HCM Newsletter

Ψ_k Network

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

Number 18 December 1996

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Contents

1 Editorial

Finally, as you probably noticed by now, we have a page with the Newsletter content. We hope that it will help you to find easily the places of interest. However, please do read the **News from the Network Section**. In the **Editorial** we will no longer summarize the content of the *Newsletter*. We will just bring to your attention the more important parts of the *Newsletter* or issues discussed.

Some of you may know that the original '*Magnetism Working Group*' of our Network has started a separate TMR Network on *'Interface Magnetism'*. In this Newsletter we publish a report, including programme and abstracts of presented papers, of their first workshop that took place in Jülich on November 25–26, 1996. There you can also find information on their future workshops. Please note, that our *Newsletter* will cover also this TMR Magnetism Network.

Another important news is that this *Newsletter* contains altogether 60 interesting abstracts (10 in the report of the TMR Magnetism Network), and we would like to invite you to at least browse through them.

In this *Newsletter*, the **Highlight of the Month Section** contains an article by P.J.D. Lindan (*Daresbury, UK*), N.M. Harrison (*Daresbury, UK*) and M.J. Gillan (*Keele, UK*) entitled *'Paint by Numbers: Oxide surface Chemistry using First-Principles MD'*.

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

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

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

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

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

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

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

2 News from the Network

As the end of the calendar year is approaching we are concentrating on preparing an annual report on the Network's activity this year. The report has to be submitted to Brussels first thing in January 1997. To make this report look as impressive as many of our activities throughout the year, we would need your help. If you have not done it yet, but you have submitted or published papers that acknowledge the Network, please do contact us and provide this information as soon as possible. The only way we can monitor the impact of the Network on your research is through your input. Moreover, if you are involved in a collaboration within the Network, please submit a contribution, to the annual report and the first Newsletter of next year, describing the essence of the project and results. We intend to have a section containing highlights of all collaborations of the Network. The contributions need not be long, just a page or so, but we welcome also those more ellaborate ones, including figures, etc., however, all in LATEX format only. Deadline for these contributions is the end of December 1996. Here we wish to thank those of you who have already provided this information.

The EU funding of the Network will finish at the end of next year. However, as written in the special issue of the newsletter, distributed early November, we are working on preparing an application to the TMR programme to continue our activity in the present and other forms. We will definitely want to keep the Newsletter going, and to make it a success we will need a continuous support from you. Please keep on submitting your abstracts (the abstract template can easily be extracted from any of the *Newsletters*) and other contributions. It is by sharing scientific information that we make progress and help our community flourish.

Finally, since it is the last Newsletter of this calendar year, we would like to thank all of you for all kinds of contributions to the past Newsletters and wish you all **Merry Christmas** and **Happy New Year**.

3 News from the Working Groups

3.1 Reports on Collaborative Visits

Report on secondment of Andrés Mujica (La Laguna, Spain) to Cambridge, UK

3 July – 6 September, 1996

Andrés Mujica from La Laguna, Tenerife, Spain, visited the Theory of Condensed Matter group at the Cavendish Laboratory, Cambridge from 3rd July 1996 to 6th September 1996. Of this period Andres spent some 6 weeks working in Cambridge. The remainder of the time was spent at two conferences in Germany (VII International Conference on High Pressure Semiconductor Physics, July 28th-31st Schwăbisch-Gmŭnd) and Seattle (XVII Congress and General Assembly of the International Union of Crystallography, August 8th-17th, Seattle), at which he presented some of the work from the collaboration. Short accounts of the work presented will appear in two conference proceedings papers [1, 2].

During his time in Cambridge, Andrés worked on two separate projects. The first was on the calculation of high pressure phases in III-V compounds, while the second was on a new method for calculating defect energies.

Our work on phases of III-V compounds was stimulated by experimental and theoretical work over the last two years which has turned the hitherto accepted sequence of high pressure phases of III-V and II-VI compounds on its head. The β-tin phase, once thought to be ubiquitous, may never be stable, and the rocksalt structure is probably much less common than once thought. It seems that these high symmetry phases are often unstable to symmetry lowering distortions. In our work we have (1) investigated these distorted structures using plane-wave pseudopotential total energy calculations, (2) studied the driving forces for the distortions, (3) compared our results with the experimental data, and (4) predicted new distorted phases of III-V compounds for experimentalists to look for. Our final aim is to construct a new systematics of the high pressure phase diagrams of III-V (and later II-VI) compounds. Our work relates very directly to the experiments done by Prof. Richard Nelmes (Edinburgh University) and coworkers, who perform high resolution powder X-ray diffraction studies at the Daresbury Laboratory. These experiments have achieved much higher resolution than previous experiments, which has revealed the existence of the distorted structures. During the visit we travelled to Daresbury to meet Prof. Nelmes and Dr. McMahon and discuss the project. We learnt how the experiments are done and what new techniques have enabled them to achieve the improved resolution.

Last year we carried out a study of GaAs [3] and we have now completed studies of GaP, InP, and InAs. The LDA plane-wave pseudopotential calculations were performed on the local computing facilities in Cambridge. The unit cells contain only small number of atoms, but the numerical accuracy must be very good to resolve the small energy differences between phases. Obviously full relaxation of the structures is necessary. We studied numerous structures, including the *Cmcm* phase which is a distortion of rocksalt, the body-centred orthorhombic *Imm2* structure, which is related to the β-tin structure, and the sc16 structure, which is the binary analogue of bc8. We found thermodynamically stable *Cmcm* phases in InP, InAs, and GaAs, and a stable or nearly stable *Cmcm* phase in GaP. This is in line with recent experimental investigations by Prof. Nelmes and coworkers [4]. We have also found stable *Imm2* phases in InP, InAs, GaP, and GaAs. At the moment there is no experimental evidence for the existence of *Imm2* phases in these compounds, so that our work stands as a prediction to be tested by new experiments. Our prediction of a stable sc16 phase for GaP increases the mystery surrounding this elusive phase. This phase has not been observed experimentally in any III-V compound, even though the relevant pressure range has been studied extensively. It is quite likely that the transition to the sc16 phase is strongly kinetically hindered, but it may be possible to make sc16 phases by high temperature treatment under pressure. Our theoretical work on the high pressure phases of these III-V compounds is by far the most complete to date. During the visit we wrote up this work and have submitted it for publication [5].

We also worked on the formulation of a new method for calculating defect energies using supercell techniques. We derive Kohn-Sham equations via minimisation of a functional which contains the effect of the "perfect crystal" which surrounds the "central" supercell in which the defect is situated, but the potential is periodic so that many of the standard techniques can still be used. Our method should be superior to the sort of non-self-consistent corrections that are sometimes added to standard supercell calculations, and it should be particularly suited for studying charged defects. During the visit we formulated the problem more precisely and convinced ourselves that it ought to work! We are now implementing the method.

Our collaborative research programme has been helped significantly by this visit, and we are very grateful to the Ψ_k network for providing the funding for it.

References

[1] A. Mujica, R.J. Needs, and A. Muñoz, to appear in *Phys. Status Solidi (b).*

[2] A. Mujica, A. Muñoz, and R.J. Needs, to appear in *Proceedings of the ICPS-23.*

[3] A. Mujica, R.J. Needs, and A. Muñoz, *Phys. Rev.* B **52**, 8881 (1995); A. Mujica and R.J. Needs, *J. Phys.: Condens. Matter* **8**, L237 (1996).

[4] M.I. McMahon and R.J. Nelmes, *J. Phys. Chem. Solids* **56**, 485 (1995).

[5] A. Mujica and R.J. Needs, submitted to *Phys. Rev.* B.

(R. Needs)

Report on the secondment of H.G. Bekker (University of Twente) to N.E. Christensen (Aarhus University)

September 2 to September 29 1996

The visit took place as part of a joint project to develop a full potential first principles electronic structure method based on the CLOPW basis set (see abstract by H.G. Bekker, C.M.J. Wijers and N.E. Christensen in the Ψ_k−Newsletter 10, 1995).

The original goal of this visit was to do a comparative study of CLOPW calculations and FP-LMTO calculations on MgTe. We also planned to study a number of other model systems where linearised electronic structure methods like LMTO have problems with higher lying semi-core states which hybridise with valence states (e.g. Zn and Sn). We hope that a comparison of the results between CLOPW and FP-LMTO will give information on 1) the effect of mathematical modifications in the LMTO method (downfolding / two panel calculations) on the calculated properties of those materials and 2) the ability of the CLOPW basis set to describe semi-core states with sufficient accuracy.

However during the initial calculations we encountered some unespected problems in the description of the exchange correlation potentials in the CLOPW code. To cure these problems we discussed and tested several ways to combine the advantages of the conventional linear least square fit methods with the concept of confinement.

One idea being tested at the moment is the decompositon of the exchange correlation potential into a spherically symmetric confined part around the atoms and a remaining part which is smooth enough to be accurately fitted by a limited number of plane waves.

Unlike methods like LMTO, CLOPW does not use so-called empty spheres to get a close packed filling of the Wigner Seitz cell. This leads to a larger number of plane waves required for an accurate fit than expected originally. The number of plane waves remains however within very reasonable limits.

The results up until now are still unpublishable due to the uncertainties in the code but they look promising. We hope to do the originally planned study in the nearest future.

(H.G. Bekker)

Report on a Collaborative Visit of K.P. Bohnen (Karlsruhe) to J. Hafner and A. Eichler (Vienna)

August 24 to September 5, 1996

During the past two years a fruitful collaboration between the Vienna group and my own group in Karlsruhe has emerged. The common interest is concentrated around *ab-initio* pseudopotential calculations of bulk and surface phonons. For the bulk the aim has been to calculate dispersion curves in high-symmetry directions. An especially demanding system is Rhodium for which no experimental results were available when we started the project. The calculations were carried out independently by both groups using different pseudopotentials and basis functions. While the results of both calculations indicated phonon anomalies in the same region in the Brillouin zone, the absolute frequencies differ by roughly 6%. Some time during this visit has been used to try to understand this difference. It is linked to the slightly different lattice constant and bulk modules which the two pseudopotentials give rise to. FLAPW calculations are presently carried out to determine the proper "LDA" lattice constant, bulk modules and zone boundary phonon. During extensive discussions a preliminary draft of a publication has been established which, besides giving phonon dispersion relations for Rhodium in excellent agreement whith new experimental results, addresses in detail the question of the origin of the anomalies and also the question of accuracy which can be obtained today with state of the art pseudopotential calculations. This visit was crucial for clarifying remaining questions and deciding on the material which should be included in the paper. Due to the support we hope to submit the paper still this year.

(K.P. Bohnen)

Report on a Collaborative Visit of A. Svane (Aarhus) Daresbury Laboratory (UK)

November 15–18, 1996

This visit was used to discuss two joint papers on applications of SIC-LSD and to discuss future joint efforts in this field. One development considered during the visit was the fully relativistic and spin–polarized SIC code (LMTO-ASA) by S. V. Beiden, W.M. Temmerman and Z. Szotek, which currently is running and being tested. Several attempts at performance improvements were discussed. Furthermore, ongoing research on the computation of physical properties of rare-earth systems (notably Ce and Yb compounds) with the SIC-LSD approach was debated and coordinated.

(A. Svane)

Report on a Collaborative Visit of A. Lichtenstein (Jülich) to Materials Modelling Laboratory, Department of Materials, University of Oxford

July 7–14, 1996

During this short visit we established a general program of work aimed at applying the rotationally invariant LSDA+U scheme to the investigation of the electronic structure of the (100) surface of nickel monoxide.

This problem is strongly linked to the project currently pursued theoretically by Dr. S.L. Dudarev and Dr. A.P. Sutton and experimentally by Dr. M.R. Castell, Ms. C. Muggelberg and Dr. G.A.D Briggs at the Department of Materials. Our idea was to perform *ab-initio* studies to understand the origin of states existing on the surface of NiO and to analyze the dependence of magnetic moments and orbital ordering in the direction normal to the surface. No similar calculation has ever been performed for a surface of transition metal monoxide and we expected that our project would be of considerable value to academic community and that it would assist in our work towards understanding of the electronic structure of this class of materials.

Following the agreed program of work, over the last four months we have carried out a series of calculations using the full-potential implementation of the LDA+U method. The calculations have been performed for slabs containing various numbers of NiO and empty layers and we have found that a calculation involving a periodic continuation of a seven–layer (100) antiferromagnetic slab (two NiO units per layer) separated by six layers of empty spheres provides a reasonably good approximation to the case of a free (100) surface. The band gap obtained from the slab calculation was found to be substantially reduced ($E_{g_{surface}}$=3.33 eV) in comparison with the result of an LSDA+U calculation done for bulk NiO (E_g=3.8 eV). Our analysis of the partial density of states evaluated both for atomic sites and for empty spheres shows that there are two localized band gap states resulting from Ni-d_{z^2} and O_{p_z} orbitals of surface nickel and oxygen atoms, respectively. We have further applied our results to simulate STM images of the NiO (100) surface and have found that they agree well with experimental data obtained recently at the Department of Materials by Dr. M.R. Castell, Ms. C. Muggelberg and Dr. G.A.D Briggs.

The results of the work have been submitted for presentation at the CMMP96 meeting. We are currently preparing a paper for submission to one of the physical journals.

(A. Lichtenstein)

3.2 Reports on Workshops

Report on Computer Course on Molecular Dynamics

Berlin, November 4–8, 1996

The second Ψ_k computer course on molecular dynamics was held in Berlin from November 4 to 8, 1996, in the Fritz-Haber Institute of the Max-Planck Geselschaft. It had 22 participants, 12 from the European Union and the others from other European countries, United States, Brazil, Argentina and China, selected from 51 applications. After the deadline there were still another 8 inquiries about the course. Many applicants that looked excellent could not be accepted due to the strict limitations in the number of participants of an 'hands-on course'. Most applicants made a ten minutes presentation of their research interests, which covered a wide range of materials and applications, in semiconductors, magnetic materials, minerals, electrochemistry, etc.

The course was organized by Jorg Neugebauer, Jose Luis Martins and Matthias Scheffler. The lectures were given by the organizers and by members of the theory group of the Fritz-Haber Institute. The course covered the basic concepts of density functional theory, and an introduction to the use of the '**fhi96md**' program. The program allows calculations for molecules, perfect crystals, defects in crystals, and crystal surfaces for materials as different as semiconductors, simple and transition metals, insulators, etc, with a pseudopotential, plane-wave scheme. The code is available on the web at **http://www.fhi-berlin.mpg.de/th/fhi96md/code.html**.

(J.L. Martins)

TMR-Network on 'Interface Magnetism'
Workshop on Interlayer Exchange Coupling

November 25 - 26, 1996

Institut für Festkörperforschung, IFF Conference Room N-219

At the first meeting of the TMR network management board in Schwäbisch-Gemünd it was decided that the network should organize miniworkshops on the different network projects. The aim would be to review recent progress in the filed, to identify interesting projects and to start international collaborations within the network resulting in common publications. In particular, the last point is one of the main aims of the TMR Networks of the European Union and the success of the network will be judged by the EU on the basis of international collaborations.

The first workshop on **'Interlayer Exchange Coupling'** took place at Jülich on November 25-26, 1996. It was attended by about 20 participants, with at least one representative from each node. The program of the workshop and the abstracts of all talks are attached. There was plenty of time for discussions and all talks were well received. Of particular interests were the presentations of the experimental colleagues R. Coehoorn, C. Carbone and P. Grünberg (who discovered the effect in 1986). In total we believe that the workshop was quite successful and that we are on a good course.

The next workshop on "KKR Methods" is scheduled for February 16 - 17, 1997 and will be organised by Peter Weinberger at the Technical University in Vienna.

Walter M. Temmerman
coordinator TMR Network

Peter H. Dederichs
chairman TMR Network

Programme

Monday, November 25, 1996

9.45 - 10.00	Welcome and organizational remarks
10.00 - 11.00	P. Bruno: Approximation schemes for calculating interlayer magnetic interactions in metals and alloys
11.00 - 12.00	V. Drchal: Effect of alloying and ordering in magnetic layers on interlayer exchange coupling
12.00 - 14.00	Lunch at Seecasino

14.00 - 15.00	R. Coehoorn: Interlayer exchange coupling across Cu and FeSi: experimental results and opportunities for first principles theory
15.00 - 15.30	J. Kudrnovský: Effect of cap-layers on interlayer exchange coupling
15.30 - 16.00	A. Niklasson: Ab-initio investigation of the interlayer exchange coupling in magnetic multilayers
16.00 - 17.00	Coffee
17.00 - 17.30	P. Grünberg: Experiments on biquadratic exchange and antiferromagnetic bias
17.30 - 18.00	P.H. Dederichs: Interface reflectivity and interlayer coupling in Co/Cu (001)
19.00	Network-dinner at Hotel Hexenturm

Tuesday, November 26, 1996

9.00 - 10.00	D. Stoeffler: Ordered compounds and interlayer exchange coupling: Co/Ru, Co/Rh and (FeCo)/Mn
10.00 - 10.30	Coffee
10.30 - 11.30	C. Carbone: Spectroscopy of spin-polarized quantum-well states
11.30 - 12.00	R. Kläsges: Spin resolved photoemission study of the interface formation and growth of Fe on Si(100)
12.00 - 14.00	Lunch at Seecasino
14.00 - 15.00	Discussion about future projects

Workshop Abstracts

Effect of alloying and ordering in magnetic layers on interlayer exchange coupling

V. Drchal[a,b]
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[b]CMS, Technical University, A-1060 Vienna, Austria

An *ab-initio* theory of the interlayer exchange coupling (IEC) in metallic multilayers which employs the spin-polarized Green function technique, the Lloyd formulation of the IEC, and the coherent potential approximation together with the vertex-cancellation theorem to describe the effect of disorder is developed. The formalism is applied to study amplitude and phase of the IEC between Fe-Co-Ni alloy layers across a Cu spacer layer. The multiplicative character of the complex phase ascribed to each of magnetic subsystems is verified in terms of realistic calculations. It will be demonstrated that the formation of an ordered superstructure in alloyed magnetic layers induces new periods of the IEC whose origin can be correlated with a new caliper of the spacer Fermi surface when folded down to the Brillouin zone of corresponding complex superlattice.

Ab-Initio Investigation of the Interlayer Exchange Coupling in Magnetic Multilayers

A.M.N. Niklasson
Condensed Matter Theory Group, Physics Department,
Uppsala University, S-75121 Uppsala, Sweden

A first-principles LMTO Green's function method utilizing the principal layer technique and the coherent potential approximation has been used to calculate the interlayer exchange coupling in magnetic multilayers. Especially the effects on the magnetic interlayer coupling due to interface intermixing are investigated. Moreover, the dispersion of quantum-well states in the two-dimensional Brillouin zone as well as their periodic behaviour as a function of spacer thickness has been calculated. Their relations with the Fermi surface of the spacer material and the the magnetic interlayer coupling are discussed.

Approximation schemes for calculating interlayer magnetic interactions in metals and alloys

P. Bruno
Institut d'Électronique Fondamentale, CNRS URA 22
Bât. 220, Université Paris-Sud, F-91405 Orsay France

The various level of approximations that can be used to calculate the interlayer exchange interactions in metal and alloys magnetic multilayers are discussed.

The simplest approach consists in calculating total energy differences between self-consistent F and AF configurations; this approach, however, is very demanding on the computational point of view.

A more convenient approach consists in computing non-self-consistently the band energy difference between F and AF configurations. This approach, usually called "force theorem", can

be justified by using the variational properties of Harris functionals. The freedom in the choice of the Harris functional can be used to reduce significantly the required amount of numerical calculations. Although this has be done seldom, the magnetic torque (instead of the magnetic energy) can be computed directly, without calculating energy differences.

In the case of disordered alloys, one has to perform some configurations averaging. By using Ducastelle's "alloy force theorem" and the "vertex cancellation theorem", together with the CPA, the magnetic interlayer coupling in disordered systems can be computed with almost the same numerical effort as for pure metals.

Finally, in the limit of large spacer thicknesses, asymptotic approximations can be used. Periods of oscillation of the interlayer exchange coupling are relate to the (bulk) Fermi surface of the spacer. In the case of an alloy spacer, an analog result is obtained by using an appropriate complex generalization of the concept of Fermi surface.

Spectroscopy of Spin Polarized Quantum Well States

C. Carbone
Institut für Festkörperforschung, Forschungszentrum Jülich,
52425 Jülich, Germany

A review will be given of recent progress in photoemission studies of ultrathin films in connection with the interlayer exchange coupling. Quantum-size and magnetic effects are spectroscopically found to modify the electronic structure of non-magnetic spacers. Spin and angle resolved photoemission has been used to probe the electronic states of Cu films on fcc Fe(100), Co(100) and Ni(100) in the k-space regions associated to the two periods of the oscillatory coupling. Spin polarized quantum well states are observed in films of thickness up to 50 atomic layers. The density of states and spin-polarization show at the two stationary points of the Fermi surface a modulation which corresponds to the short (2.5 ML) and to the long (5.9 ML) coupling period.

Effect of cap-layers on interlayer exchange coupling

J. Kudrnovský[a,b]
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[b]CMS, Technical University, A-1060 Vienna, Austria

The effect of non-magnetic cap-layers on periods, amplitudes, and phases of oscillations of interlayer exchange coupling (IEC) is studied theoretically on *ab initio* level. We employ the spin-polarized surface Green function technique within the tight-binding linear muffin-tin orbital method and the Lloyd formulation of the IEC. Application is made to Co/Cu/Co(001) trilayers with Cu-cap layer interfacing the vacuum through the dipole barrier. We investigate in detail both the asymmetric case with one semiinfinite Co-slab and other Co-slabs five monolayers thick as well as symmetric cases of Co-slabs each of which is thick one or five monolayers.

In all cases we have found pronounced oscillatory behavior of both the amplitudes and phases of the IEC oscillations with the cap-layer thickness. For the thick cap-layer standard results of corresponding infinite systems are recovered.

Ordered Compounds and Interlayer Exchange Coupling: Co/Ru, Co/Rh and (FeCo)/Mn

Daniel Stoeffler
IPCMS, Univeriste Louis Pasteur, Strasbourg, France

We present recent calculations of the role of ordered compounds on the Interlayer Exchange Coupling and the magnetic moment distributions in metallic multilayers. First, we study Co/Ru and Co/Rh multilayers presenting Interfacial Ordered Compounds to model interfacial mixing over 3 atomic planes with the first principle Augmented Spherical Wave method. Our calculations show a preserved magnetism on the Co atoms at the Co/Rh interface whereas magnetically dead Co atoms are found at the Co/Ru interface. We discuss the strength of the Interlayer Exchange Coupling in these systems resulting from the previous calculated magnetic moments profiles in relation with experimental data exhibiting a 7 to 8 times larger saturation field for Co/Rh than for Co/Ru. Second, we study (FeCo)/Mn multilayers where the ferromagnetic layer is an iron-cobalt ordered compound. We present first principle calculations allowing to determine the strength of the interfacial and interlayer couplings for collinear magnetic order as a function of the iron concentration. Using a tight-binding approach for describing non collinear magnetic order, we determine the self-consistent vectorial magnetic moment distributions in these (FeCo)/Mn multilayers. We show that the most stable magnetic configuration switches from collinear to non-collinear when the Co concentration increases.

Interlayer exchange coupling across Cu and FeSi: experimental results and opportunities for first principles theory

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

In the talk I will first review experimental results, obtained mainly by MBE deposition, on (i) the dependence of the oscillatory interlayer exchange coupling across Cu on the layer thicknesses, ferromagnetic layer composition and crystal orientation, and (ii) the superexchange-like coupling across FeSi (dependence on film composition and spacer layer thickness). Attention will be given to structural effects, as studied e.g. by in-situ STM. Subsequently, some simple ideas and models that may at least qualitatively explain the observations made will be discussed. Based on these results, proposals for first principles computational studies of RKKY-like and superexchange-like interlayer exchange coupling will be presented.

Interface reflectivity and interlayer coupling in Co/Cu(001)

P.H. Dederichs
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The reflectivity at the interface between a nonmagnetic and a magnetic layer represents the key quantity for the understanding of interlayer coupling and quantum well states in magnetic layers. We present ab-initio calculations for the reflection coefficient of a Cu Bloch electron at the (001)-interface of fcc Fe, Co and Ni layers, using a "one-dimensional" representation of the Cu Green's function. The main emphasis lies on the dependence of the reflectivity on the thickness of the magnetic layers. The reflectivity and the corresponding phase shifts show similar size oscillations as the local density of states of the magnetic layers. We discuss the importance of these oscillations for the interlayer coupling in two different asymptotic limits and the smearing of these effects due to temperature and disorder.

Experiments on biquadratic exchange and antiferromagnetic bias

P. Grünberg
Institut für Festkörperforschung, Forschungszentrum Jülich,
D-52425 Jülich, Germany

Many results on interlayer exchange coupling show biquadratic exchange- in particular in the transition regions between ferro- and antiferromagnetic type coupling. Furthermore often an antiferromagnetic bias is superimpoesed to the otherwise oscillatory coupling. The origin of these phenomena to our knowledge is still rather unclear. In our investigations on the Fe/Au/Fe- and the Fe/Cr/Fe system we found that biquadratic exchange is a bias, superimposed to oscillations between F- and AF coupling. This bias shows a strong temperature dependence and becomes weaker at higher temperatures. For the Fe/Ag/Fe system we performed experiments where we introduced additional Fe in the midplane of the Ag interlayer. It produced additional biquadratic coupling as predicted by Slonczewski in his loose spin model. Our results on Fe/Cr/Fe are compared with those by the group at NIST and in Burnaby which were obtained from samples grown on Fe whiskers and had extremely good quality.

Spin Resolved Photoemission Study of the Interface Formation and Growth of Fe on Si(100)

R. Kläsges
Institut für Festkörperforschung, Forschungszentrum Jülich,
D-52425 Jülich, Germany

The observation of antiferromagnetic interlayer coupling in Fe/Si multilayers has stirred up the need to characterize the chemical and magnetic composition of these multilayers in order to understand the coupling mechanism. We have studied the formation of the Fe/Si interface by spin- and angle-resolved photoemission. By deposition of Fe on Si(100) at room temperature a ferromagnetically ordered metallic layer of ca. 20 $\AA$ thickness is formed with composition and electronic structure close to Fe_3Si. Above 20 $\AA$ the silicide formation stops and subsequently deposited Fe layers contain little or no interdiffused Si. Deposition of Si on a thick Fe overlayer results in a number of compositionally different silicide phases with increasing Si content for thicker films. At liquid nitrogen temperature the interdiffusion between Fe and Si and the formation of silicides is reduced.

4 Workshop/Conference Announcements

4.1 Workshop in Darmstadt

First Circular

Workshop on Various Aspects of Noncollinear Magnetism

Darmstadt, 25-26 January 1997

organized by L. Sandratskii and J. Kübler

Workshop partially supported by the EU HCM Ψ_k−Network

The aim of the workshop is to bring together researchers from all over Europe active in the field of **non-collinear magnetism** which rapidly developed in the last years. The following topics are suggested:

- *new technical developments*
- *noncollinear magnetism of bulk, surfaces and multilayers*
- *noncollinear magnetism of non-perfect systems (amorphous systems, defects)*
- *noncollinearity and relativistic effects*
- *non-Stoner thermodynamics of itinerant electron systems*
- *noncollinearity and spin dynamics*

Most of the time of the workshop will be reserved for long (invited) talks of about 45 minutes. This will allow the speakers to discuss approximations and technical details more extensively than at a usual conference. Sufficient time will be devoted to discussions.

Long talks will be given by:

H. Dreyssé (*Strasbourg*)
H. Eschrig (*Dresden*)
J. Hafner (*Wien*)
B.L. Gyorffy (*Bristol*)
U. Krey (*Regensburg*)
J. Kübler (*Darmstadt*)
A. Liechtenstein (*Jülich*)
L. Nordström (*Uppsala*)
L. Sandratskii (*Darmstadt*)
P. Weinberger (*Wien*)

If the final program of the workshop will allow, the list of invited speakers may be extended by one to two names. The workshop is planned to have about 30 participants in total.

All participants will have the opportunity to present their contributions as a short oral talk (20 minutes) or a poster. Posters as supplements to both long and short talks are also welcome. The number of short talks will be restricted to avoid the programme to be too exhausting and reserve some time for informal discussions.

The workshop will start early in the morning on Saturday January 25 and end in the evening on Sunday January 26.

The transportation and local expenses should be covered by the participants themselves. However, the participants coming from the non-German nodes of the EU HCM Ψ_k−Network will be supported by the Network. Please, contact the organizers to find out whether you are eligible for financial support. Depending on the financial situation the participants might be asked to pay a small conference fee (20-30 DM) to cover the cost of beverages and snacks. The conference fee will be collected on a voluntary basis. The organizers hope to be able to supply reasonable and inexpensive hotel accommodation.

Anyone interested in participating in the workshop should send e-mail to L. Sandratskii with the following information:

- *title of the presentation*
- *desirable form of the presentation (short talk/poster)*
- *dates of arrival and departure*
- *maximum affordable price for a hotel per night*
- *will your institution reimburse the conference fee payment*

Participants supported by the Network do not need to answer the last two questions. The maximum financial support provided by the Network cannot exceed 60 ECU per diem plus cheap travel. Network members from Austria, Finland, Sweden and Switzerland need to apply for support to their national coordinators.

Deadline for sending applications: December 20, 1996.

We are looking forward to seeing you in Darmstadt.

With best regards,

Leonid Sandratskii and Jürgen Kübler

Please use for communications:
Email: dg5m@mad1.fkp.physik.th-darmstadt.de (L. Sandratskii)
Tel.: 49-6151-163581
Fax.: 49-6151-163681

4.2 Symposium in Strasbourg

Symposium D - 1997 ICAM and E-MRS Spring Meeting:

"Computational Modeling of Issues in Materials Science"

Strasbourg (France) 16-20 june 1997

Partially supported by the HCM network
"Ab-initio calculation of complex processes im materials".

"Computer experiments" are amongst the most rapidly growing techniques to study the statics and dynamics of materials in a variety of situations. The description of the relevant features and parameters may be at the atomic level, based on quantum mechanics or more classical approaches, or it may be at some more coarse-grained level, all the way up to continuum models. Computer simulation allows one to test hypotheses, to predict properties of existing or novel materials, and to perform procedures that may not be feasible in the laboratory. Moreover, through the use of animation and visualization computational modeling has great educational power. Much of the progress in the field is due to the tremendous advances in computer performance, notably the use of parallel computing, but new theoretical insights and improved computer algorithms have also propelled the subject.

This symposium intends to bring together researchers from a wide range of subfields in materials science. The aim is to discuss common trends and problems, but also to produce cross-fertilization between disciplines. The emphasis will be on actual materials problems, studied in a realistic way, and on systems of processes of industrial or technological importance. New algorithms and implementations as well as novel theories are also welcome provided they have the potential of applicability to real-world problems. Issues of particular interest are:

- relating the electronic structure of materials to simulation parameters
- comparing and contrasting ab-initio and semi-empirical approaches
- addressing the relation between atomic and continuum models
- describing algorithms for parallel and other high-performance computers, in particular O(N) methods
- Monte Carlo, molecular dynamics, and other simulation techniques.

Phenomena to be covered include:

- mechanical properties, such as fracture, crack growth and propagation, instabilities, stress, etc.

- electronic structure and its macroscopic effects
- growth and evolution of microstructure
- thermodynamics and kinetics of phase transformations, including metastable phases
- magnetism.

Systems of interest range over metals and semiconductors (as well as their alloys), polymers, composites, and biological systems. These may take the form of small clusters or nanoparticles, or may be in bulk form. Of equal relevance are surface and interface phenomena, including multilayers and thin films.

Please note that the **DEAD-LINE** for abstract submission is:

February 1, 1997.

* To submit a paper:

Send one original + 6 copies to:
ATTENTION: ABSTRACT ENCLOSED
E-MRS 1997 Spring Meeting
BP 20
67037 Strasbourg Cedex 2
France
Fax: (+33) 03 88 10 63 43
E-mail: EMRS@FRCPN11.IN2P3.FR

* All abstract should be typed according to a model.
This model and the 2nd announcement can be obtained by writing to:
P. Siffert
E-MRS
BP 20
67037 Strasbourg Cedex 2
France

* For further informations concerning precisely the symposium D, contact:
Hugues Dreysse
IPCMS-GEMME
23 rue du Loess
BP 20 Cr
67037 Strasbourg - France
Tel: (+33) 03 88 10 70 83
Fax: (+33) 03 88 10 72 49
E-mail: hugues@lugh.u-strasbg.fr

CHAIRPERSONS

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4.3 Workshop in Corfu

TOTAL ENERGY METHODS TO STUDY THE DYNAMICS OF SURFACE PROCESSES

A number of Euroconferences under the general title: *"Dynamics and Kinetics of Bond Making and Breaking at Surfaces: from Chemisorption to Catalysis"* will be funded by the EC under the TMR programme.

A small conference on **TOTAL ENERGY METHODS TO STUDY THE DYNAMICS OF SURFACE PROCESSES**, will be held on the island Corfu in Greece in the village Dassia at the Hotel Corfu Chandris from Wednesday 25 June to Friday 27 June 1997, coordinated by H.M. Polatoglou (*Aristotle University of Thessaloniki, Greece*) and M. Scheffler (*Fritz-Haber Institute, Berlin*).

SCIENTIFIC AND ORGANIZING COMMITTEE:

Professor G. Allan (University of Lille)
Professor EJ. Baerends (University of Amsterdam)
Professor S. Holloway (University of Liverpool)
Professor RM. Nieminen (Helsinki University of Technology)
Professor J. Norskov (Technical University of Denmark)
Professor GF. Tantardini (University of Milan)

For more informations e-mail: **H.M. Polatoglou at hariton@donoussa.physics.auth.gr or polatoglou@olymp.ccf.auth.gr**. A WWW site will soon be available.

5 Job Announcements

Associate Professor of Theoretical Condensed Matter Physics

Department of Physics, Osaka University, Japan

The Department of Physics of the Graduate School of Science at Osaka University invites application for a position beginning Spring 1997. The position is in theoretical condensed matter physics and intended at the associate professor level. The appointment will either be permanent or three-year contract depending on the qualifications and experience of the individual. Applicants should have a PhD and must be able to initiate an active research program that will contribute substantially to our theoretical and experimental condensed matter physics research efforts. Applicants must be interested in teaching at both the undergraduate and graduate levels including that for general education in the 1st and 2nd grades. The language ability of Japanese, enough to communicate with undergraduate level students, is desirable. Applicants should send a curriculum vitae with a resume of their research and a research plan, and arrange to have 3 letters of recommendation sent to (or give the names of 3 references) the address below. The deadline for receipt of application is January 31, 1997.

Osaka University,
Department of Physics,
Graduate School of Science
1-16 Machikaneyama Toyonaka
Osaka 560, Japan
Attention: Hisazumi Akai
Telephone: [+81] 6-850-5738
Fax: [+81] 6-850-5764
E-mail: akai@fuji.phys.wani.osaka-u.ac.jp
Posted: November 20, 1996

Postdoctoral Research Officer in Theoretical Surface Physics
University of Bath, School of Physics

Applications are invited for an EPSRC-funded postdoctoral researcher to work on surface state mediated interactions at metal surfaces. This post, available for up to three years, is supervised by Dr S Crampin. The project aims to quantify the role of surface states in interactions at metal surfaces, with a particular focus on the interactions between adsorbates and/or steps and their role in a variety of physical processes such as epitaxial growth. The project involves both the development and application of ab-initio methods for large-scale surface electronic structure calculations.

Closing date for applications is **12th December 1996**.

Informal contact may be made with **Dr S Crampin, School of Physics, University of Bath, phone (01225) 826826 ext. 4808, e-mail s.crampin@bath.ac.uk**.

Application forms may be obtained from the **Personnel Department, University of Bath, Claverton Down, Bath BA2 7AY or 'phone the 24 hr answer-phone service on Bath (01225) 826924 (e-mail A.J.Witcombe@bath.ac.uk) quoting Ref No 96/254**.

Ph. D. Position

Max–Planck–Institute for Metal Research, Stuttgart

Starting from about April 1997, there is a position (BAT IIa/2) for a Ph. D. study at the Max-Planck-Institut für Metallforschung in Stuttgart, Germany. It is intended to develop an *ab-initio* molecular dynamics programme for the investigation of dynamical and thermodynamical processes in transition metals. The programme will be based on a computer code for the effective and accurate calculation of *ab-initio* forces by an *ab-initio* pseudopotential method with a basis set of plane waves and few localized orbitals per atom, which has been further developed in recent years in Stuttgart. The applicants should have some experience with electron theory and with the handling of big computer codes. The position is first for two years, with an option to extend it up to at most three years. Please send your applications to:

Prof. Dr. M. Faehnle,
Max–Planck–Institut für Metallforschung,
Heisenbergstr. 1, D-70569 Stuttgart, Germany
E-mail: faehn@physix.mpi-stuttgart.mpg.de

Postdoctoral Position

Research Group TSM, Department of Physics

University of Antwerp (RUCA), Belgium

Applications are invited for a postdoctoral position with the group (TSM) of P.E. Van Camp and V.E. Van Doren to do research on density functional theory in polymers and bio-polymers. The appointment is expected to start on January 1, 1997 and is for a period of two years. The monthly salary is about 60000 BEF. The topics of part of the theoretical research of the TSM-group for this position are :

- Research on improving the exchange-correlation potential in density functional theory. Implementation of the optimized effective potential model (OPM) and of the Moeller-Plesset many-body perturbation theory with Kohn-Sham orbitals in the case of polymers.
- Calculation of the total ground state energy of several polymer and bio-polymer systems within the local density approximation (LDA) and beyond in order to predict structural, electronic and optical properties.

Candidates should have an excellent knowledge of computer programming.

The TSM-group has currently collaborations with :

Dr. J.W. Mintmire, NRL, Washington DC, USA.
Prof. J.M. Martins, INESC, Lisbon, Portugal.
Prof. J. Ladik, University of Erlangen, Erlangen, Germany.
Dr. G. Straub, Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM, USA.

Candidates should send an application to :

P.E. Van Camp - V.E. Van Doren
Research Group TSM
Department of Physics
University of Antwerpen (RUCA)
Groenenborgerlaan 171
B - 2020 Antwerpen , Belgium
E-mail : vancamp@nets.ruca.ua.ac.be

Post-doctoral Position

Condensed Matter Theory

Strasbourg, France

Applications are invited from European Union nationals, excluding French residents, for the above post funded by a European Training and Mobility Award. The TMR network is supported for a duration of 4 years. The appointment will be funded for a period of 2 years, extendable on mutual agreement. The successful applicant would be expected to work on the **development of a RS-TB-LMTO (Real-Space Tight-Binding LMTO) method and application to interface and thin film magnetism** under the supervision of Prof. Dreyssé. It is expected that it will be an intense collaboration with the group in Vienna leaded by Prof. J. Hafner, including a long stay in Vienna in the first stage of the project. Some experience in electronic structure calculations is essential. The salary will be on the Research Assistant scale, according to French regulations. Interested candidates should contact Prof. Dreyssé for further information and send a C.V. with names of two references.

Closing date 15 January 1997

Professor H. Dreyssé
Institut de Physique et de Chimie des Matériaux de Strasbourg
Groupe d'Etude des Matériaux Métalliques
23, rue du Loess
67037 Strasbourg, France
tel: (33) 03 88 10 70 83
fax: (33) 03 88 10 72 49
email: hugues@lugh.

6 Abstracts

Theoretical study of the high pressure phase stability of GaP, InP, and InAs

A. Mujica
Departamento de Física Fundamental y Experimental,
Universidad de La Laguna, La Laguna E-38205, Tenerife, Spain
R.J. Needs
Theory of Condensed Matter Group, Cavendish Laboratory,
University of Cambridge, Cambridge CB3 0HE, United Kingdom

Abstract

We report a first-principles study of the high pressure structural properties and phase diagrams of GaP, InP, and InAs. The present study includes the *Cmcm* phase which is a distortion of the rocksalt structure, and the *Imm2* and sc16 phases, which have been suggested as stable high pressure phases of III-V compounds. Our work relates directly to recent experimental work on III-V compounds which has indicated that the previously reported high pressure phase diagrams of these compounds should be reconsidered. Our results support the existence of stable *Cmcm* phases in InP and InAs, and a stable or nearly stable *Cmcm* phase in GaP. We find stable *Imm2* phases in each of the compounds studied. We also find a small range of thermodynamical stability for sc16-GaP. The energy-volume curves and phase diagrams of InP and InAs, as well as those of GaP and GaAs, show remarkable similarities. Along with previous work, we now have enough theoretical results to support a new systematics of the high pressure phases of III-V compounds.

(Submitted to Phys. Rev. B)
Manuscript available from: amf@teide.dfis.ull.es

We gratefully acknowledge the financial supported of the EU HCM Ψ_k-Network on "*Ab-initio* (from electronic structure) calculation of complex processes in materials".

Electronic structure calculations for $YBa_2Cu_3O_7$ within the slave boson formalism

M. Biagini
Istituto Nazionale per la Fisica della Materia
and Dipartimento di Fisica, Università di Modena,
I-41100 Modena, Italy

Abstract

A novel method for self-consistent electronic structure calculations for correlated metals is presented. This approach takes into account on-site Coulomb repulsion among localized electrons and is based on the slave boson formalism. The method proposed herein has been applied to the study of the electronic structure of $YBa_2Cu_3O_7$: the on-site Coulomb repulsion of Cu3*d* electrons gives origin to a flat band at the Fermi level, as observed in experiments. A sharp van Hove singularity has been found 25 meV below the Fermi energy.

(Accepted to Phys. Rev. Lett.)
Manuscript available from: biagini@imoax1.unimo.it

Electronic structure of rare earth arsenide/gallium arsenide superlattices

M. Said[1,2], C. M. Bertoni[1], A. Fasolino[1,3], S. Ossicini[1]
[1] *Istituto Nazionale per la Fisica della Materia (INFM)*
and Dipartimento di Fisica, Università di Modena, 41100 Modena, Italy
[2] *Institut Preparatoire aux Etudes d'Ingenieur, 5019 Monastir, Tunisia*
[3] *Dept. Theor. Physics I, University of Nijmegen,*
6525 ED Nijmegen, The Netherlands

Abstract

We present linear-muffin-tin-orbital calculations of the energy band structure and of the density of states of semimetal-semiconductor superlattices made of rare earth arsenide (ErAs and YbAs) and of GaAs. The effect of size quantization and the possibility of a semimetal-semiconductor transition is studied by varying the number of rare earth arsenide monolayers buried in GaAs. We find that indeed a gap opens up in the band structure for the case of a single monolayer of YbAs embedded in GaAs, albeit well above the Fermi energy. The chances to induce a transition to a semiconductor are discussed.

(submitted to Phys. Rev. Lett.)
Manuscript available from: ossicini@imoax1.unimo.it

Non-collinear order contribution to the exchange coupling in Fe/Cr(001) superlattices

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Groupe d'Etude des Matériaux Métalliques,
UMR 46 du CNRS-Université Louis Pasteur
23, rue du Loess, 67037 Strasbourg Cedex, France

Abstract

By means of a d-band tight-binding hamiltonian, we calculate the non-collinear distribution of magnetic moments in Fe/Cr superlattices, as a function of the relative orientation $\Delta\varphi$ of the magnetic moments at the centre of two adjacent Fe layers. All magnetic moments are computed selfconsistently in both magnitude and angle. We find that for thick layers of Cr spacer, the total energy varies parabolically as a function of $\Delta\varphi$, in accordance with the phenomenological proximity magnetism model proposed by Slonczewski. However, this model is not entirely satisfied for small Cr thicknesses because of the assumptions made in it.

(to be published in Phys. Rev. B Rapid Comm. November 1996)
Manuscript available from: freyss@belenus.u-strasbg.fr

The Adsorption of Atomic Nitrogen on Ru (0001): Geometry and Energetics

S. Schwegmann, A. P. Seitsonen, H. Dietrich, H. Bludau,
H. Over, K. Jacobi, and G. Ertl
Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4-6, D-14 195 Berlin-Dahlem, Germany

Abstract

The local adsorption geometries of the (2×2)–N and the $(\sqrt{3}\times\sqrt{3})$R30°–N phases on the Ru (0001) surface are determined by analyzing low-energy electron diffraction (LEED) intensity data. For both phases, nitrogen occupies the threefold hcp site. The nitrogen sinks deeply into the top Ru layer resulting in a N–Ru interlayer distance of 1.05 Å and 1.10 Å in the (2×2) and the $(\sqrt{3}\times\sqrt{3})$R30° unit cell, respectively. This result is attributed to a strong N binding to the Ru surface (Ru–N bond length = 1.93 Å) in both phases as also evidenced by ab-initio calculations which revealed binding energies of 5.82 eV and 5.59 eV, respectively.

(Chem. Phys. Lett., in print). Contact person: over@fhi-berlin.mpg.de
Paper available from: http://www.fhi-berlin.mpg.de/th/paper.html

On Tilted Magnetization In Thin Films

L. Udvardi[a], R. Király[a], L. Szunyogh[a,b], L. Denat[c], M.B. Taylor[c],
B.L. Györffy[c], B. Újfalussy[b,d] and C. Uiberacker[b]
[a] *Department of Theoretical Physics, Institute of Physics,*
Technical University of Budapest
[b] *Institut für Technische Elektrochemie, Technical University of Vienna*
[c] *H.H. Wills Physics Laboratory, University of Bristol*
[d] *Research Institute for Solid State Physics, Hungarian Academy of Sciences*

Abstract

We suggest a new mechanism for explaining the tilt of the magnetization away from the surface normal in certain magnetic ultra–thin films. Our arguments are based on a simple classical spin Hamiltonian in which the magneto–crystalline surface anisotropy is described by $H_a = -\sum_i \lambda_i \left(s_i^z\right)^2 + \sum_i \gamma_i \left(s_i^z\right)^4$, where λ_i and γ_i are non–negative phenomenological constants, s_i^z denotes the z–component (normal to the surface) of the spin at the site labelled by i. In this paper we study only the ground state. In contrast to the usual explanation which attributes the experimentally observed tilted magnetization to the fourth order term involving γ_i, we show that the second order term alone can lead to this interesting phenomenon. Our explanation implies that the magnetization of the successive layers are not collinear. As an illustration of our arguments we discuss the experimentally observed orientational transition of the Co/Au(111) system in quantitative details.

(submitted to JMMM, 22 Oct 1996)
Postscript preprints available from: `szunyogh@newton.phy.bme.hu`

(This paper acknowledges the Ψ_k–Network)

Ab-initio calculations of one-dimensional band structures of mixed-stack molecular crystals

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Université Rennes-1, 35042 Rennes-Cedex, France
P.E. Blöchl
IBM Research Division, Zurich Research Laboratory,
8803 Rüschlikon, Switzerland

Abstract

We present the first ab-initio calculation of one-dimensional band structures of two mixed-stack molecular crystals: TTF-CA and TTF-2,5Cl$_2$BQ. We discuss the intra-chain coupling and derive hopping parameters to be used in model calculations. Our calculations reveal that the dispersion differs qualitatively from existing model calculations. Implications of our findings on the charge transfer are discussed.

(Submitted to Phys. Rev. B)
Manuscript available from: katan@univ-rennes1.fr

The financial support of the EU HCM Ψ_k-Network is acknowledged.

Band theory of induced magnetic moments in CoM (M=Rh, Ru) alloys

G. Moraïtis, H. Dreyssé and M.A. Khan
Institut de Physique et Chimie des Matériaux de Strasbourg,
23, rue du Loess, 67037 Strasbourg, France

Abstract

Experimentally observed induced magnetism on Rh and Ru when alloyed with Co is studied within tight binding linear muffin-tin orbital (TB-LMTO) method in atomic sphere approximation (ASA). Different possible crystal structures of Co_3M ($M = Rh, Ru$) are considered and it is shown that the hexagonal close packed (hcp) structure is the most stable with induced magnetic moments on Rh and Ru. Some other off-stoichiometric structures such as $Co_{71}M_{29}$ and $Co_{67}M_{33}$ are also considered. The band theory explains quite well the observed induced magnetism in different cases.

(in Phys. Rev. B (Oct. 1996))
Preprint available from: georges@nantos.u-strasbg.fr

This work was partly supported by Ψ_k-Network (contract $N^0CHRX - CT93 - 0369$).

Ab-initio study of the structural distortion and its influence on the magnetic properties of metallic dilute alloys

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D-52425 Jülich, Germany
N. Stefanou
University of Athens, Section of Solid State Physics,
Panepistimioupolis, GR-15784 Athens, Greece

Abstract

We report a systematic study of lattice relaxation effects around $3d$ and $4sp$ impurities in aluminum, using the full-potential Korringa-Kohn-Rostoker Green function method. Our results for the magnetic properties of the impurities seem to resolve the discrepancy between experiment and previous calculations. In addition, the calculated atomic displacements and total volume changes are in good agreement with the corresponding experimental data.

(To appear in Comp. Mat. Sci.)
Manuscript available from: nikos@iff126.iff.kfa-juelich.de

Interlayer Exchange Coupling and Interface Reflectivities in Fe/Cu, Co/Cu and Ni/Cu (001) Layers

P.H. Dederichs, K. Wildberger, and R. Zeller
Institut für Festkörperforschung, Forschungszentrum Jülich,
D-52425 Jülich, Germany

Abstract

We present ab-initio calculations for the interlayer exchange coupling of fcc Fe, Co and Ni layers in Cu (001) which have been performed by a KKR Green's function method for planar defects. The calculations show strong differences in the amplitudes for the short and long oscillation periods, which in a first approximation can be understood from the bulk bandstructures of Fe, Co and Ni. We discuss results for the quantum well states in the Cu spacer layers and their relation to interlayer coupling. In detail we investigate the effect of the finite thickness of the magnetic layers and present calculations for the reflectivity of a Cu Blochwave at a magnetic layer of finite thickness. We discuss the temperature dependence of the coupling and the transition from finite to infinite layer thickness.

(To be published in J. Magn. Magn. Mat.)
Manuscript available from: L.Gerken@kfa-juelich.de

Study of Magnetic Clustering Using a Tight Binding Molecular Dynamics Approach

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Foundation for Research and Technology-Hellas,
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P.O. Box 1470, Heraklio,Greece 71409
[c]*Department of Physics andAstronomy, and Center for Computational Sciences,*
University of Kentucky, Lexington, KY 40506-0055

Abstract

The tight-binding molecular-dynamics (TBMD) method has been proved to be a useful tool in the study of semiconductors. Recently, we extended this method to the study of transition metal systems. Our applications to non-magnetic clusters of transition metal atoms gave results for the binding energies, bond lengths and vibration frequencies of Ni_n clusters (n upto 55) in very good agreement with both theory and experiment. In the present work we extend the applicability of the formalism to include the study of magnetic properties of the Ni_n, Fe_n and Co_n clusters ($n \leq 55$). This is achieved by incorporating an exchange splitting term in the TBMD Hamiltonian. It is shown that the results obtained for the magnetic moment (per atom) for Ni, Fe and Co clusters are in very good agreement with recent experimental data, thus establishing the validity of our scheme in the treatment of magnetic systems and/or their alloys.

(Accepted for publication in Proc. 1st International Alloy Conference,
Athens 1996, A.Gonis,A.Meike, P.Turchi Eds., Plenum Press)
Manuscript available from: andriot@iesl.forth.gr

(The paper aknowledges support of the Ψ_k–Network)

The Charge on a Single Impurity in a Metal

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Florida Atlantic University Boca Raton, Florida 33431, USA

Abstract

The techniques for calculating the electronic states of an impurity in a metal from first principles are well understood and have already been implemented. An approximate method that leads to much simpler calculations has been proposed recently. We investigate this method within the framework of the quadratic Korringa-Kohn-Rostoker formalism, and show that it produces surprisingly good predictions for the charge on the impurity.

(Accepted for publication in Proc. 1st International Alloy Conference,
Athens 1996, A.Gonis,A.Meike, P.Turchi Eds., Plenum Press)
Manuscript available from: andriot@iesl.forth.gr

(The paper aknowledges support of the Ψ_k−Network)

Magnetic Properties of Ni and Fe Clusters: A Tight Binding Molecular Dynamics Study

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P.O. Box 1527, Heraklio, Crete, Greece 71110
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P.O. Box 1470, Heraklio,Greece 71409
[c] *Department of Physics andAstronomy, and Center for Computational Sciences,*
University of Kentucky, Lexington, KY 40506-0055

Abstract

We introduce an efficient approach to incorporate magnetic ordering in transition metal clusters. The method is based on the tight binding molecular dynamics technique employing a minimal basis set. The computational efficiency of the scheme allows applications to cluster sizes well beyond the range of *ab initio* techniques. Excellent agreement is obtained with *ab initio* results when comparison is made for small clusters of Ni and Fe for which *ab initio* results are available. Applications of the present scheme to Ni_n ($n \leq 7$), and Fe_n ($n \leq 5$) clusters show that while magnetic ordering does not affect the geometric ordering of Ni clusters, inclusion of magnetic effects significantly affects Fe clusters, forcing them to attain geometric configurations of higher symmetry than paramagnetic states.

(Chem. Phys. Letters, **260**, 15 (1996))
Reprints available from: andriot@iesl.forth.gr

Magnetic Properties of Clusters of Transition Metal Atoms

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[a] *Institute of Electronic Structure and Laser,*
Foundation for Research and Technology-Hellas,
P.O. Box 1527, Heraklio, Crete, Greece 71110
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[c] *Department of Physics andAstronomy, and Center for Computational Sciences,*
University of Kentucky, Lexington, KY 40506-0055

Abstract

Using a newly proposed calculational scheme that combines the Hubbard approximation with the tight-binding molecular dynamics method, we obtain the magnetic moments of Fe_n and Ni_n clusters with cluster size upto n=55 in a systematic way. Our results indicate that the average magnetic moment per atom is significantly higher in the cluster than in the bulk, in agreement with recent experimental data for Fe and Ni clusters. Furthermore, it is found that magnetic effects stabilize the clusters in geometries that were found to be completely unstable when magnetism is ignored. In general, magnetic effects drive Fe (and to a lesser extent Ni) clusters into geometries of higher symmetry than that of the corresponding singlet states.

(Europhysics Letters, **36**, 37 (1996))
Reprints available from: andriot@iesl.forth.gr

Dependence of Onset Optical Absorption on Interface Diffusion in $\mathrm{Si}_n\mathrm{Ge}_m$ Superlattices

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Abstract

The optical absorption coefficient, α(E), of $\mathrm{Si}_n\mathrm{Ge}_m$ superlattices depends strongly on the quality of the Si-Ge interfaces. Interdiffusion along the Si-Ge interfaces is reflected on the variation of α(E) with energy for energies near the energy gap, E_g. Using the Coherent Potential Approximation for simulating the interdiffusion along the Si-Ge interfaces and the Kubo-Greenwood formula for the optical absorption, we show that for $\mathrm{Si}_5\mathrm{Ge}_5$, $\alpha(E) \approx (E-E_g)^\kappa$ where the exponent κ takes values in the range 0.5-2.0 depending on the degree of interdiffusion along the Si-Ge interfaces. The value $\kappa = 0.5$ reflects abrupt Si-Ge interfaces while the value $\kappa = 2$ corresponds to highly diffused Si-Ge interfaces. The case $\kappa = 2$ fits very well the available experimental data.

(submitted to Phys. Rev B - Rapid Communication)
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(The paper aknowledges support of the Ψ_k-Network)

Magnetic Structure and Anisotropy in Fe/Cu(001) over– and interlayers: The Low–Moment Antiferromagnetic Phase

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Abstract

A first principles study of the ground state and the magnetic anisotropy of antiferromagnetic fcc Fe/Cu(001) over– and interlayers is presented using the fully relativistic spin-polarized Screened KKR method. It is found that, contrary to a previous study of the ferromagnetic state, for all considered cases, namely up to seven layers of Fe, the magnetization is oriented along the surface normal. The crucial role of the volume (lattice spacing) on the formation of the antiferromagnetic ground state is also studied.

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Metric as the dynamical variable for variable cell-shape molecular dynamics

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Abstract

We propose a new variable cell-shape molecular dynamics algorithm where the dynamical variables associated with the cell are the six independent dot products between the vectors defining the cell instead of the nine cartesian components of those vectors. Our choice of the metric tensor as the dynamical variable automatically eliminates the cell orientation from the dynamics. Furthermore, choosing for the cell kinetic energy a simple scalar that is quadratic in the time derivatives of the metric tensor, makes the dynamics invariant with respect to the choice of the simulation cell edges. Choosing the densitary character of that scalar allows us to have a dynamics that obeys the virial theorem. We derive the equations of motion for the two conditions of constant external pressure and constant thermodynamic tension. We also show that the choice of metric as variable is convenient for structural optimization under those two conditions. We use simulations for Ar with Lennard-Jones parameters and for Si with forces and stresses calculated from first-principles of density functional theory to illustrate the applications of the method.

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Interface Resistances of Magnetic Multilayers

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Abstract

Perpendicular transport in disordered magnetic multilayers is studied by solving a Boltzmann equation based upon parameter-free local-spin-density approximation electronic structure calculations. For Co/Cu multilayers it is shown that the experimentally observed interface resistance can be explained in terms of specular interface scattering in combination with diffuse bulk scattering.

(Submitted to Phys. Rev. Lett.)

Preprints available from: schep@natlab.research.philips.com

Calculation of the phonon frequencies of $\gamma - Fe$ in an anharmonic model

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Abstract

The equilibrium lattice constant and the bulk modulus of fcc Fe are calculated by the FP-LMTO method. The use of the generalized gradient approximation in calculating the electron structure and lattice properties of $\gamma - Fe$ is discussed. A local minimum is observed on the curve of total energy versus the amplitude of atomic displacements corresponding to transverse vibrations at W point of the Brillouin zone. The temperature dependence of the anharmonic mode effective frequency calculated within the framework of the pseudoharmonic approximation is found to qualitatively agree with the experimental one. The possibility to interpret the structural phase transition as a transition of the "active" phonon mode from the excited to the basic state is discussed.

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Manuscript available from: ost@otf.fti.udmurtia.su

Localized and itinerant character of electron states in the photoemission from $CuGeO_3$

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Abstract

It is shown that electron correlation among Cu d-electrons explains the photoemission data of $CuGeO_3$ and is responsible of the insulating behaviour and of the observed complex satellite structures. The analysis and interpretation of the experiments require the use of a multi-band Hamiltonian which explicitly includes both on site electron correlation and a detailed description of the single-particle band states.

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Manuscript available from: manghi@unimo.it

$TiFe_{1-x}Co_x$ alloys and the influence of anti-structural atoms

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Abstract

Ferromagnetism in $TiFe_{1-x}Co_x$ alloys is investigated first by using the virtual crystal approximation in the ASW method and then, to investigate the role of anti-structural atoms and to go beyond the virtual crystal approximation, supercell calculations are used. The itinerant picture suffices to explain ferromagnetism in these alloys, but anti-structural atoms play a role as well, which can be better described by the localised moment picture. We find both a rigid band shift and shifts in spectral weight to be responsible for the magnetic moment, which, in the case of Fe rich alloys, results in the occurence of covalent magnetism. The anti-structural Fe atom has a magnetic moment (1.71 μ_B), close to the experimental value (1.59 μ_B), and our results show a considerable magnetic moment for anti-structural Co (0.65 μ_B) as well.

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Manuscript available from: spxhps@astro.cf.ac.uk

A Transferable Model for the Atomistic Simulation of Al_2O_3

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Abstract

We calculate the energies of different solid phases of Al_2O_3 using a shell model, a compressible ion model and a new compressible ion model which includes both dipole and quadrupolar polarisability of the O^{2-} ions. Compressible oxygen ions are found to stabilise the corundum structure with respect to the θ form of alumina. The observed corundum structure is nevertheless unstable with respect to the bixbyite structure until quadrupolar polarisability of the oxygen is also included. Entropy differences are estimated with a lattice dynamics calculation and are found to make an insignificant contribution to stabilising corundum. We also calculate the relative energies of corundum and bixbyite structures using the ab initio pseudopotential method, within the local density approximation for exchange and correlation. The resulting self-consistent electron density shows graphically how the quadrupolar distortions around the oxygen develop as the basis is made more complete (the plane wave cutoff is increased from 500eV to 700eV), which at the same time brings the energy of the corundum structure below that of the bixbyite structure.

(To appear in Phys. Rev. B)
Manuscript available from: M.Finnis@Queens-Belfast.AC.UK

Density functional calculations for rare earth atoms and ions

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Abstract

Relativistic local spin density (RLSD) and self interaction corrected (SIC) RLSD calculations were performed for the whole series of the rare earth elements. Ionisation potentials and radial expectation values with the $4f$ density were calculated. Improvement on nearly all quantities is found for SIC. Comparison with other calculational methods shows that for the description of rare earth elements SIC-RLSD competes well in accuracy with all of them including the most accurate quantum chemical approach. This is important since SIC has the advantage of being suited for a description of localized f states in solids with comparatively moderate effort.

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Manuscript available from: forst@tmps10.mpg.tu-dresden.de

KKR-ASA method in the exact exchange potential band-structure calculations

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Abstract

We present a new method of the electronic band-structure calculation which incorporates the exact Kohn-Sham density-functional exchange (EXX) potential approach with the Korringa-Kohn-Rostoker (KKR) method in the atomic sphere approximation (ASA). It takes full account of the energy dependence of the radial functions, and hence, provides more accurate treatment in principle than our previous one based on the linearized muffin-tin orbital method [Phys. Rev. Lett. **74** (1995) 2989]. In this method, we treat C, Si, Ge, MgO, CaO, and MnO (Antiferro-II), which were previously studied in the framework of LMTO with EXX. The results are basically in agreement with the old one though small differences produce unnegligible effects on the results. Some numerical points as well as strict formulation of KKR in ASA are discussed.

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Manuscript available from: kotani@phys.wani.osaka-u.ac.jp

Mott Transition in Degnerate Hubbard Models: Application to Doped Fullerenes

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Abstract

The Mott-Hubbard transition is studied for a Hubbard model with orbital degeneracy N, using a diffusion Monte Carlo method. Based on general arguments, we conjecture that the Mott-Hubbard transition takes place for $U/W \sim \sqrt{N}$, where U is the Coulomb interaction and W is the band width. This is supported by exact diagonalization and Monte Carlo calculations. Realistic parameters for the doped fullerenes lead to the conclusions that stoichiometric $\mathrm{A_3C_{60}}$ (A=K, Rb) are near the Mott-Hubbard transition, in a correlated metallic state.

(submitted to Phys. Rev. B)
Manuscript available from: gunnar@and.mpi-stuttgart.mpg.de

Important role of alkali atoms in $A_4\mathrm{C}_{60}$

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Abstract

We show that hopping via the alkali atoms plays an important role for the t_{1u} band of $A_4\mathrm{C}_{60}$ (A=K, Rb), in strong contrast to $A_3\mathrm{C}_{60}$. Thus the t_{1u} band is broadened by more than 40% by the presence of the alkali atoms. The difference between $A_4\mathrm{C}_{60}$ and $A_3\mathrm{C}_{60}$ is in particular due to the less symmetric location of the alkali atoms in $A_4\mathrm{C}_{60}$.

(submitted to Phys. Rev. B)
Manuscript available from: gunnar@and.mpi-stuttgart.mpg.de

Pauli susceptibility of A_3C_{60} (A=K, Rb)

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Abstract

The Pauli susceptibility of A_3C_{60} (A= K, Rb) compounds is calculated. A lattice quantum Monte Carlo method is applied to a multi-band Hubbard model, including the on-site Coulomb interaction U. It is found that the many-body enhancement of the susceptibility is of the order of a factor of three. This reconciles estimates of the density of states from the susceptibility with other estimates. The enhancement is an example of a substantial many-body effect in the doped fullerenes.

(submitted to Phys. Rev. B)
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Superconductivity in Fullerides

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Abstract

Experimental studies of superconductivity properties of fullerides are briefly reviewed. Theoretical calculations of the electron-phonon coupling, in particular for the intramolecular phonons, are discussed extensively. The calculations are compared with coupling constants deduced from a number of different experimental techniques. It is discussed why the A_3C_{60} are not Mott-Hubbard insulators, in spite of the large Coulomb interaction. Estimates of the Coulomb pseudopotential μ^*, describing the effect of the Coulomb repulsion on the superconductivity, as well as possible electronic mechanisms for the superconductivity are reviewed. The calculation of various properties within the Migdal-Eliashberg theory and attempts to go beyond this theory are described.

(submitted to Rev. Mod. Phys.)
Manuscript available from: gunnar@and.mpi-stuttgart.mpg.de

Calculation of the paramagnetic susceptibility and specific heat in UGa_2 and UPd_2Al_3 from *ab initio* crystal field theory

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Abstract

In the framework of the self-interaction corrected local density approximation, *ab initio* calculations have been carried out to obtain crystal field parameters for the paramagnetic state of UGa_2 and UPd_2Al_3. In two sets of calculations localized 5f states with occupation two and three, respectively, have been assumed. Using these parameters and adjusted anisotropic molecular field constants, the paramagnetic susceptibility for both compounds and the Schottky contribution to the specific heat in UPd_2Al_3 have been obtained by crystal field model calculations. Very good agreement between theoretical and experimental data is found for $5f^2$ occupation in UGa_2. For UPd_2Al_3, the $5f^2$ assumption yields qualitatively reasonable results as well, but it does not explain the $T = 50$ K maximum in the experimental data.

(Physica B, in press)

Manuscript available from: manuel@tmps06.mpg.tu-dresden.de

A Screened KKR-Green's Function Method for Layered Systems

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Abstract

A Green's function method for layered systems based on screened Korringa-Kohn-Rostoker structure constants is presented. The screened structure constants are calculated in real space and the interlayer structure constants are obtained by a two-dimensional Fourier transform. As reference potentials we use repulsive muffin-tin and atomic-sphere potentials of various height. Performing test calculations for Cu (001) slabs we demonstrate that for the angular-momentum decomposed local charges a typical accuracy of 10^{-3} electrons can be obtained, so that for practical applications the screening approximation can be used without loss of numerical accuracy. This precision can only be obtained, if the screened structure constants include coupling to next nearest neighbors and if the reference potentials are sufficiently repulsive. It is demonstrated in slab calculations that the numerical effort scales linearly with the number of layers, allowing accurate, self-consistent calculations for very large systems.

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Manuscript available from: Ru.Zeller@kfa-juelich.de

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Evaluation of the screened Korringa-Kohn-Rostoker method for accurate and large-scale electronic-structure calculations

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Abstract

The recently proposed concept of a reference system with repulsive, nonoverlapping, spherical potentials as a tool to transform the traditional Korringa-Kohn-Rostoker (KKR) method into a first-principles tight-binding method was investigated numerically. The tests included density-of-states calculations for free space and self-consistent full-potential total-energy calculations for Al, Cu, and Pd. It was found that the densities of states are accurate for energies up to about 3 Ry and that the results for total energies, lattice constants, and bulk moduli excellently agree with the ones obtained by the traditional KKR method. Supercell calculations with up to 500 atoms per unit cell were also done and show that the screened KKR method is advantageous for large-scale density-functional calculations.

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This work acknowledges the benefits from collaborations within the Ψ_k−Network.

Molecular dynamics study of the vibrational and transport properties of copper adatoms on the (111) copper surface; comparison with the (001) face

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Abstract

The vibrational properties and the self-diffusion process of single adatoms on the Cu(111) surface have been studied and compared with the corresponding ones of the Cu(001) face, using molecular dynamics simu- lation based on a n-body potential. From the calculated phonon spectral densities it comes out that the adatoms modify the surface phonon spectrum and introduce new vibrational modes. The frequencies of these new modes suggest, in the in-plane directions, looser coupling of the ada- toms with the surface atoms of the (111) than those of the (001) face and stronger coupling in the perpendicular direction. This is in agree- ment with the temperature dependence of the relaxed positions of both surface atoms and adatoms. The effect is more pronounced for the (001) face, indicating that this surface presents anharmonic behavior at high temperatures. In addition, the mean-square-dispacements of the surface atoms in the normal direction, are greater in the case of the (001) fa- ce. The vibrational amplitudes of the adatoms on the (111) surface are smaller than those of the surface atoms, for a wide temperature range. The adatom self-diffusion on the (111) surface is a thermally activated process, exhibiting Arrhenius behavior at two distinct temperature re- gions. The detailed analysis of the diffusion process revealed a new hopping mechanism.

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Manuscript available from: nikpap@cc.uoi.gr

Di-carbon defects in annealed highly carbon doped GaAs

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Abstract

Formation of bonded di-carbon C-C centers is deduced by the observation of Raman lines at 1741, 1708 and 1674 cm^{-1} in GaAs co-doped with ^{12}C and ^{13}C after annealing at 850 °C with concomitant loss of vibrational of vibrational scattering from C_{As}. The frequencies agree with results of *ab initio* theory for a split C–C interstitial (deep donor) formed by the trapping of a mobile interstitial C (displaced C_{As}) atom by an undisplaced C_{As} acceptor. Other mechanisms of carrier loss are inferred since a weaker Raman triplet is detected at 1859, 1824 and 1788 cm^{-1} from a different C–C complex.

(Phys. Rev. Lett., accepted 1996)
Manuscript available from: C.D.Latham@exeter.ac.uk

Carbon atoms catalyse fullerene growth

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Abstract

The fullerene road to C_{60} must proceed through isomers which do not obey the Isolated Pentagon Rule (IPR). Stone Wales (SW) transformations are required to redistribute the pentagons to obtain the almost exclusively observed IPR icosahedral C_{60}. We find a very high barrier for these transformations (over 6 eV), which make their occurrence rare during the annealing phase of C_{60} formation. Earlier we reported that the presence of a loosely bound single carbon atom reduces this barrier to 3.9 eV, making frequent pentagon rearrangements possible. Here we review this process and show how carbon atoms bind preferentially to paired pentagon regions, diffuse easily and exchange with C_{60} host atoms.

(Fullerene Science and Technology, accepted, 1996)
Manuscript available from: C.D.Latham@exeter.ac.uk

First-principles studies of materials properties of refractory compounds

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Abstract

In certain types of steel small grains of refractory compounds occur which significantly influence the phyiscal properties of the steel. Because it is rather difficult to obtain suitable experimental data for the refractory compounds of interest, first-principles methods are needed for reliable estimates of important materials properties. Based on density functional calculations for TiC, TiN, VC, VN and $VC_{0.75}$ we derived data for quantities such as elastic properties, thermal expansion coefficients and critical cleavage stresses. The results are discussed and analyzed in our study.

(Conf. Proceedings of 6th Italian-Swiss Workshop on Comp. Mat. Science,
to appear in: Nuovo Cimento)
Preprints available from: raimund@calvin.tssc.univie.ac.at

Linear-response calculation of the electron-phonon coupling in doped $CaCuO_2$

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Abstract

Using density–functional linear–response theory we calculate the electron–phonon interaction for s– and d–wave pairing in the 12 per cent hole doped infinite–layer compound $CaCuO_2$. We find $\lambda_{x^2-y^2} \sim 0.3$ to be positive and only slightly smaller than $\lambda_s \sim 0.4$. This suggests that the electron-phonon mechanism *alone* is insufficient to explain the high T_c but could *enhance* another d-wave pairing mechanism. Results of calculated lattice–dynamics and transport properties are also presented and discussed. Out–of–plane distortions are found essential for the stability.

(To be published in Phys. Rev. Lett.)

Manuscript available from: savrasov@anpow4.mpi-stuttgart.mpg.de

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Can a Spin Antiferromagnet Exhibit the Magneto-Optical Kerr Effect?

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Abstract

It is shown that antiferromagnetic spin order coupled through the spin-orbit interaction with the lattice distortion can lead to a nonvanishing ferromagnetic component of the orbital magnetization and strong optical nonreciprocity in transition-metal perovskite oxides with the orthorhombic structure. This new magneto-optical effect is expected to display very peculiar orientation dependence and disappears for particular directions of the antiferromagnetic spin magnetization. Based on the first principles band structure calculations, elements of the conductivity tensor relevant for this phenomenon are evaluated for the series of LaMO$_3$ oxides with M=Cr, Mn and Fe.

(Submitted to Phys. Rev. Lett.)

Manuscript available from: igor@jrcat.or.jp

Linear-response theory and lattice dynamics: a muffin-tin-orbital approach

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Abstract

A detailed description of a method for calculating static linear-response functions in the problem of lattice dynamics is presented. The method is based on density functional theory and it uses linear muffin-tin orbitals as a basis for representing first-order corrections to the one-electron wave functions. This makes it possible to greatly facilitate the treatment of the materials with localized orbitals. We derive variationally accurate expressions for the dynamical matrix. We also show that large incomplete-basis-set corrections to the first-order changes in the wave functions exist and can be explicitly calculated. Some usefull hints on the **k**-space integration for metals and the self-consistency problem at long wavelengths are also given. As a test application we calculate bulk phonon dispersions in *Si* and find good agreement between our results and experiments. As another application, we calculate lattice dynamics of the transition-metal carbide *NbC*. The theory reproduces the major anomalies found experimentally in its phonon dispersions. The theory also predicts an anomalous behavior of the lowest transverse acoustic mode along the $(\xi\xi0)$ direction. Most of the calculated frequencies agree within a few percent with those measured.

(To be published in Phys. Rev. B)
Manuscript available from: savrasov@anpow4.mpi-stuttgart.mpg.de

Electron-phonon interactions and related physical properties of metals from linear-response theory

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Abstract

Spectral distribution functions of electron-phonon interaction $\alpha^2F(\omega)$ obtained by *ab initio* linear–response calculations are used to describe various superconducting and transport properties in a number of elemental metals such as $Al, Cu, Mo, Nb, Pb, Pd, Ta$, and V. Their lattice dynamics and self–consistently screened electron–phonon coupling are evaluated within local density functional theory and using linear–muffin-tin–orbital basis set. We compare our theoretical $\alpha^2F(\omega)$ with those deduced from the tunneling measurements and find a close agreement between them. Temperature dependent electrical and thermal resistivities as well as transport constants λ_{tr} also agree well with the experimental data. The values of λ_{tr} are close to the electron-phonon coupling parameter λ. For the later a very good agrement with specific-heat measurements was found without any paramagnon contribution, except in Pd. We conclude that our method provides the description of electron-phonon interactions in tested materials with the accuracy 10%.

(To be published in Phys. Rev. B)
Manuscript available from: savrasov@anpow4.mpi-stuttgart.mpg.de

Tight-binding interatomic potentials based on total-energy calculation: Application to noble metals using molecular-dynamics simulation

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Abstract

We present an alternate approach to parametrizing the expression for the total energy of solids within the second-moment approximation (SMA) of the tight-binding theory. In order to obtain the necessary parameters, we do not use the experimental values of the lattice constant, the elastic constants and the cohesive energy, but we fit to the total energy obtained from first- principles augmented-plane-wave calculations as a function of volume. In addition, we shift the total-energy graphs uniformly so that at the minimum they give the experimental value of the cohesive energy. We have applied the above methodology to perform molecular dynamics simulations for the noble metals. For Cu and Ag our results for vacancy formation energies, relaxed surface energies, phonon spectra and various temperature- dependent quantities are of comparable accuracy to those found by the standard SMA , which is based on fitting to several measured data. However, our approach does not seem to work as well for Au.

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The Equilibrium Shape of Quantum Dots

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Abstract

The formation of dislocation-free three-dimensional islands during the heteroepitaxial growth of lattice-mismatched materials has been observed experimentally for several material systems. The equilibrium shape of the competition between the surface energy and the elastic relaxation energy of the islands as compared to the uniform strained film. As an exemplification we consider the experimentally intensively investigated growth of InAs quantum dots on a GaAs(001) substrate, deriving the equilibrium shape as a function of island volume. For this purpose InAs surface energies have been calculated within density-functional theory, and a continuum approach has been applied to compute the elastic relaxation energies.

(Nouvo Cimento, in print)
Paper available from: http://www.fhi-berlin.mpg.de/th/paper.html
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Theory of self-diffusion in GaAs

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Abstract

Ab initio molecular dynamics simulations are employed to investigate the dominant migration mechanism of the gallium vacancy in GaAs as well as to assess its free energy of formation and the rate constant of gallium self-diffusion. Our analysis suggests that the vacancy migrates by second nearest neighbour hops. The calculated self-diffusion constant is in good agreement with the experimental value obtained in ^{69}GaAs/^{71}GaAs isotope heterostructures and at significant variance with that obtained earlier from interdiffusion experiments in GaAlAs/GaAs-heterostructures.

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Strain-Dependence of Surface Diffusion: Ag on Ag (111) and Pt (111)

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Abstract

Using density-functional theory with the local-density approximation and the generalized gradient approximation we compute the energy barriers for surface diffusion for Ag on Pt (111), Ag on one monolayer of Ag on Pt (111), and Ag on Ag (111). The diffusion barrier for Ag on Ag (111) is found to increase essentially linear with increasing lattice constant. We also discuss the reconstruction that has been found experimentally when two Ag layers are deposited on Pt (111). Our calculations explain why this strain driven reconstruction occurs only after two Ag layers have been deposited.

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Ab initio study of step formation and self-diffusion on Ag(100)

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Abstract

Using the plane wave pseudopotential method we performed density functional theory calculations on the stability of steps and self-diffusion processes on Ag(100). Our calculated step formation energies show that the {111}-faceted step is more stable than the {110}-faceted step. In accordance with experimental observations we find that the equilibrium island shape should be octagonal very close to a square with predominately {111}-faceted steps. For the (100) surface of fcc metals atomic migration proceeds by a hopping or an exchange process. For Ag(100) we find that adatoms diffuse across flat surfaces preferentially by hopping. Adatoms approaching the close-packed {111}-faceted step edges descend from the upper terrace to the lower level by an atomic exchange with an energy barrier almost identical to the diffusion barrier on flat surface regions. Thus, within our numerical accuracy ($\approx \pm 0.05$ eV) there is no additional step-edge barrier to descent. This provides a natural explanation for the experimental observations of the smooth two-dimensional growth in homoepitaxy of Ag(100). Inspection of experimental results of other fcc crystal surfaces indicates that our result holds quite generally.

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Application of current density functional theory to spontaneously magnetized solids

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Abstract

The first application of current density functional theory CDFT to spontaneously magnetized solids is presented. For this purpose, a finite orbital current is assumed to be present as a consequence of spin-orbit coupling. This situation is described in the framework of a corresponding extension of the Dirac formalism for spin-polarized solids making use of relativistic multiple scattering theory. In accordance with experiment an enhancement of the spin-orbit induced orbital magnetic moment is found for the ferromagnets Fe and Co while for Ni only a minor change was found compared to a plain calculation done within spin density functional theory (SDFT). However, the enhancement for Fe and – even more pronounced – for Co turned out to be too small. Nevertheless, the first results presented here demonstrate the applicability of CDFT to magnetic solids as well as the need for more accurate parametrisations of the corresponding exchange-correlation potentials.

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Quantum many-body potentials in a tight-binding-bond approximation: Application to the phase stability of carbon and silicon

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Abstract

The importance of quantum many-body forces for understanding the relative structural stability of s,-p-bonded solids is studied on the basis moment-expansions of the bond-order within a tight-binding framework. Detailed results for the phase-stability of silicon and carbon under high pressure are presented. The so called ring-term approximation combined with simplified symmetric response functions is shown to be inadequate for quantitative predictions of structural energy differences. More accurate response functions and consistence between the on-site and inter-site moments are required. This leads to a better convergence of the bond-order expansion, but an accurate prediction of the high-pressure phase diagramm requires eight-moment terms. This can be related to the topological properties of the competing structures.

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A theoretical study of the H-induced reconstructions of the Pd(110) surface

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Abstract

It is now established by experiments that the chemisorption of hydrogen on the Pd(110) surface can induce reconstructions. Under different conditions of coverage and temperature, two types of reconstructions have been found: pairing-row and missing-row. Although the way in which the substrate reconstructs is clearly deduced from experiments, the in which the H atoms are arranged on the reconstructed surfaces is not well established. This is due to the difficulty to "see" directly H atoms by experimental methods. In this work, we report on a systematic study of the reconstructions on Pd(110) by *ab initio* calculations based on density functional theory within the local density approximation (LDA) and generalized gradient corrections (GGC) and ultrasoft pseudopotentials. A variety of models is studied in detail. We show that only particular arrangements of the H atoms can induce the considered surface reconstructions. The driving force for the reconstructions is analyzed.

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Dissociative adsorption of H_2 on the Pd(111) surface

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Abstract

In the present work we apply an *ab initio* approach to the study of the dissociative adsorption of a hydrogen molecule on the palladium (111) surface. Our approach is abased on local density functional (LDF) theory with generalized gradient corrections. The wave functions are expanded in a plane-wave basis and the electron-ion interaction is described by ultrasoft pseudopotentials. Several pathways for the dissociative adsorption are studied in detail and the potential energy surface for each path is determined. Spontaneous dissociation channels are found which have only a very small barrier of the order of 70 meV. This agrees fairly well with the estimation of 50 meV based on molecular beam experiments. We find that the geometric factor plays an important role: a larger stretching of the hydrogen molecule leads to a higher barrier. Our results give also some indication for the existence of a precursor state.

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Ab-initio simulation of the metal/nonmetal transition in expanded fluid mercury

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Abstract

We present an investigation of the variation of the structural and electronic properties of liquid mercury for states along the liquid-vapor coexistence line, spanning the range from the triple-point to the critical point. Our study is based on ab-initio density-functional molecular dynamics on the Born-Oppenheimer surface. Of central interest is the metal/nonmetal transition occurring at densities approximately twice the critical densities. We show that the density-functional calculations describe the atomic structure very accurately over the entire range from the triple point to the critical point. We find that a single-particle gap between the 6s and the 6p band opens at a density of about 8.8 gcm^{-3}, i.e. very close to the density where optical measurement locate the onset of the formation of an optical gap. The detailed investigation of the band edges and of the participation ratio of the eigenstates suggests that the metal/nonmetal transition is best described as a simple band-crossing transition and that electron localization and many-body effects may not be as important as assumed in current scenarios for the transition.

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Frustrated exchange interactions at the interface of antiferromagnetic films with ferromagnetic substrates

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Abstract

Detailed investigations of the frustration of the magnetic exchange interactions at the interface between an antiferromagnetic monolayer of Mn and a body–centered–cubic Fe(100) substrate have been performed via selfconsistent spinpolarized tight–binding linear muffin–tin orbital calculations and the calculation of the exchange pair–interactions via a real–space Greens–function technique. We find that while the Mn–moments in the monolayer are strongly enhanced compared to those in bulk Mn. The moments in the top layer of the substrate are reduced by as much as forty percent due to the competition between the antiferromagnetic nearest-neighbour Mn-Fe and ferromagnetic Fe-Fe interactions. The strongest frustration effects arise from the strong ferromagnetic coupling between the Mn atoms in the overlayer and the Fe–atoms in the second layer of the substrate which tends to induce an antiferromagnetic component in the magnetic polarization of the top layers of the substrate. The possibility to reduce the frustration by the formation of a non–collinear magnetic structure has been investigated.

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7 HIGHLIGHT OF THE MONTH

Paint by Numbers: Oxide surface Chemistry using First-Principles MD

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Abstract

We discuss the motivation for using first-principles molecular dynamics to study surface chemistry, and highlight the strengths of the method. Water adsorption on the TiO_2 (110) surface is investigated, and the results show that the molecule dissociates on the defect-free surface. Analysis of the vibrations of the adsorbed species reveals a surprisingly complex spectrum for one of the surface hydroxyl groups. This is used to show how first-principles simulations can help in the interpretation of experimental results.

7.1 Introduction

It's a safe bet that you know someone who is studying Titanium Dioxide, or that you are doing so yourself. A good reason why is that everyone uses TiO_2 in surprisingly large quantities: If recently you have painted your house, took a holiday in the sun, carried home shopping in plastic bags, brushed your teeth or sucked a polo-mint, you used a product containing the stuff, and failing all these then the paper upon which Ψ_k newsletter is printed probably contains TiO_2. This wide-ranging utility stems from the the powder being an ideal white pigment (almost all manufactured things white contain it), and therefore an equally good opacifier (coloured plastic, for example, needs to have an opaque base for the coloured pigment). Titanium is the ninth most abundant element in the Earth's crust, and its ores, including ilmenite ($FeTiO_3$) and naturally-occuring rutile are processed worldwide to yield over \$6Bn-worth of TiO_2 each year.

Aside from good commercial reasons to study TiO_2, it is a very tough problem for condensed-matter theory. The production and uses of TiO_2 all rely in some way on its surface properties. It is commonly acknowledged that our understanding of oxide surfaces is quite rudimentary when compared with that of metals or semiconductors [1]. Transition-metal oxides have the complication of an empty (in the case of TiO_2) or partially-occupied d-band, which for example gives rise to variable oxidation states: titanium's stable oxides include TiO_2 (rutile structure) and Ti_2O_3 (Corundum) with family of Magnéli phases which occur between, and TiO_x (rocksalt or a distortion of it) where x ranges from $0.6 < x \leq 1.28$. Concomitant is a variety of electronic and magnetic properties. The interplay of electronic and physical structure remains largely unexplored, and even basic questions of surface structure and chemistry are open. This is well illustrated by the question of water adsorbtion on the surfaces. Water is always present in air and therefore reacts with TiO_2 powders during processing and storage. In addition, the observation [2] of photoelectrolysis of water by TiO_2 stimulated much effort to understand adsorption, and it must be remembered that water is a good experimental probe of the surface. However, (metaphorically) ask four experimentalists what happens to water at the (110) surface and you may hear:

> "The surface is completely inert"
>
> "It adsorbs only dissociatively"
>
> "It adsorbs both dissociatively and molecularly"
>
> "It adsorbs only molecularly"

As Henrich and Cox note (ref. [1], pp321), this sees to cover most possibilities! This is not to decry experiments on oxide surfaces, which are notoriously difficult; rather it reflects the problems inherent in the material and in interpretating the experimental results. The vexed question of water dissociation has been addressed by many groups and reviewed by Henrich and Cox in their excellent book, and we have given a brief, up-to-date review [3].

This whole situation sounds like a clarion-call for first-principles simulations, and indeed there have been many impressive works recently on oxides [4], including MgO surfaces [5], water on MgO using Hartree-Fock [6] and first-principles dynamics [7], Al_2O_3 surfaces [8], SnO2 stoichiometric and reduced surfaces [9] and TiO_2 surfaces [10, 11, 12, 13]. We are working on several aspects of TiO_2 surface structure and chemistry [14, 15], and here we will describe some surprising results from first-principles molecular dynamics calculations of water on the (110) surface [3].

7.2 Why use first-principles molecular dynamics?

Molecular dynamics (MD) has been around for a long time, and it is almost 40 years since the first report of an MD simulation of condensed matter [16]. If one is interested in thermal properties it is perhaps the most obvious way of using a computer to generate a phase-space trajectory for an assembly of interacting atoms, and amounts simply to the stepwise integration of Newton's equations of motion from a completely specified starting point. The ergodic principle guarantees that time averages over these phase-space trajectories are equivalent to ensemble averages, and we have, therefore, every macroscopic observable that can be related to atomic motions through statistical mechanics [17]. These include time dependent quantities such as transport coefficients which explicitly involve the dynamical motion of the atoms and their correlation in time [18, 19]. Also, MD can also be used to investigate relaxation towards equilibrium, and as such is a way to explore the configuration-space of a system so as to find the global minimum. The techniques of MD and the many algorithmic innovations which have been made are described in the books by Mike Allen and Dominic Tildesley [20] and Jim Haile [21].

The problem has always been that the only tractable prescriptions for the atomic interactions were simple potential models, and for a long time MD taught us rather more about statistical-mechanics and thermodynamics than it did about real materials. To be fair, many very sophisticated and accurate potentials have been derived for every class of material and applied to great effect, but the ubiquitous stumbling block has been the treatment of systems in which chemical bonding changes. While the effects of changes in bonding may be taken into account in an average way so that e. g. phase transitions may be approximately treated, there is no way to replace the quantum mechanics when one is interested in molecular reactions at surfaces.

This was the situation until the mid-80's, when Car and Parrinello published their seminal work on a unified approach to electronic structure and MD [22]. This synthesis of ideas is by now very familiar and has been well-reviewed in the literature [23, 24]. The following decade saw a quite remarkable increase in the ambitions and achievements of first-principles calculations, fuelled by algorithmic developments and computer speedup, the latter providing a huge impetus through the advent of massively parralel machines. The abstracts of the recent Ψ_k Network Conference report Car-Parrinello MD calculations on metals, semiconductors and insulators, surface reactions, carbon polymorphs and even biological systems. Car-Parrinello style simulations, be they static or dynamic, are capable of describing the quantum mechanical behaviour of valence electrons — the chemical bond — through density-functional theory. The method is also efficient enough to be used for the many evaluations of energy and forces which are needed for MD. In short, the MD technique can be used to treat the making and breaking of chemical bonds.

It is generally true that most things can be calculated using static simulations, and that they are usually much more cost-effective — so why do dynamical simulations? There are two reasons which we have already mentioned: firstly, MD provides an unbiassed way to both sample phase space (to calculate statistical- mechanical quantities) or to explore configuration space (finding the best geometry), and secondly it yields time-dependent quantities. The first reason is not neccessarily a very good one in all cases, since Monte Carlo methods are in general far superior in the calculation of statistical-mechanical quantities in solids and liquids [1]. However, because of the small number of degrees of freedom and the low energy barriers encountered, the configura-

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[1] There are no special technical reasons to favour MD or Monte Carlo when using potential models. However, *First-principles* MD is different: a crucial aspect of the technique is the extrapolation of the wavefunctions after each increment of the atomic positions. This is naturally achieved, and in fact in the original Car-Parrinello prescription both the atoms *and* the wavefunctions are evolved through equations of motion, via the trick of associating a fictitious mass with the wavefunction coefficients.

tion space of a small molecule on a surface is readily sampled by quite short MD simulations. In the present case, where we are interested in the adsorption and possible dissociation of water on TiO_2 (110), this means that we can find adsorption geometries in an automatic way, rather than by guessing the most favourable configuration(s) and relaxing them to mechanical equilibrium. Therefore, one type of simulation we report here involves simply starting with a water molecule above the surface and letting it go to see what happens. By using several starting positions and orientations of the molecule, we can investigate the possible adsorption mechanisms. The second reason to do MD is often not so strong either. Take the case of the vibrations of a crystal: these can readily be calculated by MD, but so can they by diagonalization of the dynamical matrix, and to boot the latter is in general cheaper to do and more accurate. However, static methods do not give information about anharmonic effects, or equivalently about the effect of the ionic configuration on vibrational frequencies. So the justification for the calculation of vibrational frequencies by MD is that anharmonic effects might be significant. In the other class of simulation we report here we have used MD to calculate the frequencies of vibration of the adsorbates, and as will be shown we find some very surprising results which would not be given by a lattice-dynamical method.

7.3 Surface chemistry experiments

Experimental studies of surface chemistry gain indirect information about the adsorbed species. This includes even the modern microscopies such as scanning-tunneling microscopy — witness the effort being made to understand STM images. This means that the results must be interpreted in terms of systems in which the signal for the particular experimental technique is known, or alternatively, in terms of a model of the system being studied. For example, temperature-programmed desorption (TPD) measurements show that adsorbed species are bound at certain energies, but does not give enough information to say what it is that is bound with those energies. As another example, high-resolution electron-energy loss spectroscopy (HREELS) reveals the vibrational spectrum of a surface with an adsorbed molecule, but features in the spectrum must be interpreted in terms of the known vibrational signals of the clean surface, those of molecules in the gas phase, and those taken from other adsorption experiments with the same molecule.

The water molecule has three normal modes of vibration, two high-frequency "stretch" modes in which the length of the stiff hydrogen bonds vary, and one "bending" mode in which the lengths of these bonds are basically constant and the angle between them is varying. The stretch modes are usually well separated from crystal phonon modes which makes them a clear signal in experiment. The presence or absence of the bending mode is often taken as sufficient evidence for molecular or dissociative adsorbtion of water on a surface, and in addition it is assumed that the two different types of hydroxyl group formed upon dissociation will produce two distinct, sharp, high-frequency signals.

Both TPD and HREELS have been used by Henderson *et al* [25] in a recent study of water adsorbtion on TiO_2 (110). Henderson argues that at 130 K, water dissociation occurs only at rather low coverages ($\sim$ 0.1 monolayer (ML)) and suggests that this occurs at defect sites. The vibrational spectra were used to support the view that the majority of first-layer adsorption was molecular, in particular, a feature at 1625 cm^{-1} identified as the water bond-bending mode, and features around 3400 cm^{-1} which were assigned to the O-H stretch modes of the molecule. Dissociative adsorption was linked with an O-H stretch feature at 3690 cm^{-1} and it was noted that *two distinct O-H frequencies expected from the two types of hydroxyl formed by dissociated water could not be observed.*

Simulations can help to interpret experiments. To go further, this is one of the most important uses of simulation, since working in tandem the two approaches both benefit, and the end result is greater than they can achieve apart. As a corollary, it is certainly not possible to answer all questions by one technique alone. In this work we have attempted to make contact with the HREELS experiments on the water-TiO_2 system, and while we cannot offer a full interpretation of the experimental results we can certainly help to understand part of them.

7.4 Techniques

We have used a variant of the `cetep` code (Cambridge and Edinburgh Total Energy Package [26]), the parallel version of `castep` (CAmbridge Sequential Total Energy Package [23]), running on the 512-node CRAY T3D at the Edinburgh Parallel Computer Centre, to perform our calculations. The generalised-gradient approximation (GGA, [27]) is used in preference to the local density approximation (LDA) as it provides a more accurate description of molecular dissocation energies and of hydrogen bonding [28]. A plane wave cutoff energy of 750 eV was found to converge the total energy of the 6-ion TiO_2 unit cell to 0.07 eV. The calculated lattice parameters (experimental values [29] in parenthesis) are 4.69 (4.594) and 2.99 (2.959) Å for a and c respectively, while the internal coordinate u was 0.306 (0.305). The slight overestimation of the lattice parameters (2% for a) is typical for the GGA.

A 3D supercell was used to model the surface, with a 2×1 area exposed on each side of a slab separated by a vacuum region. The (110) surface has rows of oxygen ions along [001] which are called bridging oxygens: these sit above the flat surface which contains fivefold- and sixfold-coordinated titanium ions. In order to minimise the computational cost the Brillouin zone sampling was restricted to the Γ-point and the hydrogen mass was set to 3 a.m.u. This higher mass allows a longer time step to be used in the MD simulation without affecting configuration energies or equilibrium statistical averages such as vibrational mean-square displacements. The overall shape of the hydrogen vibrational spectra will also be unaffected, but the frequencies will be lower. This is taken into account when interpreting frequencies. The vibrational frequencies of a single water molecule have been computed within the harmonic approximation in order to validate this approach, and are shown in table 1. With a mass of 1 a.m.u excellent agreement with experiment is obtained. A mass of 3 a.m.u lowers the angle-bending frequency to 29 THz, still well clear of the TiO_2 lattice vibrations, and allows us to use a time-step of up to 2 fs in the MD. The bond length and bond angle of the water molecule were found to be 0.967 Å and 105°, again in excellent agreement with the experimental values of 0.957 Å and 104.5° [30].

Other aspects of the simulations are quite standard, and full technical details have been published elsewhere [3].

Mode	Expt.	$M_h = 1$	$M_h = 3$
Sym. stretch	109.6	111	66.6
Asym. stretch	112.6	114	70.9
Bond bend	47.82	46.6	28.8

Table 1: Calculated DFT-GGA harmonic frequencies for the three vibrational modes of water. The values obtained for two hydrogen masses M_h are shown, along with the experimental values from reference [30].

7.5 Simulation results

7.5.1 Stage 1: adsorption

After relaxation and equilibration of the ions in the slab at 500 K, a water molecule was placed on each surface in the simulation box in a variety of initial configurations. This corresponds to a coverage of half a monolayer. Initial, random velocities corresponding to a temperature of 500 K were assigned for all the ions; the water molecules were *not* given an overall velocity directed towards the surface to hasten adsorption.

The behaviour observed in the dynamical simulations was as follows: in the early stages the molecule was drawn down to the surface rapidly, and its favourable orientation was in the (001) plane, with the oxygen atom pointing towards the the surface; when the oxygen atom is within about 2.7 Å of a bridging oxygen ion, there is strong interaction between a hydrogen and the bridging oxygen; this hydrogen atom is captured by the bridging oxygen, and the hydroxyl remnant of the water molecule adsorbs above the fivefold Ti site. It was noticable that while the hydroxyl remnant is rather free with respect to its orientation, the hydrogen ion bonded to the bridging oxygen prefers to point towards the "water" oxygen from whence it came. This pattern of dissociative adsorption was seen for several initial orientations of the water molecules, and is apparently insensitive to the hydrogen positions as long as the molecule is near to a fivefold Ti site. The dissociation described took about 0.4 ps, and during a further 0.8 ps simulation time there was no change in the average hydroxyl positions. Almost identical behaviour was observed in similar simulations of water adsorption on SnO_2 (110), which has the same rutile crystal structure as TiO_2.

We have performed similar calculations starting with water molecules over the 6-fold coordinated Ti site. Here, we chose orientations in which the hydrogen ions were closest to the bridging oxygens, but we could not find a position in which the molecule was attracted to the surface. This is in contrast to the 5-fold site simulations. MD simulations did not result in either physisorption or dissociation at the 6-fold site. Instead, the water molecule drifted away from the site and would presumably dissociate at the 5-fold site given sufficient simulation time.

After relaxation of the ions at the end of these simulations, the geometry confirms that the water molecule is dissociated. For convenience we will use the term "terminal hydroxyl" to describe the O-H fragments which originate from the water molecule, and "bridging hydroxyl" to indicate the O-H group formed by a bridging oxygen and a hydrogen ion. The terminal hydroxyl bond length of 0.97 Å is little changed from that in the water molecule while in the bridging hydroxyls it is somewhat longer - 1.00 Å. The distance between the oxygen of the terminal hydroxyl and the hydrogen of the bridging hydroxyl is about 1.8 Å, and the H-O-H angle is about 120°. The energy of adsorption obtained from our Γ-point calculations is 1.35 eV per H_2O at half-ML coverage. Our calculated geometry is in good agreement with static, multiple k-point DFT-GGA calculations [12]. The static calculations yielded an adsorption energy of 1.08 eV at monolayer coverage, and also indicated that at lower coverages the adsorption energy should increase. Our dynamical calculations provide strong support for the dissociation geometry being the most favouable, since we did not observe physisorption in our simulations.

7.5.2 Stage 2: vibrational spectra for the adsorbates

We have used MD to calculate the vibrational power spectra of the hydrogen atoms from the temporal Fourier transform of their velocity autocorrelation function (vacf). We recall that, since we are using a hydrogen mass of 3 a.m.u., our calculated frequencies are lower than those that would be obtained with normal H_2O, and must be corrected for purposes of comparison. The harmonic analysis (table 1) indicates a correction factor of 1.61-1.67 for the water molecule stretch frequencies, which we will use here. The vacf's were calculated up to 1.05 ps, with time origins at every time-step, giving a resolution of ±0.5 THz. The vacf's were multiplied by a windowing function prior to transformation, in order to suppress termination ripples.

Before considering the hydroxylated surface, we report calculations on an isolated water molecule, which provide both a check on our methods and a necessary reference point. The computational details were the same as already described, except that a cubic simulation box of 7 Å was used. Starting from the relaxed geometry, the ions were given random velocities in the plane of the molecule. The power spectra calculated at low temperature yielded frequencies in exact agreement with those found by harmonic analysis (table 1), and no appreciable anharmonic shift was found at 500 K.

To calculate the vibrational frequencies characteristic of the adsorbed species we started from the relaxed ionic configuration of the hydroxylated surface. The power spectrum from a 120 K simulation is shown in figure 1. The contributions from terminal and bridging hydroxyls are shown separately. As well as the low-frequency vibrations of the slab, there are clearly several high-frequency modes, and an absence of any power around the 29 THz water bond-bending frequency. Notice that the sharp peak at 69 THz is associated with the terminal hydroxyl groups, and the broad, multipeak structure around 60 THz corresponds to bridging hydroxyl vibrations. The terminal hydroxyl mode frequency is very similar to those of the stretch modes in water. More surprising is the behaviour of the bridging hydroxyls: their slightly greater bond length suggests that their vibrations may be lower in frequency than the terminal hydroxyls, but quite obviously one cannot associate a single mode to their vibrations. Analysis of the ionic trajectories reveals that the broadening occurs because the hydrogen on the bridging hydroxyl interacts strongly with the terminal hydroxyl oxygen. The length of this hydrogen bond, and hence the strength of interaction, is largely determined by the low-frequency motions of the oxygen ions. Using the correction factor of 1.61-1.67, we estimate that the vibrational spectrum of the hydroxylated surface would exhibit a sharp peak between 111-115 THz (3800-3930 cm^{-1}), and a broad feature spanning 89-100 THz (2970-3330 cm^{-1}).

7.6 Conclusions

Our results show that water does dissociate on the non-defective TiO_2 (110) surface. This is really a re-statement of the conclusion drawn from previous static calculations, but it does strengthen those conclusions since we have made a thorough search to find other adsorption geometries. We have not explicitly dealt with inter-molecular interactions in these calculations. Of course, the water molecule on the surface interacts with its periodic images, but the latter are at a fixed spacing and orientation with respect to the molecule. This means that the effects of hydrogen bonding between adjacent molecules cannot be investigated in our system. In previous studies [6] we have estimated the inter-molecular interactions as a function of separation, and for this situation the energies involved are small compared to the dissociation energy. Our finding dissociative adsorption in these circumstances is consistent with Henderson *et al* [25].

An important conclusion from our work is that the vibrational spectrum of dissociated H_2O on TiO_2 (110) does not contain two clear hydroxyl stretch mode frequencies. Rather, there is a sharp feature around the H_2O stretch frequencies associated with terminal hydroxyl modes, and a broad range of frequencies associated with the vibrations of bridging hydroxyls. The broadening of the bridging hydroxyl frequencies is due to hydrogen bonding between the dissociation fragments. This underlines the fact that the vibrational behaviour of a molecule cannot neccessarily be interpreted through simple arguments or inferred from other situations. This is of course generally true for any property, but the point here is to emphasise how simulation can aid interpretation.

We hope we have demonstrated that first-principles MD is a very powerful tool for surface chemistry investigations, and that for appropriate systems and problems, its particular strenghts make it the technique of choice for the theorist. Finally, why not take a look at some vidoes made from these simulations, which are on the web site:

`http://www.dl.ac.uk/TCS/Staff/Lindan_P_J_D/`

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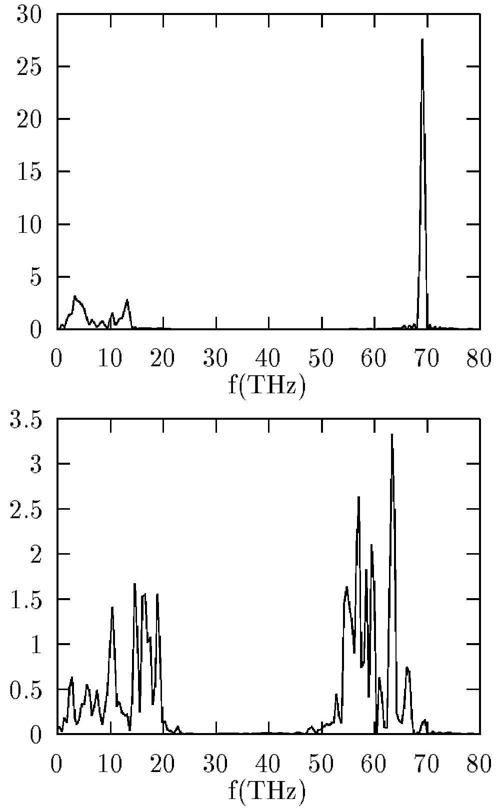

Figure 1: Power spectra for the hydrogen ions in the terminal hydroxyl (upper panel) and bridging hydroxyl (lower panel) groups after water dissociation. The simulation was at 120 K. Note that the frequencies are shifted because of the use of a large hydrogen mass. Note also the different y-scales used.