-hole at this level. The effect of screening is shown by the increased occupation of the local valence band DOS in (b) compared to (a).

$$E_{CLS}^{is} = -\varepsilon_i + \varepsilon_i^{ref}. \tag{4}$$

In E_{CLS}^{is} all final state effects are neglected, and it should therefore be used with some caution, especially considering that the eigenenergies of the Kohn-Sham orbitals strictly speaking don't have any physical meaning, and correspond to an auxiliary system of quasiparticles designed to produce the ground state charge density of a true many-body system.

3 Transition state model

The transition state model is based on an extension to DFT made by Janak [39], introducing the occupation numbers η_i ($0 \leq \eta_i \leq 1$) for the Kohn-Sham orbitals in the expression for the charge density,

$$n(\mathbf{r}) = \sum_i \eta_i |\psi_i(\mathbf{r})|^2. \tag{5}$$

Now the Kohn-Sham equation can formally be solved self-consistently for a non-integral electron occupation. The introduction of the occupation numbers yields a modified total energy functional $\tilde{E}$. In general $\tilde{E} \neq E$, but if η_i have the form of the Fermi-Dirac distribution, $\tilde{E}$ is numerically equal to E. *Janak's theorem* states that

$$\frac{\partial \tilde{E}}{\partial \eta_i} = \varepsilon_i, \tag{6}$$

independent on the exchange-correlation functional. It follows from the equation that when η_i have the form of a Fermi-Dirac distribution, $\tilde{E}$ is minimized at the end-points (η_i is equal to 1 or 0) and then it is equal to the ground-state energy of the system.

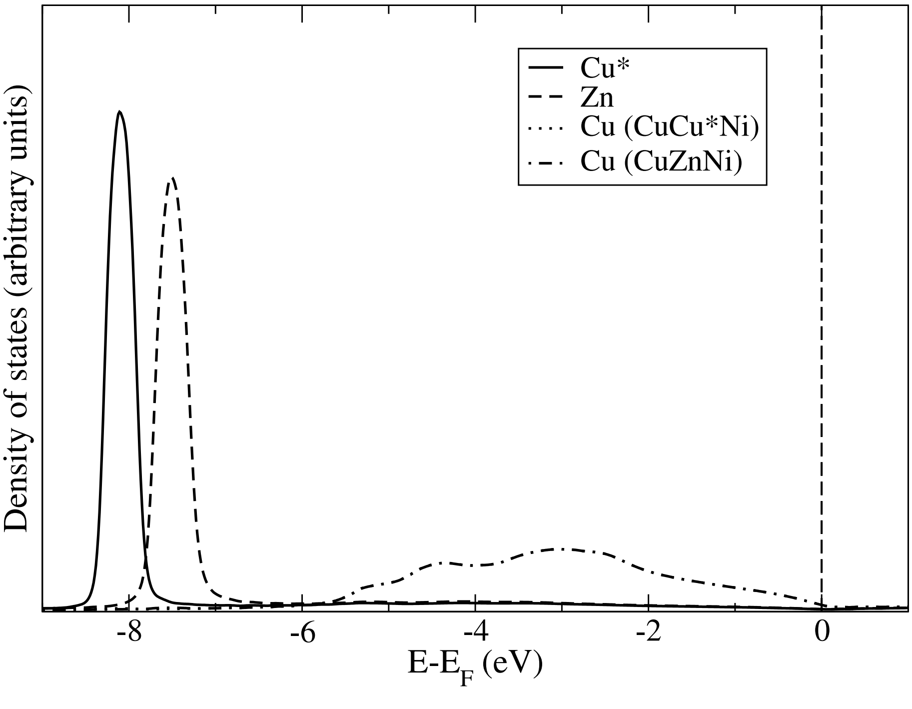

Figure 2: Site-projected valence band density of states for ionized Cu sites (Cu*) in equiatomic CuNi alloy. It is compared to DOS for Zn atoms in CuNi alloy that model Cu* sites within the Z+1 approximation.

From an integration of Eq. (6) it is possible to connect the ground states for two systems with N respectively $N+1$ electrons by inserting η electrons in the lowest unoccupied state,

$$E_{N+1} - E_N = \int_0^1 \varepsilon_i(\eta_i) d\eta_i. \tag{7}$$

This integral can be identified as the binding energy E_i for the highest occupied valence electron,

$$E_{N+1} - E_N = -E_i. \tag{8}$$

If the one-electron eigenenergy ε_i depends *linearly* upon the occupation number η_i, the integral in Eq. (7) can be written (assuming that the eigenvalues are aligned with the Fermi-level zero),

$$\begin{aligned} E_{N+1} - E_N &\approx \varepsilon_i(1/2) & (9) \\ &\approx \varepsilon_i(0) + \frac{1}{2}[\varepsilon_i(1) - \varepsilon_i(0)], & (10) \end{aligned}$$

with the $\varepsilon_i(1/2)$ evaluation “at midpoint”, known as the *Slater-Janak transition state* [39, 40], carried out under the assumption that the core-level is occupied by half an electron. The last equality is very useful as it splits E_i into contributions from the initial and final states explicitly. In order to retain the charge neutrality of the system, the occupation for the valence band in the whole system should be increased with the missing amount of electrons in the core-region. Eqs. (9) and (10) will yield the same values, if the above-mentioned assumption of the Kohn-Sham eigenvalues as linear functions of the occupation numbers is true.

The evaluation at midpoint was used to calculate CLSs according to the transition state model in Ref. [29],

$$E^{ts}_{CLS} = -\varepsilon_i(1/2) + \varepsilon_i^{ref}(1/2), \tag{11}$$

with fewer calculations needed compared to the last scheme in Eq. (9). Notice the similarity to the initial state shift in Eq. (4). The difference is that the energy eigenvalues here are obtained from core-levels with half an electron promoted to the valence band, and that the corresponding sites are considered as impurities in systems with conventional occupation at core levels at all other atoms. It was shown [29] that the results for the transition state model, Eq. (9), compare well with the complete screening picture, which will also be illustrated in the next section.

One can also use Eq.(10) when calculating the CLSs, which will yield the equation

$$E^{ts}_{CLS} = \frac{1}{2}\big[-\varepsilon_i(0) + \varepsilon_i^{ref}(0)\big] + \frac{1}{2}\big[-\varepsilon_i(1) + \varepsilon_i^{ref}(1)\big]. \tag{12}$$

Since Eqs. (11) and (12) will only yield the same result if the Kohn-Sham eigenvalues are linear functions of their corresponding occupation numbers, comparing these two equations provides us with a way to evaluate the assumption of the linear dependence of ε_i on η_i.

Apart from the transition state CLS calculations, we have (see Ref. [33]) performed calculations on different core-levels in several alloy systems in order to verify the above-mentioned assumption of linearity. For each core-level and system the Kohn-Sham eigenvalues have been calculated for $\eta = 0.0, 0.1, \ldots, 0.9, 1.0$. The results have then been used for linear interpolations, where the norm of residuals have been calculated. This means 11 different self-consistent calculations have been done for each core-level and system.

The Kohn-Sham eigenvalues for Cu $2p_{3/2}$ and Pt $4f_{7/2}$ in $\mathrm{Cu}_{50}\mathrm{Pt}_{50}$ as functions of their occupation numbers are shown in Fig. 3. For the sake of brevity, we present only one alloy system; more calculations can be found in Ref. [33]. Though the graph indicate a linear relationship between $\varepsilon(\eta)$ and η, the norm of residuals is 0.07 Ry for Cu and 0.02 Ry for Pt.
However, since the energy level is much higher for Cu $2p_{3/2}$, this does not mean that the dependence of the eigenvalue for this electronic state on the occupation number is less linear than that for Pt $4f_{7/2}$. It is shown in Ref. [33] that the deeper in the core the electronic state is, the more linear the corresponding Kohn-Sham eigenvalue.

As reference for the CLS we have also used these results to numerically evaluate the integral in Eq. (7) by using all 11 points or by using 3 points (i.e. $\eta = 0, 1/2, 1$). A comparison of different schemes for the calculations of hte CLS is given in the next section.

4 Comparison of different theoretical models

In order to compare different schemes for the calculation of the CLS, we present in Fig. 4 the results obtained for the CuPt fcc alloy as function of the Pt concentration. Here upwards triangles denote transition state CLS obtained from Eq. (11) ["TS(1,0)"] and downward triangles

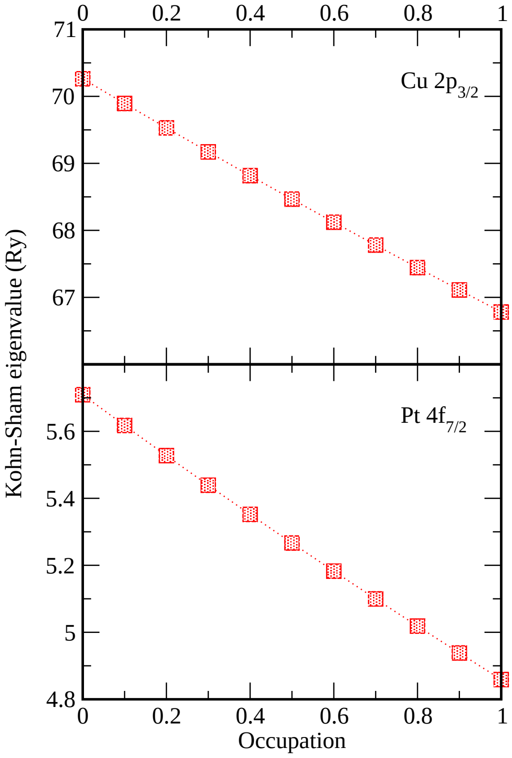

Figure 3: Kohn-Sham eigenvalues in $Cu_{50}Pt_{50}$ as functions of the occupation number.

denote transition state CLS from Eq. (12) [”TS(1/2)”], squares denote the initial state (IS) shifts, diamonds complete screening (CS) shifts, circles transition state calculations with 11 point numerical integration, crosses (black) transition state calculations with numerical integration over 3 points $(0, 1/2, 1)$ using the Simpson's rule. Red crosses and plusses denote experimental results from Refs. [41] and [42], respectively.

For the Cu shift, we see that there is a noticeable difference between the TS(1/2) and TS(1,0), up to around 0.2 eV. One may also notice that this difference increases with the Pt concentration, which is verified by the increasing deviation from the linear dependence of the core eigenstates on the occupation number, as discussed in Ref. [33]. It is also interesting to note that the numerical integration using 11 or 3 points are in very good agreement with each other and lies between TS(1/2) and TS(1,0). Also, the numerical integrations are in reasonable agreement with experiments. We see that the IS and CS shifts are quite close to each other, but the numerically integrated TS shifts are not very far away either. The difference between the two experimental sets makes it difficult to draw conclusions about which of the theoretical models is the most accurate.

Further, if we turn to the Pt shift we may notice that the difference between the transition state shifts are smaller than in Cu, but this is because the binding energies and the shifts are smaller. The agreement with experiments is reasonable, but one should once again notice the difference between the two experimental sets. The numerically integrated TS shifts are in good agreement with the CS shifts, although the difference between the two increases with decreasing Pt concentration. Both the CS and TS models yield a considerable final-state contribution for the Pt shift. The initial state shift is not in good agreement with the other theoretical models, and with experiment, which indicates that it is important to include the final state contributions in the treatment of the CLS.

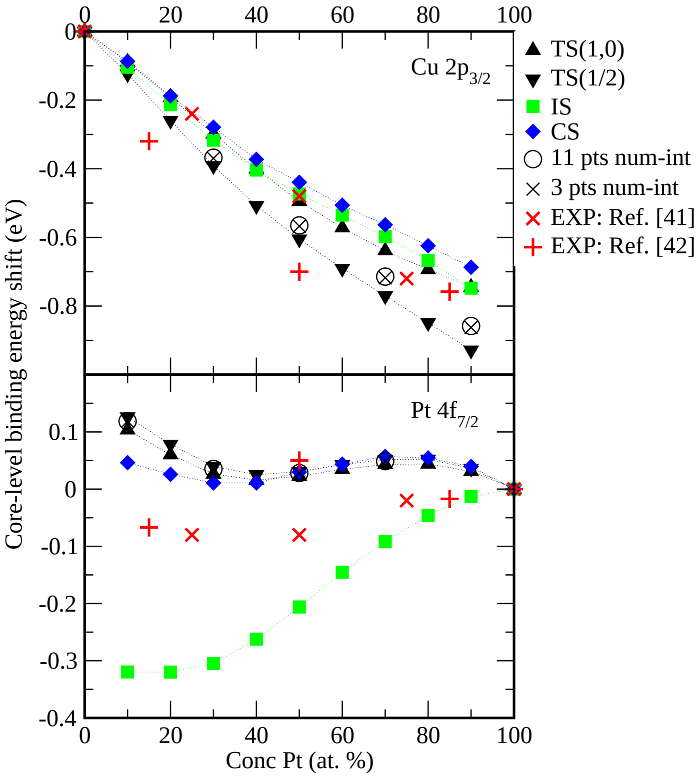

Figure 4: Core-level shifts in CuPt using different theoretical models. Experimental CLS from Refs. [41, 42] are also shown. See text for more details.

5 Core-level shifts in fcc disordered alloys: the effect of composition variation

Studies of the core-level shifts in fcc binary substitutionally random alloys can be found in Refs. [22, 23, 29]. One of the motivations for an investigation came from the ongoing discussion regarding different models for calculating CLS, namely an approach based on charge transfer in the potential model by Cole *et al.* [6, 7], compared to a first-principles approach within the initial state model [see Eq. (4)] by Faulkner *et al.* using the locally self-consistent multiple scattering (LSMS) supercell method [43]. It seemed that it would be of interest to include both inital and final state effects in a study, by employing the complete screening picture for the random alloys, considering for instance Refs. [44, 45].

In Ref. [23] the calculational result of the complete screening picture and initial state shift was compared to experiment, for Cu $2p_{3/2}$, Ag and Pd $3d_{5/2}$ in CuPd and AgPd alloys. It was found that the complete screening picture leads to an improved agreement with experiment, compared with the initial state approach. In particular this was found for Pd in both alloys, with a smaller effect for Ag at high Pd concentrations. A more detailed study was conducted for the AgPd alloys in Ref. [22], where it was shown that the changes of the initial state shift followed the shift of the valence d-band center. The latter, in its own turn, depends on the *intra-site* charge redistribution due to hybridization. By studying the unoccupied states at the Fermi-level one can draw a conclusion from "rule of thumb" about the influence of the orbital character of the *screening* charge on the importance of the final state contribution to the CLS. There is a pronounced difference in the bonding for the delocalized *sp*- and tightly bounded *d*-like electrons, leading to differences in final state contributions between pure metal Pd (*d*-screening) and Pd at low concentration in the alloy (*sp*-screening).

A more extended study was presented in Ref. [29]. The binding energy shifts were calculated over the whole concentration interval for fcc CuPd, AgPd, NiPd, NiPt, CuPt, CuNi, CuAu and PdAu, for Cu and Ni $2p_{3/2}$, Ag and Pd $3d_{5/2}$, Pt and Au $4f_{7/2}$ core-levels. The selection of the binary alloys was based on the availability of experimental results. One of the aims was to show that accurate first-principle calculations of the CLS in disordered alloys can be readily performed in the framework of DFT using the complete screening picture and the CPA. Compared to Refs. [22, 23] the basis set cutoff of the linear muffin tin orbitals was increased from $l_{max} = 2$ to $l_{max} = 3$, the multipole corrections to ASA were included within ASA+M method and the GGA exchange-correlation function was employed. The increased basis set gave a better agreement with experiment, e.g. in the case of CuPt.

The result obtained within the complete screening picture is compared to experiment for binary alloys AB in Fig. 5. Experimental values are denoted by red symbols, results from the classical article by Steiner and Hüfner[3] are shown by × (A) and + (B). Other experimental values are represented pairwise by the symbols triangle up △ and circle ◯, as well as triangle down ▽ and square □, and show data for: AgPd [41, 46], CuPd [2, 47], CuPt [42, 47], CuNi [46], CuAu [48, 49], PdAu [50, 51] and NiPt [47, 52]. Also see Refs. [53, 54].

In general the difference between the calculated and the experimental results is in the order of 0.1 eV, with the exception for Ni in NiPd and NiPt alloys. It is also interesting to notice that in the case of AgPd and CuAu the experimental series that diverge from E^{cs}_{CLS} are taken from Steiner and Hüfner [3]. The origin of this difference could be due to the sample preparation in the form of thin film alloys, as remarked by Barbieri *et al.* [46]. Also note that more recent experiments carried out for CuAu alloys give better agreement with the first-principles calculations.

Initial and final state effects were investigated, and local DOS calculated for Pd in NiPd, CuPd and PdAu. In line with the earlier results, obtained for AgPd alloys [22], differences between E^{is}_{CLS} and E^{cs}_{CLS} occur in systems with a change in the orbital character of the unoccupied states at the Fermi-level, with alloy composition like CuPd and PdAu. On the contrary, if the orbital character of the screening charge at E_F is the same for alloys at all concentrations, like for Pd in the NiPd alloys, a much smaller final state effects are observed, as compared to the three other alloys. It is interesting to note that it is the final state effects that contribute to the nearly zero Pt $4f_{7/2}$ shift in CuPt, and also to the slightly curved Pd $3d_{5/2}$ shift in CuPd. A direct numerical comparison was made between the total energy approach in form of the complete screening calculations and the Slater-Janak transition state model, giving an overall close agreement between the models, though some differences were noted, especially for Cu $2p_{3/2}$. For AgPd, NiPd, PdAu and NiPt it was difficult to separate the results from the two calculational methods.

In addition to the results for CLSs calculated by the scalar relativistic method, AgPd and PdAu alloys were selected as trial examples to investigate possible effects of calculating the CLS

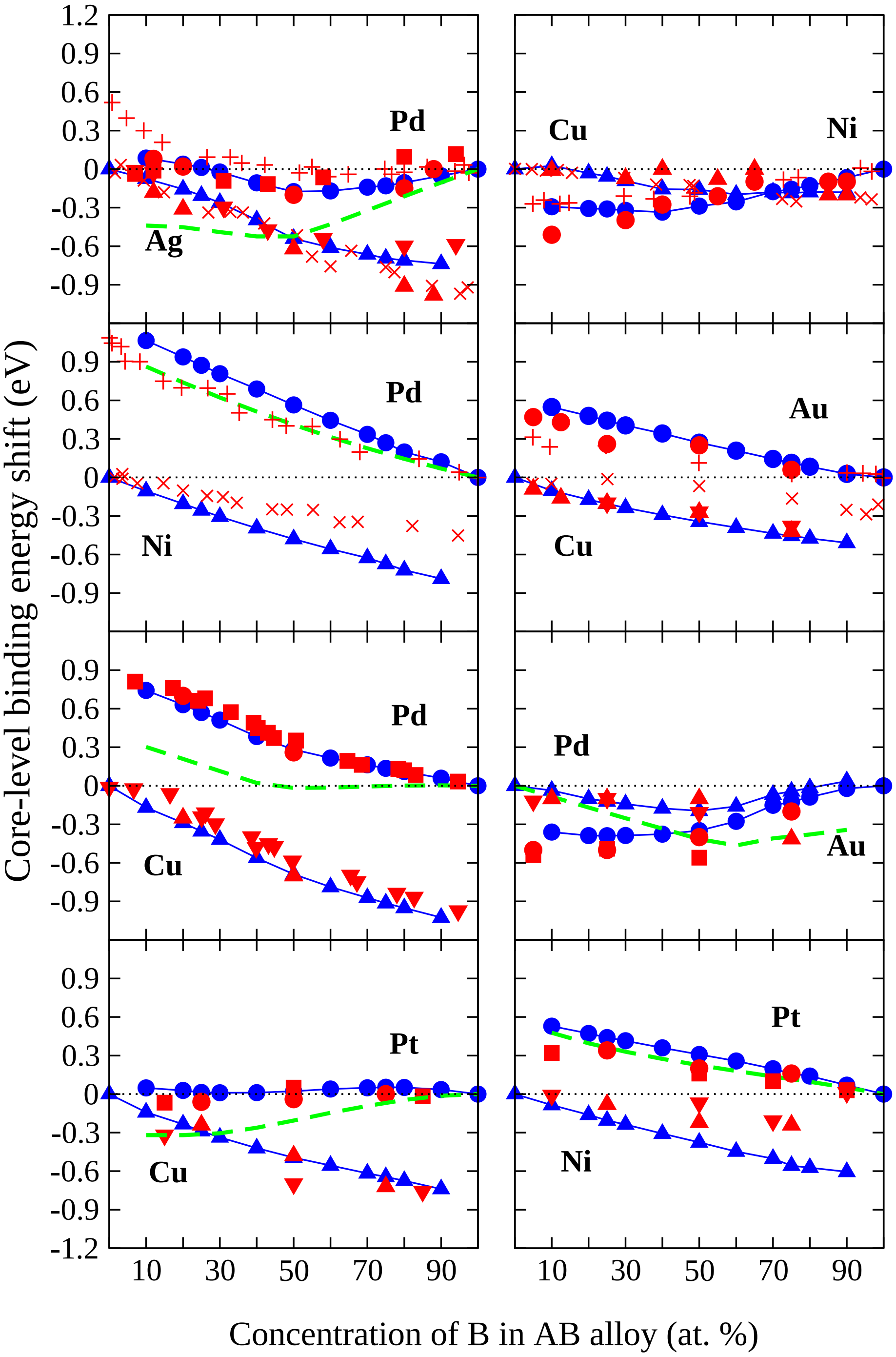

Figure 5: CLS in fcc random alloys AgPd, NiPd, CuPd, CuPt, CuNi, CuAu, PdAu and NiPt. E^{exp}_{CLS} is denoted by disconnected red symbols, E^{cs}_{CLS} full line connected blue symbols, E^{is}_{CLS} dashed green lines for Pd $3d_{5/2}$ and Pt $4f_{7/2}$. See text for further details.

according to fully relativistic theory. Only small differences were noted, which might also be related to the numerical accuracy of the computations. Core-level shifts were also investigated in ferromagnetic systems. Substantial effects due to magnetism was observed in CuNi, on Cu and Ni $2p_{3/2}$ CLS for the alloy concentration $> 50\%$ of Ni, in agreement with the result from experiment for both alloy components.

6 Sensitivity of the CLS to local environment effects

6.1 Disorder broadening of core photoemission spectra

A fundamental feature of random alloys is that chemically equivalent atoms are located in different *local environments*, opposed to the situation in an ordered compound. In the previous section only results from CPA calculations were considered, that effectively average the local effects. Binding energies, and hence CLSs, tend to give different values depending on the specific chemical environment around an atom. With some generalization this would also seem plausible to hold in the case of different local environments in a random alloy. One of the likely consequences that can be predicted is that the spectral line of a core-level attains a larger width in a random alloy, if compared to the corresponding line-width in the pure metal. This difference is called *disorder broadening*. It is in fact only quite recently in XPS experiments with very high resolution that disorder broadening has been detected, first for Cu $2p_{3/2}$ in fcc CuPd random alloys by Cole *et al.* [7], and thereafter the same group has obtained additional results for Cu $2p_{3/2}$ in CuPd, CuZn and CuPt, and Ag $3d_{5/2}$ in AgPd [41, 53, 55, 56].

6.2 Experimental deduction of disorder broadening

The analysis starts with numerically fitting a Doniach–Šunjić (DS) [57] lineshape to the measured XPS line of the pure metal. DS lineshapes are characterized by two parameters, the lifetime parameter and the assymetry index. The DS lineshape is broadened by a Gaussian to simulate the instrumental broadening. The lineshape parameters are then determined by numerical fitting. Upon alloying one assumes that the lifetime parameter is unchanged, which leaves the assymetry index as the only parameter to simulate the XPS alloy spectra. A satisfactory fitting between simulation and experimental data can be obtained by artificially increasing the Gaussian broadening. This indicates that the additional source of broadening present in alloys, not included in the simulation, is Gaussian in character. Knowing the instrumental- and the total broadening mechanism one can isolate and deduce the disorder broadening of the CLS. A more detailed description can be found in the literature, for instance in Refs. [55, 56].

6.3 A theoretical approach

Disorder broadening was investigated theoretically in Ref. [34], using the complete screening picture according to Eq. (3) by introducing a single core-ionized atom at a time at each lattice site in the supercell for the perturbed system. Actual calculations were done by means of the LSGF approach [16, 17], and by calculations in `VASP` [18, 19, 20, 21] where additionally the (Z+1)-

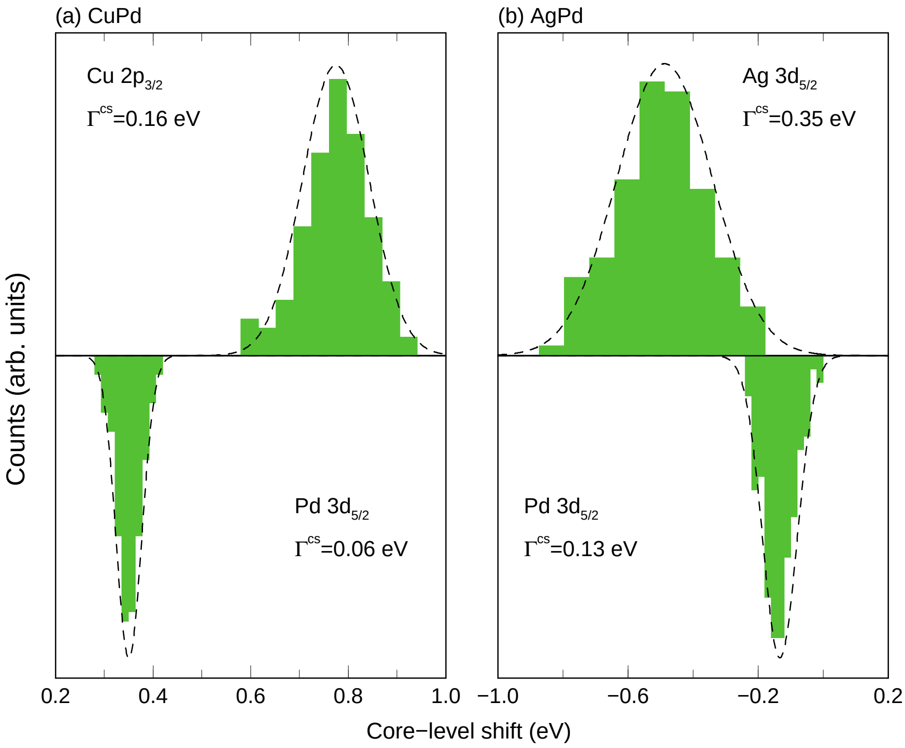

Figure 6: Disorder broadening of CLS in the equiatomic (a) CuPd and (b) AgPd alloys.

approximation was employed to simulate the core-hole screening effect. Previous theoretical estimations of the disorder broadening effect include a model based on charge transfer, by Cole *et al.* [6], and initial state calculations using LSMS, by Faulkner *et al.* [43]. An advantage in the present description is that also final state effects are considered in the total energy scheme. The disorder broadening, Γ, is given for the full width at half maximum (FWHM). The complete screening picture produces a good agreement compared to experimental values, Cu $2p_{3/2}$ in $\mathrm{Cu_{50}Pd_{50}}$, $\Gamma^{cs} = 0.16$ eV, $\Gamma^{exp} = 0.23$ eV, and Ag $3d_{5/2}$ in $\mathrm{Ag_{50}Pd_{50}}$, $\Gamma^{cs} = 0.35$ eV, $\Gamma^{exp} = 0.38$ eV. In Fig. 6 we present these dispersions. One should remark that the absolute values of the Cu $2p_{3/2}$ CLSs are plotted in order to facilitate the illustration of different FWHM. The initial state disorder broadening CLSs agrees well with the previous results in Ref. [43]. To the best of our knowledge no experimental study of the disorder broadening of the Pd $3d_{5/2}$ core spectral line has been published. In these alloys theoretical calculations predicts very narrow distributions for the Pd component, which implies that the Pd $3d_{5/2}$ core-electrons are not so sensitive to the surrounding chemical environment.

It is interesting to notice that the final state effect in the case of Pd $3d_{5/2}$ leads to a smaller overall disorder broadening, due to that the more negative initial state shifts are compensated with the more positive final state contributions, and vice versa. In the cases where the final state contributions to the binding energy in alloy and metal are more similar, as for Cu $2p_{3/2}$ and Ag $3d_{5/2}$, the final state effects come into play as an additional broadening instead. This can actually be shown to correlate with the results for the global composition variation (CPA effective medium) when considering the tendencies around the equiatomic concentration for the initial and complete screening shifts [22, 29]. Once again, this illustrates the importance of including final state effetcs in the analysis of CLSs. For more details see Ref. [34].

Moreover, the influence of local lattice relaxations on the CLS in the CuPd alloy was studied by means of the projected-augmented wave [58, 59] (PAW) method, implemented in `VASP`. We find that the average CLS, for both components, remain the same when we allow for the local lattice relaxations compared to an unrelaxed underlying lattice. Considering the average CLS as a function of nearest neighbors (NNs) of the opposite kind in the first coordination shell, we find that close to the equiatomic distribution the unrelaxed and relaxed lattice gives the same CLS. However, deviations from local equiatomic compositions causes differences in the average CLS per NN, resulting in an increased disorder broadening. The FWHM parameter Γ increases by 0.04 eV and 0.06 eV for Cu and Pd respectively comparing to calculations for unrelaxed and relaxed underlying lattice. Allowing the bond length in the random alloy to relax really brings the theoretical results in better agreement with experiment. The effect of increasing FWHM due to local lattice relaxations was also suggested by Faulkner and co-workers in their theoretical study [43]. Local lattice relaxations might be of more importance for systems with larger size-mismatch between the atoms that constitute the alloy.

7 Interface structures

The interest in studying interface core-level shift (IFCLS) is motivated by possible applications. For instance, a question can be asked if it is possible to detect any difference between whole embedded metal monolayers and various stages of intermixing – or a completely disordered sample. This further leads to the question if theoretically predicted differences between interface qualities could be detected in experimental measurements (with a sufficiently high resolution). If so, theoretical IFCLSs could be used in conjunction with experiment to assist the structure characterization of complex materials.

From a theoretical point of view, it is straightforward to model systems in question, calculate IFCLSs and make a direct comparison. This was done for some trial structures in Refs. [31, 32]. For our calculations of surface and interfaces, the Green's function technique [14] was employed. No steps and no surface or local lattice relaxation was permitted, which is usually a reasonable approximation considering the aim, which is to capture general trends. In particular, the above assumption allows for relatively fast calculations, especially compared to supercell methods.

In Ref. [31], the Cu $2p_{3/2}$ IFCLS for 1-3 whole monolayers (MLs) of Cu embedded in ferromagnetic metals, bcc Fe, fcc Co and Ni, was investigated. Some of the results are displayed in Fig. 7.

It was noticed that the 2-dimensional 1-2 ML Cu embedded into the Ni and Co systems, display a very small difference compared to model shifts based on CLS in the disordered bulk alloy. However, for the case of Fe/Cu/Fe a large difference between model and IFCLS, $\Delta E^{cs}_{CLS} \approx 0.2$ eV, was attributed to interface states. For 3 MLs there were also differences between the results for the Cu-Co and Cu-Ni systems, which could possibly be detected as a broadening effect on the spectral core-line in an experiment compared to the disordered case, if not directly resolved (considering the difference between the outer and inner layer shifts).

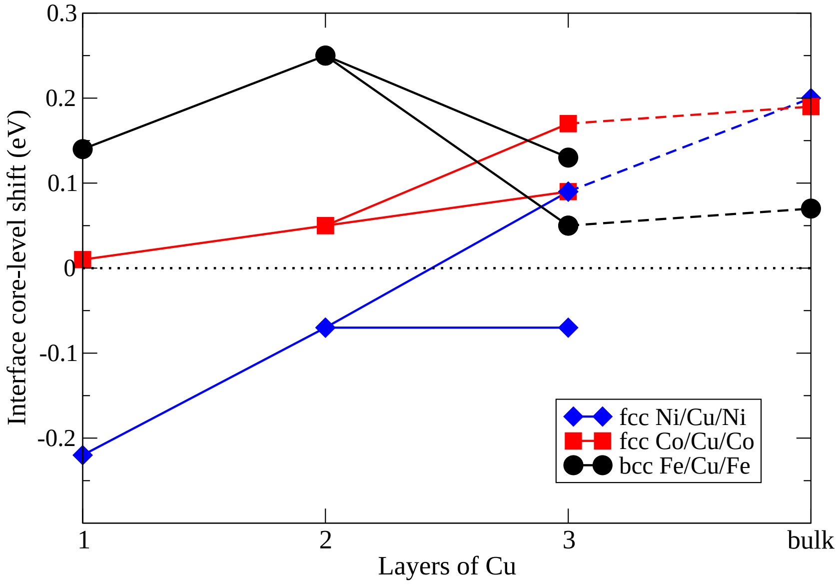

Figure 7: Layer resolved Cu $2p_{3/2}$ IFCLS (eV) for 1-3 MLs of Cu in Me/Cu/Me, Me = Ni, Co and Fe. Cu bulk CLSs at volume of the surrounding metals is given on the right hand side. Dashed lines are drawn between *inner* layer shifts for 3 MLs and bulk CLS, the remaining IFCLS for 3 MLs represents the *outer* layer shift.

In the further work [32], a more extensive theoretical study is made regarding the Cu $2p_{3/2}$ IFCLS for the bcc Fe/Cu/Fe, fcc Co/Cu/Co and Ni/Cu/Ni systems. Here the Cu layers vary in thickness between 1-10 MLs, for the cases of no intermixing and two choices of interface qualities. Different trends are captured for the systems. While in Ni/Cu/Ni a large spread is found in the IFCLSs over the total number of Cu layers and at different degrees of intermixing, which would seem possible to detect experimentally, the effect is smaller in Co/Cu/Co. As in Ref. [31], the results for the Fe/Cu/Fe systems differ from the other systems. It is found that the effect on Cu CLS exists at the sharp Fe-Cu interfaces (no intermixing), and is attributed to interface states, mentioned above. The latter disappear with mixing of Fe and Cu.

To summarize, while it has been shown that theoretical results for layer resolved interface core-level shifts are readily calculated, it would be of high interest to investigate the experimental detectability of different interface qualities in future work.

8 Thin film surface structures

In Refs. [24, 30] take into account applicational aspects of the theoretical determination of core-level shifts for the case of thin film surface structures, attempting their structural characterization based on the comparison between calculated and experimental measurements.

Indeed, in Ref [60] measured binding energy shifts of Pd $3d_{5/2}$ were presented in the near surface region of Pd(100) with a thin magnetic layer of Mn; 1 ML Mn on Pd(100) and a PdMn overlayer on top, obtained by annealing. One of the interesting questions that arised was the determination of the annealed structure.

As in the case of interface structures in the previous section, the surface and interface Green's function technique was used. As a first test of the accuracy of the complete screening picture computations, SCLSs were calculated and compared with experiment for the case of pure Pd(100) and the 1 ML Mn/Pd(100) system. It was found that theory gave reasonable shifts compared with experiment and previous calculations in the literature. In the experiment it was deducted that Mn formed 'checkerboard' pattern (C) together with Pd (P) in a layer, resulting in 2 C-layers after annealing. In Ref. [24] experimental results were compared to the theory by calculating the near surface CLSs of Pd for the candidate systems suggested in Ref. [60], namely I C/C, II $C/P/C$ and III $P/C/P/C$ on Pd(100), see Fig. 8.

The layer resolved CLS compared to experiment is displayed in Fig. 8, layers are numbered from the surface, S, and downwards. In addition, the difference in total energy, ΔE, against a 1 ML Mn/Pd(100) system is given. From the figure it is indeed very easy to single out the structure I as the one reached after annealing. A direct comparison between the experimental and theoretical SCLSs, clearly leads to this conclusion. One sees that the presence of Mn atoms in a layer leads to a significantly different CLS at the Pd atoms. For instance notice the differences between the CLS at the surface Pd atoms as Mn goes deeper into the bulk. Also notice that structure I has a higher total energy as compared with the energetically more favourable structures II and III. They are however not formed due to kinetic limitations [60]. A natural extension of the study would be to continue the annealing of PdMn/Pd(100), and make a further comparison between theory and experiment. In brief, this example shows the possibility to use theoretical CLSs *together* with experimental results to make a prediction for metastable structures obtained in experiment.

In Ref. [30], this idea was further investigated in a combined theoretical and experimental study

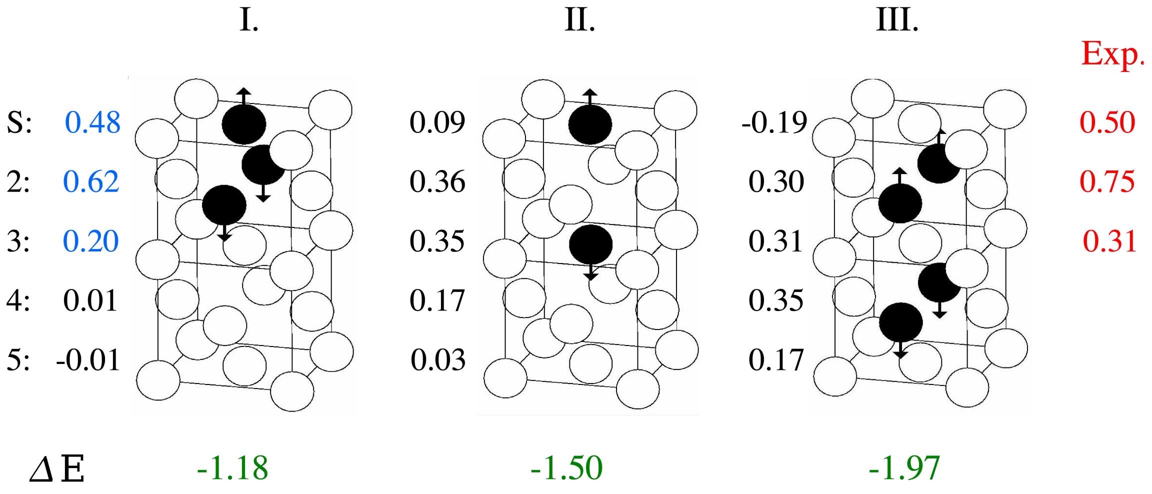

Figure 8: Layer resolved Pd $3d_{5/2}$ CLS (eV) for the PdMn/Pd(100) structures I. - III. Pd (white spheres) and Mn (black spheres) with arrows indicating the magnetic moment. ΔE gives difference in total energy compared to a 1 ML Mn/Pd(100) system. All values are given in eV.

of Pd thin films, CuPd and AgPd surface alloys, on an inert Ru(0001) surface. To test the employed complete screening calculations, the surface and subsurface CLS for pure Ru(0001) was calculated to -0.45 respectively 0.09 eV, and found to be comparable with both experiment, -0.37 and 0.13 eV and transition state calculations within FP-LAPW, -0.38 and 0.12 eV, by Lizzit *et al.* [61]. In the experiment for the CuPd films, a change in the concentration dependence of the Cu $2p_{3/2}$ CLS in alloy films with different thickness, between 1 monolayer (ML) and up to 2-4 layers, was observed. This trend is reproduced by theory, and in addition it is noted that the layer resolved theoretical shifts for Cu atoms at the Ru interface for >1 ML systems follows the 1 ML Cu CLSs.

Another study was performed for a system of an approximately equiatomic ∼4 MLs AgPd surface alloy on Ru(0001). Experimental photoemission spectra were taken for Ag and Pd $3d_{5/2}$ core levels for samples treated at different temperatures. First, ∼2 ML Ag were deposited at Ru(0001) with a residual coverage of Pd, then a deposition of 1.8 ML Pd was made, resulting in a ∼4 MLs thick AgPd film. By comparing theoretically obtained layer resolved CLSs calculated for a number of trial concentration profiles of 4 ML AgPd/Ru(0001), with experimental shifts for Ag and Pd, an attempt is made to monitor the overall change in the film structure as the annealing progresses. We suggest that Pd goes towards the Ru interface and Ag towards the surface with increasing temperature. It is found that while one can follow the overall trends as the annealing temperature is raised, it is less straightforward to make more detailed predictions of the concentration profile. One of the reasons is the relative difficulty of comparing on one hand layer resolved theoretical CLSs, and on the other hand experimental shifts with a contribution from all the layers to the signal, which is not layer resolved. To provide a more direct comparison between theory and the experimental photoemission curves obtained at different temperatures, the calculated shifts were inserted into the model for experimental spectrum templates. Notice that the situation here is very different compared to the study above for the PdMn/Pd(100), from Ref. [24]. Instead of having a limited number of systems, the degrees of freedom for the AgPd concentration profiles are significantly larger. In order to overcome this difficulty, we are currently investigating a possibility to go along the theoretically consistent way of selecting the concentration profiles, by using the *Monte Carlo* technique with interaction parameters determined from first-principles, assuming that the structures reached in experiments are in the so-called quasi-equilibrium state. Then we compare CLSs calculated for the obtained segregation profiles with the experimental results. Our preliminary results indicate very good agreement between theory and experiment. The complete study will be presented elsewhere.

9 Auger transition

In a recent work [28] the complete screening picture was generalized to calculate the Auger electron kinetic energy (E_{KIN}) shifts from first-principles using the model originally proposed in Ref. [62]. Auger kinetic energy shifts were first calculated in metals using the phenomenological approach via Born-Haber cycles and the equivalent core approximation [2, 62]. By studying the kinetic energy of photoelectrons and Auger electrons in the same experiment, uncertainties in energy reference can be minimized. In addition, relaxation effects due to screening of the core-hole can be investigated directly from the so-called Auger parameters [28, 64].

The Auger ijk core-core-core transition can be decribed as a two-step process, shown schematically in Fig. 9. The first step, Fig. 9(a), consists of the photoemission of a core-elecron from the i:th orbital with a binding energy E_i, leaving a core-hole. This is the final state in the photoemission process. In the second step, Fig. 9(b), an electron at the j:th core-level, with lower binding energy compared to i, fills the core-hole, while in the same immediate process the electron in the k-orbital is ejected with the Auger kinetic energy

$$E_{KIN} = E_i - E_{jk}. \tag{13}$$

Note that E_{KIN} is determined solely by the binding energies E_i and E_{jk}, which corresponds to the double core-hole binding energy required to move the j and k electrons from their respective core-levels. The Auger kinetic energy *shift* for an atom A in the pure metal, respectively binary alloy $\mathrm{A}_{1-x}\mathrm{B}_x$, ΔE_{KIN}, can be interpretated as a combination of a single-hole metal-to-alloy shift ΔE_i and a corresponding double-hole shift ΔE_{jk} [62], such that $\Delta E_{KIN} = \Delta E_i - \Delta E_{jk}$. The double-hole shift ΔE_{jk} can be calculated as in the case of the core-level shift, i.e. as a *total energy* difference between two systems, one with a doubly ionized atom A^{**} in an alloy $A_{1-x}B_x$ and a doubly ionized impurity atom A^{**} in the pure A metal. The double-hole shift is then given by

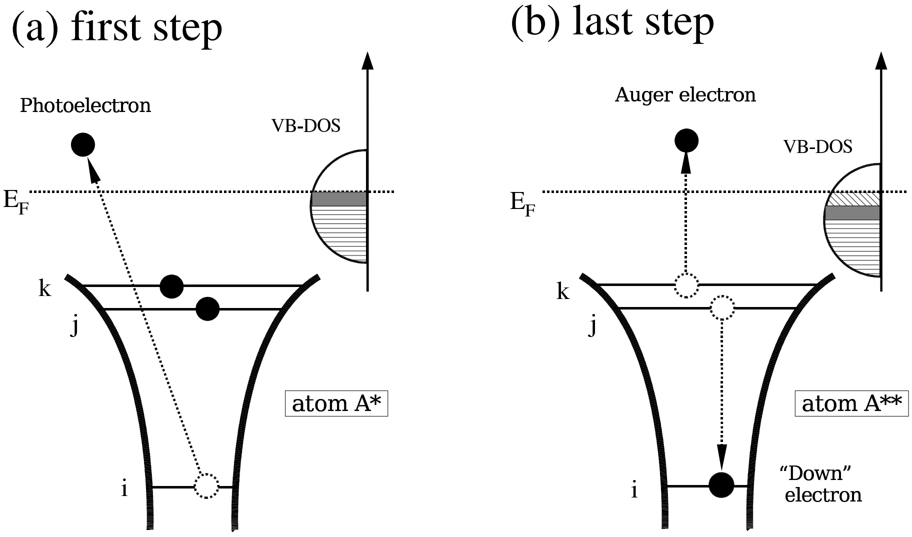

Figure 9: The two steps in the ijk core-level Auger transition, in which a core-hole is created by photoemission in the first step. See text for more discussion.

$$\Delta E_{jk} = \mu_{jk}^{alloy} - \mu_{jk}^{metal} = \Delta\mu_{jk}, \tag{14}$$

and the Auger kinetic energy shift is written,

$$\Delta E_{KIN} = \Delta\mu_i - \Delta\mu_{jk}. \tag{15}$$

Here one immediately notes that the first term is the core-level shift, while the second term corresponds to the double-hole binding energy shift for the two core-holes at j respectively k.

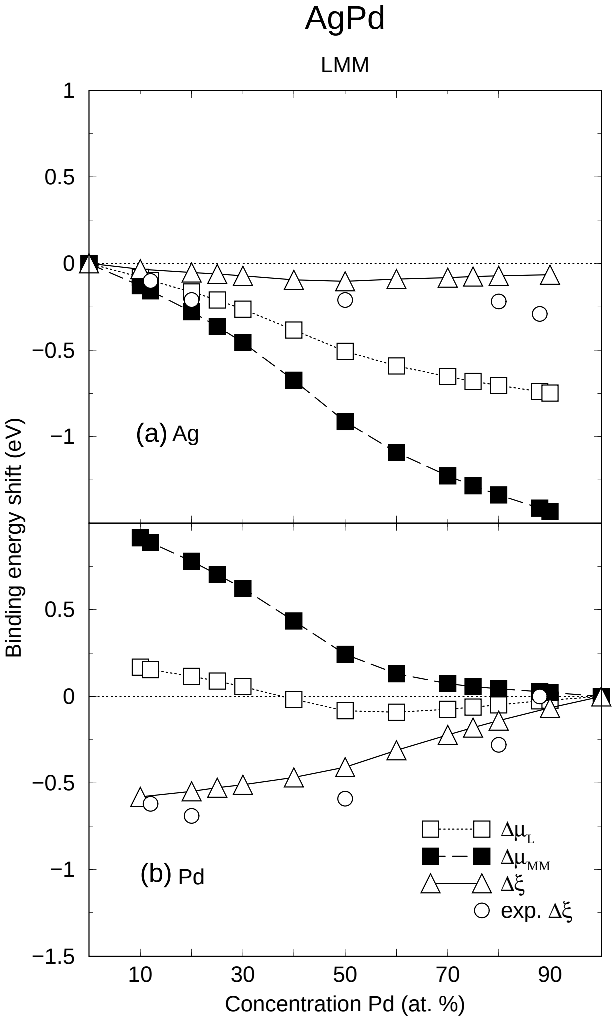

Figure 10: The Auger parameter shift $\Delta\xi$ with CLS $\Delta\mu_L$ and double core-hole shift $\Delta\mu_{MM}$.

Another possibility offered by the theory, as well as experiment, is to calculate the Auger parameter ξ. Its shift is given by the sum of the core-level shift and Auger shift. ξ is used in experimental works and has become an important tool for characterizing the response of materials to electron excitations [63, 64],

$$\begin{aligned} \Delta\xi &= \Delta E_{KIN} + E_{CLS} \\ &= 2\Delta\mu_i - \Delta\mu_{jk}. \end{aligned} \tag{16}$$

In experiment it is frequently extracted as an estimate of the relaxation effects.

Let us now consider Auger kinetic energy shifts in fcc disordered AgPd alloys [28]. The task of analyzing the Auger shift can be broken down into an investigation of the core-level $\Delta\mu_L$ ($2p_{3/2}$) and double-hole shifts $\Delta\mu_{MM}$ ($2\times3d_{5/2}$) for Ag and Pd at different concentrations. An analysis of the different binding energy shifts can also be split into a comparison of initial state effects (core-electron energy eigenvalues), and final state effects (relaxation from the screening of the core-holes). If the difference in final state effects are small, the shifts are determined mainly by positions of the one-electron eigenstates, and one gets the simple relation $\Delta E_{jk} \approx 2\Delta E_i$, because deeply laying core states feel a change of the crystal potential as a rigid shift. In this case one obtains $\Delta\mu_{MM} \approx 2\Delta\mu_L$, leading to very simple anti-symmetry relation between the Auger kinetic energy shift and the core-level shift, $\Delta E_{KIN} = \Delta\mu_L - \Delta\mu_{MM} \approx -\Delta\mu_L$. This can be confirmed in the case of Ag by inspecting the theoretical results, and is due to that the Ag core holes are screened by mainly *sp* electrons both, in alloys and in the pure metal [28].

In Fig. 10 the separate contributions to the Auger kinetic energy and the Auger parameter shifts in fcc AgPd alloys, Eqs. (15) and (16), respectively, are shown, the calculated metal-to-alloy changes of the chemical potentials of single ionized atoms $\Delta\mu_L$, as well as that for double ionized atoms $\Delta\mu_{MM}$, together with the Auger parameter shift. Good agreement between theory and experiment is observed for the Auger parameters shifts. Also, one can clearly see a relation, $\Delta\mu_{MM} \approx 2\Delta\mu_L$, in the case of Ag, as discussed above. In the case of Pd the relation does not hold, indicating larger importance of of the relaxation effects, in agreement with larger value of the Auger parameter shift.

10 Summary

An overview is presented for the recent work on first-principles studies of core-level binding energy shifts, mainly using the complete screening picture, which includes initial and final state effects in the same computational scheme. Investigations have been made for various types of complex systems, including a number of disordered alloys, interface structures and thin films on surfaces, with good agreement between theoretical and experimental results (when available). Initial state CLSs were used to estimate the final state effects. The complete screening picture, which is a total energy approach, was compared to the transition state model, an energy eigenvalue approach which however also includes both initial and final state effects. It was found that the agreement is typically very good between the two different methods. An improvement for the use of the transition state model was suggested with minimal increase of computational costs. In addition to the study of CLS as a function of the alloy composition within the coherent potential approximation (which gives fast computation), results were obtained for the broadening of the spectral core-line due to the different local chemical environments in a disordered alloy, by using supercell methods. We also propose to using theoretical shifts together with experimental data as a tool for structural charaterization of materials. For instance we applied the methodology for the structural characterization of metastable samples obtained in experiment, as well as for the determination of the interface qualities. The continued development of x-ray photoelectron spectroscopy towards increased resolution, encourages both a direct comparison between experiment and theory, as well as an investigation of applicational purposes – using theory and experiment together.

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