HCM Newsletter

Ψ_k Network

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

Number 20 April 1997

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Contents

1 Editorial **3**

2 News from the Network **5**

3 News from the Working Groups **6**

3.1 Reports on Collaborative Visits 6

3.2 Reports on Workshops 7

4 Conference Announcements **15**

4.1 The CCP5 Annual Meeting, London, UK 15

4.2 Third Workshop Wien97, Vienna, Austria 20

4.3 Adriatico Research Conference in Miramare - Trieste, Italy 21

4.4 CECAM/Ψ_k−Network Workshop 23

5 Job Announcements **26**

6 Abstracts **32**

7 HIGHLIGHT OF THE MONTH **49**

7.1 INTRODUCTION 49

7.2 VARIABLE CELL-SHAPE MOLECULAR DYNAMICS 50

7.3 ANISOTROPIC EXTERNAL STRESS 52

7.4 STRUCTURAL OPTIMIZATION 53

7.5 APPLICATIONS 53

7.6 CONCLUSIONS 55

1 Editorial

In this *Newsletter* readers will find a report and abstracts of presented contributions of the second workshop of the TMR Network on 'Interface Magnetism'. This TMR Network has originated from the Ψ_k-Network and basically comprises the 'old' **Magnetism Working Group** of the Ψ_k-Network. As such it is closely linked with our original Network, and we shall also publish in the *Newsletter* all information on the activity of this TMR Network.

We refer our readers to the **News from the Network** section, where we give some information on the financial situation and future of the Ψ_k-Network.

Below please find a reminder of the abstract template to be used for submissions to the *Newsletters*.

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Manuscripts available from: Author's e-mail address\\
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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. Finnis (Univ. Belfast)*, *M. Gillan (Univ. Keele)*, *E.K.U. Gross (Univ. Würzburg)*, *B.L. Györffy (Univ. Bristol)*, *M. Heggie (Univ. Sussex)*, *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)*, *M. Springborg (University of Konstanz)*, *G.P. Srivastava (Univ. Exeter)*, *W.M. Temmerman (Daresbury Laboratory, UK)*, and *A. Walker (UEA Norwich)*. There also exists 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 you may remember, this year is the final year of the HCM Ψ_k- Network's activity. By the end of the year we have to use up the funds. At present, there is still a substantial amount of money available for organizing workshops and making short and longer term collaborative visits within the Network. As customary, to get hold of the funds one needs to apply by email to **psik-management@dl.ac.uk** providing a short write-up on the project of interest and the nodes to be involved in a prospective collaboration, including a sufficiently detailed cost statement of the planned visit. Visits of one month or over are strongly encouraged and are expected to lead to well established collaborations between nodes of the Network and to common publications acknowledging the support of the Network. Please do contact us concerning your applications as soon as possible.

Regarding the future of the Ψ_k-Network, a proposal for a TMR Research Network on '**Electronic Structure Calculations of Materials Properties and Processes for Industry and Basic Sciences**' was submitted to the EU Commission at the end of January as a successor to the Ψ_k-Network. TMR Networks are much more research and project orientated than HCM Networks, but we incorporated in the proposal for the TMR Network a node dedicated to training and dissemination to keep many of the present HCM Ψ_k- Network activities going.

Moreover, we have heard informally that our ESF proposal for a programme is strongly supported by the ESF secretariat. This proposal was submitted last summer and if successful would allow us to expand the Ψ_k-Network workshops and collaborative visits also to countries of Central Europe.

Finally, in order to keep the cooperation of the electronic-structure community in Europe growing we count on your continuous involvement and support.

3 News from the Working Groups

3.1 Reports on Collaborative Visits

Report on a Collaborative Visit of C.Molteni (Max Planck Institut, Stuttgart), to the Theory of Condensed Matter group, University of Cambridge

24–28 February 1997

During the last week of February I visited Prof. V.Heine and Dr. M.C.Payne at the Theory of Condensed Matter group of the Cavendish Laboratory (University of Cambridge). The goal of my visit was to discuss recent results and future developments of a collaboration on grain boundary properties which started when I was a post–doc in Cambridge.

In particular we are interested in understanding and characterizing, by means of first principles simulations, the microscopic processes that occur during grain boundary sliding in different materials and boundary geometries. After a initial study of the sliding at grain boundaries in germanium[1], chosen as an example of brittle covalent semiconductor, we are currently investigating twist and tilt boundaries in aluminium, a typical ductile metal, with the goal of studying the role of delocalized metallic bonding in the sliding process.

For our simulations, we use a recently developed scheme for metals based on ensemble density functional theory[2], able to provide the efficiency that is needed to deal with large metallic systems.

In our study we have discovered and analysed a variety of behaviours in the sliding of aluminium grain boundaries, including coupling to migration, that turn out to depend not only on the materials chosen, but also on the geometry and the presence of defects, as a vacancy at the boundary interface.

The visit has been very useful to complete a paper on the sliding mechanisms in aluminium grain boundaries, that has been submitted for publication[3], and to discuss new ideas for future calculations. We are grateful to the network for its support.

(C.Molteni)

References

[1] C. Molteni, G. P. Francis, M. C. Payne and V. Heine, Phys. Rev. Lett. **76**, 1284 (1996).

[2] N. Marzari, Ph.D. Thesis, University of Cambridge (1996); N. Marzari, D. Vanderbilt and M. C. Payne, submitted for publication (1997).

[3] C.Molteni, N.Marzari, M.C.Payne and V.Heine, submitted for publication (1997).

TMR-Network on 'Interface Magnetism'

Workshop on 'KKR-like Methods'

February 15 – 17, 1997

CMS – Technical University Vienna

Summary

The Vienna meeting was already the second meeting of the TMR-Network on '**Interface Magnetism**', which originated from the '**Magnetism Working Group**' of the HCM Ψ_k – Network. This meeting provided an excellent opportunity to present, discuss and evaluate the various stages in developing screened KKR-type computer codes, presently pursued by three of the nodes of the Network. It seems that right now all aspects of a screened scattering approach such as real space scattering, scattering using two- or three-dimensional translational invariance, including supercell techniques are in quite an advanced stage. In some applications the full potential aspects were the primary goal, in others relativistic descriptions. On top of these developments also recent theoretical improvements with respect to magnetic properties in alloyed systems, as described with standard KKR tools, were presented.

Because of the time schedule, but also because of the interest in the various aspects of the KKR-like methods, a very lively discussion seemed to characterize the meeting. In the general discussion session devoted to the logistics of scientific interrelations within the network, quite a few specific arrangements were fixed, which are necessary to monitor a broad exchange of computing techniques, but also training of young scientists. The programme of the workshop and abstracts of all presented contributions follow below.

(P. Weinberger)

Programme

Sunday, February 16, 1997

Morning session:

Chair-person: B.L. Gyorffy

9:00	9:05	**Opening: Techical details**
9:05	10:00	*Experience with Screened KKR-methods* **Zeller**

10:00	10:30	*A screened KKR-method for the slab geometry*	**Wildberger**
10:30	11:00	**coffee break**	
11:00	11:30	*Screened KKR: Application to supercells*	**Zahn**
11:30	12:30	*Full potential, forces and structural distortion*	**Papanikolaou**
12:30	14:00	**lunch**	

Afternoon session:

Chair-person: P.H. Dederichs

14:00	14:30	*Magnetic Anisotropy of Ni, Fe and Co from real space multiple scattering methods*	**Beiden**
14:30	15:30	*Magnetic anisotropy of an impurity in a semi-infinite host*	**Gyorffy**
15:30	16:00	*Failure of two-current model for alloys with strongly spin-dependent disorder*	**Banhart**
16:00	16:30	**coffee break**	
16:30	17:30	*A new method for calculating the dynamic, paramagnetic, spin susceptibility of metals and their alloys*	**Staunton**
17:30	18:30	*Spin-polarized relativistic Screened KKR for magnetic multilayer systems*	**Szunyogh**
19:00		**leave from Hotel to Sievering** (public transportation)	
20:00		**joint dinner party: Heurigen**	

Monday, February 17, 1997

Morning session:

Chair-person: W.M. Temmerman

8:30	9:30	*Layer relaxation: real space screening & 2d-translational invariant screening*	**Újfalussy**
9:30	10:30	*The Spin-polarized relativistic KKR (SPR-KKR) — new developments*	**Ebert**
10:30	11:00	**coffee break**	
11:00	13:00	**General discussion:** *Who is doing what with whom? And: When and where?*	**Temmerman**
13:00	14:00	**lunch**	

Afternoon session:

14:00	16:30	**Discussion groups:**	
		(a) TB-LMTO & SKKR interactions	**Kudrnovský**
		(b) Transport, GMR	**Mertig**
		(c) Spectroscopy	**Pustogowa**

ABSTRACTS

Experience with the screened KKR method: theoretical aspects and numerical calculations

R. Zeller

Institut für Festkörperforschung, Forschungszentrum Jülich, Germany

For occupied and low lying unoccupied electronic states it is shown how the traditional KKR method can exactly and easily be transformed into a tight-binding form. The transformation is based on a suitably chosen repulsive reference system and the tight-binding parameters (i.e.

the screened KKR structure constants) can straightforwardly be obtained in real space which is a considerable advantage compared to the complicated determination of the standard KKR structure constants. It is demonstrated that the tight-binding parameters decay exponentially and so fast that highly accurate density-functional calculations for lattice constants and bulk moduli are possible if these tight-binding parameters are determined by using rather small clusters of repulsive muffin-tin potentials. It is discussed that as a consequence of the small clusters electronic-structure calculations for very large systems can be done and that the main computational work consists in the inversion of rather sparse matrices. Algorithms for banded matrices can directly be applied and lead to favorable scalings of the computational effort with systems size, e.g. to linear scaling with the number of layers in systems with two-dimensional periodicity. It is also shown that available standard software allows to implement the necessary matrix inversions easily and efficiently on workstations, vector and parallel computers.

A Screened KKR-Green's Function Method for Slabs

K. Wildberger

Institut für Festkörperforschung, Forschungszentrum Jülich, Germany

A Green's function method for layered systems with slab geometry 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. However, 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. We will discuss the extension of the program to include the full potential.

Screened KKR: Application to supercells

P. Zahn[a], *I. Mertig*[a], *R. Zeller*[b] *and P.H. Dederichs*[b]

[a] *Technische Universität Dresden, Institut für Theoretische Physik, Dresden, Germany*

[b] *Institut für Festkörperforschung, Forschungszentrum Jülich, Germany*

A Green's function method adapted to multilayer systems is presented. The method is based on the recently proposed concept of a reference system with repulsive muffin-tin potentials. Using this technique the traditional Korringa-Kohn-Rostoker (KKR) method can be transformed into a tight-binding scheme with screened structure constants. Besides the calculation of the Green function our attention is directed to the solution of the eigenvalue problem. Because of the block-tridiagonal structure of the eigenvalue matrix the numerical effort scales linearly with the number of atoms in the unit cell. The accuracy of the method was investigated for an empty lattice. Applications to Co/Cu multilayers are presented.

Full Potential KKR Green function method: Forces and lattice distortions

N. Papanikolaou

Institut für Festkörperforschung, Forschungszentrum Jülich, Germany

We will present a full-potential Korringa-Kohn-Rostoker (KKR) Green function method for electronic structure calculations. In the full-potential treatment both the shape of the Wigner-Seitz cells as well as the non-sphericity of the potential in the cells, are taken into account exactly. The non-sphericity leads to a set of coupled radial equations, which are solved iteratively. As an advantage of the KKR method the atomic forces can be easily obtained from the Hellmann-Feynman theorem since the Pullay corrections vanish. The method was recently extended to treat small atomic displacements from the ideal lattice positions. As first application we calculate the lattice relaxation around transition metal impurities in Cu and Al and compare the results with EXAFS and lattice parameter measurements. As second example we discuss the calculation of phonons in real space, and present calculated dispersion curves for some selected metals. Both examples demonstrate the accuracy and efficiency of the method.

Magnetic Anisotropy of Ni, Fe and Co from real space multiple scattering methods

S.V. Beiden[a], *Z. Szotek*[b], *W.M. Temmerman*[b], *G.A. Gehring*[a], *Yang Wang*[c], *G.M. Stocks*[c], *D.M.C.Nicholson*[c], *W.A. Shelton*[c] *and H. Ebert*[d]

[a] *Department of Physics, University of Sheffield, UK*

[b] *Daresbury Laboratory, Daresbury, UK*

[c] *Oak Ridge National Laboratory, Oak Ridge, USA*

[d] *Institute for Physical Chemistry, University of München, Germany*

A fully relativistic and spin–polarized extension of the O(N) real space locally self–consistent multiple scattering formalism has been implemented and applied to the study of magnetic properties of Fe, Co and Ni. Here we report on the calculation of the magneto–crystalline anisotropy energy of these systems. We discuss the convergence of the latter, and of the spin– and orbital–moments, as a function of the number of shells included for self–consistency. The calculated values are in good quantitative agreement with the experimental results in case of Fe and Co, which indicates that the origin of the magneto-crystalline anisotropy is relatively local in real space. The result for Ni is in a good agreement with other first-principles calculations.

Magnetic anisotropy of an impurity in a semi–infinite host

B.L. Gyorffy[a] *and L. Szunyogh*[a,b]

[a] *H.H. Wills Physics Laboratory, University of Bristol and* [b] *Institute of Physics, Technical University Budapest*

We investigate the interaction of a magnetic (Fe) impurity with the surface of a non–magnetic (Au) semi–infinite host on the bases of fully relativistic spin–polarized first principles calculations. We show that the surface induces a magnetic anisotropy on the impurity, however, it

is questionable whether the anisotropy coupling constant K is sufficiently large to explain the thickness dependence of the Kondo amplitude B in thin films of dilute Fe_cAu_{1-c} alloys. We also find that $K(d)$ is an oscillating function of the distance d between the impurity and the surface with an amplitude which falls as $1/d^2$ and a period which is determined by the shape of the Fermi Surface of the bulk Au host.

Failure of two-current model for alloys with strongly spin-dependent disorder

J. Banhart

Fraunhofer-Institut für angewandte Materialforschung (IFAM), Bremen, Germany

The two-current model is generally considered to give a good description of the transport properties of ferromagnets. It assumes that scattering processes are spin conserving and that the electronic current can be described as the sum of two spin sub-currents. A large number of experimental investigations seem to support the application of this model to alloys such as Fe-Ni and Co-Ni.

In order to check the validity of the two-current model a series of first principles calculations was carried out. For that purpose the Kubo-Greenwood formalism was applied on the basis of electronic structure data obtained using the spin-polarized Korringa-Kohn-Rostoker Coherent Potential Approximation (KKR-CPA). One set of calculations was carried out fully relativistically, while for a second one the two-current model was used.

It was found that the two-current calculations yield spin-resolved resistivities which are more polarized than one would expect from experimental considerations and which give a much lower total resistivity than the relativistic calculations. This shows that scattering processes between the spin-systems are of crucial importance in contradiction to the basic assumption of the two-current model. Moreover, the experimental decomposition of resistivities into spin-resolved resistivities which is based on the two-current model, is shown not to give the proper values but some effective resistivities which are quite different from the calculated ones. The conclusion is that the two-current model is wrong for the alloys considered but that this failure does not become apparent in the usual interpretation of the resistivities of ferromagnetic alloys as long as the wrong assumptions are used throughout the interpretation.

A new method for calculating the dynamic, paramagnetic, spin susceptibility of metals and their alloys

J.B. Staunton

Physics Department, University of Warwick, U.K.

We describe a new method for calculating the dynamic, paramagnetic, spin susceptibility of metals and their alloys. The temperature susceptibility is formulated from 'first principles' using Spin Density Functional theory and an analytic continuation made in order to obtain the dynamic susceptibility. The approach is applied to investigate the spin fluctuations in the paramagnetic phase of Cr and in the $Cr_{95}V_5$ disordered alloy, both of which have been studied extensively by neutron scattering. We can describe for the first time several features observed in these experiments. In chromium we find incommensurate SDW paramagnons for a narrow low

frequency range and the dynamic susceptibility $\chi(\mathbf{q},\omega)$ to peak at a commensurate wave-vector $\mathbf{q} = (1,0,0)$ at higher frequencies, ω. On the other hand $Cr_{95}V_5$ exhibits a peak at an incommensurate $\mathbf{q}$ in $\chi(\mathbf{q},\omega)$ for a wide frequency range. These features are determined by the extent to which electron jack and hole octahedral pieces of the Fermi surfaces are nested. Doping Cr with V diminishes the nesting.

Spin-polarized relativistic Screened KKR for magnetic multilayer systems

L. Szunyogh[a,b], *B. Újfalussy*[a,c], *P. Weinberger*[a], *and C. Sommers*[d]

[a] *Center for Computational Materials Science, Vienna, Austria,* [b] *Institute of Physics, Technical University Budapest, Hungary,* [c] *Research Institute for Solid State Physics, Hungarian Academy of Sciences, Hungary and* [d] *Laboratoire de Physique des Solides, Orsay, France*

By utilizing the tridiagonal block–shape of the matrices of the corresponding structure constants, the screened Korringa–Kohn–Rostoker (SKKR) method is shown to be a powerful tool to calculate the electronic structure of systems with two–dimensional translational invariance. It's spin–polarized fully relativistic version enables a non–perturbative treatment of the spin–orbit coupling in the presence of spin–polarization. Some of the technical details of the method are presented with special emphasis on group theoretical aspects.

The corresponding program package has mainly been applied to study the surface/interface magnetic anisotropy energy (MAE) in layered magnetic systems. Within the "force theorem" approach the MAE is calculated as a sum of two contributions, namely, that of the one–particle energies (band–energy) and that of the magnetic dipole–dipole interaction energy. The applications include e.g. Fe over– and interlayers on fcc Au(001) and Cu(001) substrates, where the orientational switching thickness has been obtained in good agreement with experiments. In particular, the origin of the "anomalous magnetic anisotropy" is studied for the case of a Co monolayer on Au(111) substrate as capped by additional Au layers. Recent results for MCo/Cu(001) ($M = 3d, 4d, 5d$ metals) are also presented.

Layer relaxation: real space screening & 2d-translational invariant screening

B. Újfalussy[a,b], *L. Szunyogh*[a,c] *and P. Weinberger*[a]

[a] *Center for Computational Materials Science, Vienna, Austria,* [b] *Research Institute for Solid State Physics, Hungarian Academy of Sciences, Hungary and* [c] *Institute of Physics, Technical University Budapest, Hungary*

By making explicit use of the so-called "Kambe" structure constants, originally formulated in the late Sixties for a theoretical description of Low Energy Electron Diffraction (LEED), the Screened KKR Surface Green's function (*SKKR-SGF*-) method for layered systems can be conceptually extended to multilayer systems corresponding to complex two-dimensional lattices and/or showing layer relaxation. Because within the *SKKR-SGF*-method the Coherent Potential Approximation (CPA) can be applied to disordered multilayer systems, and in particular since such a description can be formulated (and programmed) in a fully relativistic spin-polarized manner, important magnetic properties of multilayer systems such as magnetic anisotropies at surfaces or interfaces can be calculated in a very realistic way, namely including layer relaxation

and interdiffusion at interfaces (surfaces). For matters of completeness a comparison to the so-called 'real space' screening approach is also given.

The Spin-polarized relativistic KKR (SPR-KKR) – new developments

H. Ebert, M. Battocletti, H. Freyer, T. Huhne, V. Popescu, J. Schwitalla, A. Vernes, and C. Zecha

Institut für Physikalische Chemie, Universität München, Germany

We report on recent activities of our group in the field of spin-polarized relativistic (SPR) KKR calculations. This band structure technique is based on the Dirac equation for magnetic solids treated within the framework of relativistic SDFT. This approach has been extended by introducing corrections to the Dirac equation according to the orbital polarization (OP) formalism, current density formalism (CDFT) and the Breit interaction. All these modifications introduce a vector potential coupling to the orbital degree of freedom of the electrons. Our scheme developed previously to manipulate the spin-orbit coupling has been extended to distinguish the influence of energy shifts and removing of degeneracies due to the presence of spin-orbit coupling. Finally, the standard description to deal with magnetic X-ray dichroism in the XANES-region has been extended to deal with the EXAFS-region in a corresponding way. For all these developments some technical details will be discussed and illustrated by appropriate examples.

4 Conference Announcements

4.1 The CCP5 Annual Meeting, London, UK

MATERIALS, MICROSTRUCTURES AND SIMULATION

The CCP5 Annual Meeting
14th - 17th September 1997
University College London, U.K.

The emphasis of the meeting will be on the structure and properties of materials (whether metals, ionics, covalent materials or soft solids). A particular emphasis will be on structures on the nanometre to micron scale; how these depend on atomistic processes and how they in turn control the properties of materials (or have interesting properties of their own). Examples might include

- Nanostructural materials
- Simulation of growth and dissolution on the atomic scale (MBE, crystal growth)
- Structure of surfaces and interfaces; roughness, calculations on STM and AFM, epitaxial matching, stress and misfit dislocations.
- Methods for simulating microstructure (large scale MD e.g. radiation damage), cellular automata, ballistic models and so on)
- Crossing the length scales; linking *ab initio* and classical methods.

As with all CCP5 Meetings, general contributions will be welcome.

Invited speakers

Prof. David Srolovitz	University of Michigan	Interfaces, stresses and modelling.
Dr Wolfgang Paul	University of Mainz	Monte Carlo methods in large-scale simulations
Professor Roger Smith	University of Loughborough	Large-scale molecular dynamics
Dr Sergei Dudarev	University of Oxford	Metal oxides containing d and f electrons: a new challenge in surface science
Dr Tuck Choy	University of Monash	Crossing the length scales.

Administrative Matters

Timetable

The meeting will start at 09.00 on Monday 15th September and finish at 13.00 on Wednesday 17th September. Accommodation is provided for the night of Sunday 14th December.

Registration and Accommodation

The registration fee is 75 pounds (provided that registration is before August 1st). This includes lunch on Monday and Tuesday and dinner on Tuesday 16th September (after the poster session). The final date for submitting an abstract for presentation at the Meeting is August 1st. People registering after August 1st will pay an supplement of 20 pounds. Anyone who registers after September 1st cannot be guaranteed accommodation or meals.

The accommodation fee is 55 pounds. Accommodation will be in Ramsay Hall, a student Hall of Residence about 5 minutes walk from the College. The accommodation fee includes dinner on the evenings of 14th and 15th and breakfast on 15th, 16th and 17th.

Presentations and abstracts

An abstract must be sent at the time of registration by electronic mail in an electronic format using either LATEX or WORD. (If you use WORD, please send the file in RTF format). The abstracts will also be published as part of an issue of the CCP5 quarterly newsletter. Delegates are also encouraged to submit a longer account of their work for publication in the newsletter. Postscript diagrams may also be accepted.

There will be both oral and poster sessions. The poster session will be before dinner on Tuesday evening (16th) in Ramsay Hall.

Travel Arrangements

Do not attempt to come by car unless you have made your own parking arrangements and even then you should think twice. There is NO PARKING at the Hall of Residence or the College.

London is well served by public transport of all kinds. Details of how to find UCL and Ramsay Hall (it is near Fitroy Square between Maple St and Grafton St) are given in maps on the UCL web site (http://www.ucl.ac.uk). This site also gives local travel information and links to train timetables. Further information will be sent with the acknowledgement of registration.

Organising Committee

J. Harding M. Leslie

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The registration and presentation forms are attached below.

REGISTRATION FORM

Materials, Microstructures and Simulation

The CCP5 Annual Meeting

14th - 17th September 1997

University College London, U.K.

SURNAME: (Prof , Dr , Mr , Mrs , Miss , Ms *) .....Male/Female*

(BLOCK letters please). * Please delete INITIALS: .....

ADDRESS: .....

.....

.....

.....

.....

Tel .....Fax .....

e-mail .....

Please indicate if you have any special requirements (Diet, disability)

.....

CONFERENCE COSTS

(Prices in Pounds Sterling)

1)	Conference Fees (including lunches and conference dinner)	£75.00	.....
1a)	Late Registration	£20.00	.....
2)	Accommodation	£55.00	.....
3)	I will require additional nights accommodation on September 13th.	£22.50	.....
	TOTAL:		.....

I enclose a cheque for £ ..... (Payable to "University College, London"). Unfortunately, the College is unable to accept credit cards.

CONFERENCE PRESENTATIONS

I would like to submit a presentation YES/NO*
I would prefer an ORAL/POSTER* presentation

TITLE .....

Lead author: .....

Affiliation: .....

Co-author(s): .....

Affiliation(s): .....

An abstract must be sent at the time of registration by electronic mail in an electronic format using either LATEX or WORD. (If you use WORD, please send the file in RTF format).

Please return this form together with abstract and a cheque made payable to "University College London":

Dr. J.H. Harding	Email:	j.harding@ucl.ac.uk
Dept. Physics & Astronomy	Phone:	(+44) (0) 171 419 3506 (Direct Dial)
University College London	Fax:	(+44) (0) 171 391 1360
Gower St.		
LONDON WC1E 6BT		
UK		

Closing date for receipt of contributed papers is 1st August 1997. The registration price after 1st August is increased by 20 pounds. No meals or accommodation can be guaranteed to anyone registering after September 1st.

4.2 Third Workshop Wien97, Vienna, Austria

THIRD WORKSHOP

WIEN97

Full-Potential LAPW calculations with the new WIEN97 code

July 1-5, 1997
Vienna University of Technology, Austria
Chairman: K.Schwarz (TU-Vienna)
Email: kschwarz@email.tuwien.ac.at

First Announcement

This third workshop is concerned with recent progress in density functional calculations using the full-potential Linearized Augmented Plane Wave (FP-LAPW) method as embodied in the new WIEN97 code (or related topics).

The workshop will be organized as follows:

- A short introduction to the LAPW method
- A brief summary of the underlying density functional theory
- The new features of the WIEN97 program package
- Introduction to the new graphical user interface
- Hands-on experience with WIEN97
- Results obtained with LAPW (WIEN95 / WIEN97) and related topics
- Poster session

Conference site:
The conference will take place at the TU Wien (Vienna University of Technology, A-1040 Vienna, Wiedner Hauptstr. 8-10, second floor (yellow tower, lecture hall 8)

Contact:
For further information look at our WWW-homepage
http://www.tuwien.ac.at/theochem/wien97/ws97/
or send email to kschwarz@email.tuwien.ac.at.

4.3 Adriatico Research Conference in Miramare - Trieste, Italy

"SIMPLE SYSTEMS AT HIGH PRESSURES AND TEMPERATURES: THEORY AND EXPERIMENT"

Miramare - Trieste, Italy

1 - 4 July, 1997

(*Organizers*: P. Loubeyre, J. Kohanoff and E. Tosatti)

The Conference will consist of keynote and invited talks. In addition, there will be a permanent Poster Session. A detailed (tentative) programme of the Conference, together with additional informations, can be found at the WEB site:

http://www.ictp.trieste.it/ kohanoff/

The topics to be treated will include:

Introductory general topics
Metals under pressure
Semiconductors under pressure
Hydrogen
Solid phases
Fluid phases
Astrophysics
Experimental advances
Minerals and Geophysics
High pressure chemistry
Hydrogen-bonded systems
Synthesis of new materials

The list of invited speakers includes:

Russell Hemley, David A. Young, Jean-Michel Besson, Guido L. Chiarotti, Friederich Hensel, Kenichi Takemura, Vadim Brazhkin, Stefano Baroni, Malcom McMahon, Pier Luigi Silvestrelli, Neil W. Ashcroft, Isaac Silvera, William B. Hubbard, Neil Holmes, Marvin Ross, Paul Loubeyre, Francesco Ancilotto, Jorge Kohanoff, Detlef Hohl, Carlo Pierleoni, Ali Alavi, Daniel Haeusermann, Mikhail Eremets, Francesco Sette, Ho-Kwang Mao, Kiichi Amaya, Reinhard Boehler, Raymond Jeanloz, Michael Haiber, Dennis Klug, Philippe Gillet, Sandro Scandolo, Renata Wentzcovitch, Katsutoshi Aoki, Michele Parrinello, Paul McMillan, John Badding, Werner Kuhs, Philippe Pruzan, Marco Bernasconi, Frederic Datchi, Maddury Somayazulu, Stephane Bernard.

Call for Contributed Posters

Abstracts must be submitted directly via e-mail to the local organizer, Dr. Jorge Kohanoff (kohanoff@ictp.trieste.it), with a subject line "submit poster smr999 author-name". Deadline for contributed posters is : 1 June 1996 . Abstracts should including title, authors and institutions, and should be written in plain text format.

Participation and Registration

There is no registration fee. As a rule, travel and subsistence expenses of the participants should be covered by their home institutions. However, limited funds are available for some participants from developing countries who will be selected by the Organizers. As scarcity of funds allows travel contributions to be granted only in a few exceptional cases, every effort should be made by candidates to secure support for their fares from their home countries.

All applicants are kindly asked to return the Registration Form (to be downloaded from *http* : *//www.ictp.trieste.it/~kohanoff/*, or asked to *smr*999@*ictp.trieste.it*) accompanied, if requesting financial help, by a list of publications relevant to the subject of the conference.

Deadlines for registration are:

→ 1 April 1997 (for applicants requesting financial help)
→ 1 June 1997 (for applicants NOT requesting financial help)

Ab Initio Calculation in Relation to Modelling Constitutive Relations and Fracture Toughness of Metals

To take place in Lyon, 20-22 October

Organisers: M.W.Finnis and A.E.Carlsson

The Ψ_k–Network is making available a number of bursaries to fund participants from Network nodes, especially for people at post-doctoral level. Applications should be made to Mike Finnis (email: **m.finnis@qub.ac.uk**), including the abstract of a poster and the names of two referees.

Scientific background

Ab initio calculation of *materials* properties has developed over recent years to such an extent that many basic properties relevant to *mechanical properties* can be calculated. Typical examples are elastic constants of metals and alloys, surface energies and vacancy formation energies. Indeed, some quantities, such as ideal cleavage energies of solids at low temperature, can probably be more accurately calculated than measured. The most successful theoretical framework for *ab initio* is the density functional theory in the local density (or spin density) approximation. This has been implemented in a variety of ways, such as pseudopotential methods and the linear augmented plane wave or muffin tin orbital methods. While the twin demands of accuracy and faster computation time are driving major developments in *ab initio* calculation, our concerns here are rather different.

There is no doubt that *ab initio* calculations have made an impact in materials science. Nevertheless it can happen at conferences that *ab initio* results are presented and experimentalists hoping for something useful are disappointed. We see a need to focus the attention of the *ab initio* community on questions of real interest to experimentalists measuring mechanical properties and modellers trying to simulate these properties.

Mechanical properties of metals such as fracture toughness, yield stress and creep rates, present peculiar difficulties, due to the simultaneous importance of two different length and energy scales. These are on the one hand the atomic scale of interatomic bonding, dislocation cores, and defect activation energies, and on the other hand the mesoscopic scale of grain boundaries, and dislocations regarded as geometrical defects interacting elastically with each other and with other defects. But there is a way forward. *Ab initio* calculations can establish atomistic energies, e.g. a gamma surface (the sliding energy of ideal semiinfinite blocks), or the activation barrier

for kink migration on a dislocation; they can also document atomistic processes, such as during grain boundary sliding, and establish data bases of energies for calibrating more empirical models of interatomic interactions. Such atomistic results can thus feed into the mesoscopic simulations at larger length scales. These simulations, in turn, are expected to yield directly observable mechanical properties such as constitutive relations and fracture toughness of metals, over the next few years.

Motivation and objectives

The aim is to discover how to bridge the gap we perceive between *ab initio* calculations and real constitutive relations and fracture toughness of metals. The key types of ab-initio calculations include: dislocation core energies and mobilities, dislocation interactions with defects, elastic constants, response of (ideal) cracks to applied stresses, surface energies, interface energies (including sliding), and others which we expect to emerge at the workshop. Progress to this end will require good collaboration between the *ab initio* calculators, mesoscopic modellers and experimentalists. The workshop will bring these communities together and identify a wish list of *relevant* calculations, which should focus future *ab initio* effort into useful directions.

Format

There will about 40 participants. We plan about 15 talks of 40 minutes plus 20 minutes discussion, and three focussed general discussions, which should result in some written conclusions. Posters will be welcome, and would be a requirement for funding from Ψ_k-Network.

Confirmed participants

E. Aifantis, *Michigan Technological University*
L. M. Brown, *MP Group, Cavendish Laboratory*
A. Carlsson, *Washington University*
B.R. Cooper, *West Virginia University*
M. Daw, *Clemson University*
B. Devincre, *ONERA*
F. Ducastelle, *ONERA*
C. Elsaesser, *Max-Planck-Institut für Metallforschung, Stuttgart*
M.W. Finnis, *Queen's University Belfast*
S.M. Foiles, *SMTS Sandia Livermore Laboratories*
P. Gumbsch, *Max-Planck-Institut für Metallforschung, Stuttgart*
J. Harris, *MSI/Biosym*
K.-M. Ho, *Ames*
R.G. Hoagland, *Washington State University*
E.A. Holm, *Sandia National Laboratories*
E. Kaxiras, *Harvard University*

R. LeSar, *Los Alamos National Laboratory*

J.L. Martins, *INESC, Lisbon*

R. Phillips, *Brown University*

S. Roberts, *University of Oxford*

K. Schwarz, *IBM*

H.L. Skriver, *Technical University of Denmark*

R.M. Thomson, *NIST*

V. Vitek, *University of Pennsylvania*

5 Job Announcements

Imperial College of Science, Technology and Medicine

Postdoctoral Position in Theoretical Condensed Matter Physics

Applications are invited for a postdoctoral position in the Condensed Matter Theory Group at Imperial College. The work will involve using quantum Monte Carlo methods, previously applied only to bulk solids and model surfaces, to study exchange and correlation at real surfaces. Some prior experience of computational electronic structure theory is desirable. The appointment will begin on or after 1st September 1997 and will be for one year initially, although an extension for a further one or two years is likely. The starting salary will be in the range £16,451 to £23,653 depending on age and experience. Applicants should send a CV, a publications list, and copies of current preprints to the address below. They should also arrange for two letters of recommendation to be sent. Email applications are encouraged.

Dr W.M.C. Foulkes
Condensed Matter Theory Group
Blackett Laboratory
Imperial College
Prince Consort Road
London SW7 2BZ
United Kingdom
phone: (+44) 171 594 7607 fax: (+44) 171 594 7604
email: m.foulkes@ic.ac.uk www: http://www.sst.ph.ic.ac.uk/

Closing date: 25th April 1997.

Postdoctoral Fellowship

University of Texas at Austin

A postdoctoral fellowship is available from the summer of 1997 to work in the group led by Prof. Leonard Kleinman. The research interests of the group include: Density functional theory; pseudopotential theory; molecular dynamics; ab initio calculations of the electronic, magnetic, and physical properties of solids, surfaces, and liquids. Applicants need to have obtained their Ph.D. qualification within the last five years to be elligible.

Please address enquiries to:

Prof. L.B. Kleinman
Department of Physics
University of Texas at Austin
Austin, Texas 78712-1081, USA
email: kleinman@mail.utexas.edu

First Principles Simulation of Surfaces

(three year fixed term appointment)

Daresbury Laboratory (UK)

The Computational Materials Science Group at Daresbury Laboratory is seeking to fill a research position in the area of first principles simulation of surface structure and properties.

The successful candidate will work closely with members of the UK collaboration in computational surface science (CCP3) which involves over 20 leading research groups. The collaboration is currently concerned with developing software for the efficient first principles simulation of surfaces. This software will be based on the CRYSTAL package which has been developed jointly by the Daresbury group and the Theoretical Chemistry Group at the University of Turin. CRYSTAL implements both density functional and Hartree-Fock approximations within a local basis set formalism (http://www.dl.ac.uk/TCS/MatSci). These simulation techniques will be applied to the interpretation of surface spectroscopic data in collaboration with CCP3 groups. A strong background in theoretical physics, chemistry or materials science and experience of large scale software development in FORTRAN or C is required. Experience of first principles methods and, in particular, local basis techniques will be an advantage.

The position will be based at Daresbury. The starting salary will be within the Council's Band 5 range: 14,828 - 24,233 pounds dependent on experience.

Further information is available from: **Dr NM Harrison (01925 603334, n.harrison@dl.ac.uk)**.

For an application form please contact the Recruitment Section, Personnel, R71, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, OX11 0QX or telephone (01235) 445435, quoting reference VN1481/97.

The deadline for applications is: **5th April 1997**.

COUNCIL FOR THE CENTRAL LABORATORY OF THE RESEARCH COUNCILS

Ph.D. Position

Institut für Festkörperforschung (IFF), Research Center Jülich, Germany

Starting now or later this year there is a position for a Ph.D. student (BAT IIa/2, 3 years) at the Institute for Solid State Research in Jülich, Germany. The aim of the project are ab-initio calculations for magnetic nanostructures on surfaces, such as adatoms, dimers, small islands, steps etc. The calculations will be performed using the full-potential KKR-Green's function methods developed at Jülich and will include structural optimisation. The work is integrated within the Sonderforschungsbereich "Mesoscopic Systems" (Aachen/Jülich/Cologne) and the TMR-Network "Interface Magnetism". The candidate should have experience with computing and/or electron theory. Please contact:

Prof. Dr. P.H. Dederichs
Institut für Festkörperforschung
Forschungszentrum Jülich
D-52425 Jülich, Germany

e-mail: l.gerken@kfa-juelich.de
phone: [+49] 2461 61 4351
[+49] 2461 61 2620

Research Studenship

University of Cambridge
Department of Materials Science
and
Daresbury Laboratory

Applications are invited for a research studentship leading to the degree of Ph.D. in the field of ab-initio electronic structure calculations and modelling of advanced structural materials. The student will join a multidisciplinary research team based in Cambridge working, in close interaction with industry, on a prestigious EPSRC Foresight Challenge project dealing with the development of new high temperature alloys. Results of the Cambridge high resolution electron microscopy experiments will be interpreted by the prospective research student on the basis of ab-initio calculations performed in collaboration with the band theory group in Daresbury. Work will involve a range of computational ab-initio techniques and will include massively parallel computing and scientific interaction with researchers at Oak Ridge National Laboratory in the USA. A good honours degree in Physics with preferably some exposure to solid state physics, electronic structure methods and some experience in experimental methods are required. The studentship is available to British Residents and EU citizens at standard U.K. rates.

Further details about the research can be obtained from Dr. G. Botton (gb10003@cus.cam.ac.uk) or Prof. W. Temmerman (W.M.Temmerman@dl.ac.uk). For application forms and a booklet with details of the research work carried out in the Department of Materials Science, contact Dr. Rosie Ward, Department of Materials Science and Metallurgy, University of Cambridge, Pembroke St., CB2 3QZ, Tel. (+44) (0)1223 331955, (remw2@msm.cam.ac.uk). Further information about the Department of Materials Science can be found at http://www.msm.cam.ac.uk and about Daresbury Laboratory at http://www.dl.ac.uk

Post-doctoral Position

University of Wales Cardiff
Department of Physics and Astronomy

Nonlinear Optical Studies of Thin Magnetic Films

A postdoctoral research associate is required, to work with John Inglesfield on the theory of the Nonlinear Magneto-Optical Kerr effect in thin magnetic films. This position is part of the NOMOKE network funded by the European Union Training and Mobility of Researchers Programme, and involves collaboration with Nijmegen (the Netherlands), groups in France and Germany, and the University of Bath.

Candidates must be nationals of a EU country other than the United Kingdom. Candidates should have experience in electronic structure theory, or some related area of condensed matter physics.

The post is available immmediately for a fixed-term period of 2 years.

Salary: £ 15159 – £ 22785 per annum.

For more information contact: John Inglesfield on +44 1222 874857,
email: J.Inglesfield@astro.cf.ac.uk

Density-Functional Theory of Surface Diffusion and Epitaxial Growth of Metals

C. Ratsch, P. Ruggerone, and M. Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4-6, D-14 195 Berlin-Dahlem, Germany

Abstract

This paper gives a summary of basic concepts of density-functional theory (DFT) and its use in state-of-the-art computations of complex processes in condensed matter physics and materials science. In particular we discuss how microscopic growth parameters can be determined by DFT and how on this basis macroscopic phenomena can be described. In order to reach the time and length scales of realistic growth conditions DFT results are complemented by kinetic Monte Carlo simulations.

(Surface Diffusion: Atomistic and Collective Processes, ed M. Tringides (Plenum Press, New York), in press). Paper available from: http://www.fhi-berlin.mpg.de/th/paper.html.
Contact person: paolo@theo24.RZ-Berlin.MPG.DE

Algorithms for Korringa-Kohn-Rostoker Electronic Structure Calculations in any Bravais Lattices

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Dipartimento di Fisica and Unità INFM
Università di Messina, Salita Sperone 31, 98166 Messina, ITALY

Abstract

We present some new algorithms for improvements of band theory calculations based on the Korringa-Kohn-Rostoker method and on the Coherent Potential Approximation, in the cases of ordered metals and random alloys. The purpose of our work was to develop a code flexible enough to deal on equal footing with any lattice geometry. The algorithms proposed are designed to achieve an arbitrary accuracy and to minimise the required computational efforts. In particular, we describe (i) an efficient and accurate method for the calculation of the KKR structure constants, and (ii) a new adaptive method for the Brillouin Zone integration. These new algorithms have been tested for a free electron Green's function and by explicit calculations for a number of systems and, when possible, discussed in comparison with other methods. Ab initio calculations for hexagonal close packed and face centered cubic Ti and for $Cu_{0.75}$-$Pt_{0.25}$ random alloy are presented.

(Accepted for publication on Phys. Rev. B15); available from: bg@ginestra.unime.it

Magnetic anisotropy of an impurity in a semi–infinite host

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[a] *H.H. Wills Physics Laboratory, University of Bristol*
[b] *Department of Theoretical Physics, Institute of Physics, Technical University of Budapest*
[c] *Centre for Computational Materials Sience, Vienna, Austria*

Abstract

We investigate the interaction of a magnetic (Fe) impurity with the surface of a non–magnetic (Au) semi–infinite host on the bases of fully relativistic spin–polarized first principles calculations. We show that the surface induces a magnetic anisotropy on the impurity, however, it is questionable whether the anisotropy coupling constant K is sufficiently large to explain the thickness dependence of the Kondo amplitude B in thin films of dilute Fe_cAu_{1-c} alloys. We also find that $K(d)$ is an oscillating function of the distance d between the impurity and the surface with an amplitude which falls as $1/d^2$ and a period which is determined by the shape of the Fermi Surface of the bulk Au host.

(submitted to PRL, 21 Feb 1997)
Postscript preprints available from: `szunyogh@phy.bme.hu`

This paper includes acknowledgement to the TMR Network on "Ab initio calculations of magnetic properties of surfaces, interfaces and multilayers" (Contract: ERB4061PL951423).

Ab-initio determination of magnetic interface coupling constants for magnetic multilayers

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[a] *Institut für Technische Elektrochemie, Technical University Vienna*
[b] *Center for Computational Materials Science, Vienna, Austria*
[c] *Laboratoire de Physique des Solides, Campus d'Orsay, Orsay, France*
[d] *Department of Theoretical Physics, Technical University of Budapest, Hungary*

Abstract

In a case study of the $Au(100)/FeAu_3Fe/Au(100)$ multilayer system the first two coefficients of an expansion of the magnetic (in-plane) interface coupling energy in polynomials in $\cos(\delta)$ are determined in terms of total energy differences using the fully relativistic spin-polarized Screened KKR method. The obtained results are compared to predictions based on the Force Theorem. It is found that only in the case of total energy differences the magnitude of the second order term is sizeable.

(Submitted to Europhysics Letters); available from: pw@ws1.cms.tuwien.ac.at

Effect of CAP-layers on interlayer exchange coupling

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[a] *Institute of Physics AS CR, CZ-180 40 Praha 8, Czech Republic*
[b] *Center for Materials Science, Technical University, A-1060 Vienna, Austria*
[c] *Institut d'Électronique Fondamentale, Université Paris-Sud, F-91405 Orsay, France*
[d] *Philips Research Laboratories, NL-5656 AA Eindhoven, The Netherlands*
[e] *Forschungszentrum Jülich, IFF, D-52425 Jülich, Germany*
[f] *Eindhoven University of Technology, NL-5600 MB Eindhoven, The Netherlands*

Abstract

The effect of non-magnetic cap-layers on the amplitudes and the phases of the oscillations of interlayer exchange coupling (IEC) is studied theoretically on *ab initio* level. We employ a 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 layers interfacing vacuum through the dipole barrier.

(submitted to **Proceedings of the MRS Sping Meeting, San Francisco 1997 Symposium M: Ultrathin Films, Multilayers, and Surfaces**)
Manuscripts available from: pw@ws1.cms.tuwien.ac.at

Both papers acknowledge benefits from TMR-Network on '*Interface Magnetism*' (Contract: ERB4061PL951423).

The optical transition in a Si wire passivated by H and O-H

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O.Bisi
Istituto Nazionale per la Fisica della Materia and Dipartimento di Fisica, Università di Trento, 38050 Povo, Italy

Abstract

We report ab-initio calculations of the electronic and optical properties of Si quantum wires with different species passivating the dangling bonds. When O-H group substitutes H atoms the band gap energy lowers and new features in the low energy side of the dielectric function arise. Our results interpret succesfully the experimental data of the oxidation induced changes in the luminescence and infrared absorption spectra of porous silicon.

(To appear in "Defect and Diffusion Forum" 1997)
Manuscripts available from: ossicini@imoax1.unimo.it

Optical emission from small Si particles

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[b]*Istituto Nazionale per la Fisica della Materia (INFM), and Dipartimento di Fisica, Università di Modena, Via Campi 213/a, I-41100 Modena, Italy*

Abstract

The optical properties of hydrogen-saturated Si clusters are studied theoretically through an approach that can treat consistently both small molecules and bulk crystals and fully includes electron-electron correlation. We find that optical spectra in the ground state cannot explain the observed luminescence of porous Si for the small particle sizes consistent with structural data. However, the same clusters in their excited state relax to highly distorted equilibrium configurations, giving rise to new transitions involving localized states that lower the emission threshold. These results allow to reconcile absorption and luminescence experiments with no need to invoke extrinsic effects.

(To appear "Solid State Communications" 1997)
Manuscripts available from: ossicini@imoax1.unimo.it

Model Hamiltonian for the conductivity oscillations of magnetic multilayers

Miguel Kiwi,[1] Ana María Llois,[2] Ricardo Ramírez,[1] and Mariana Weissmann[2]
[1] *Facultad de Física, Pontificia Universidad Católica de Chile, Casilla 306, Santiago 22, Chile*
[2] *Departamento de Física, Comisión Nacional de Energía Atómica, Avda. del Libertador 8250, 1429 Buenos Aires, Argentina*

Abstract

The behavior of the electrical conductivity as a function of layer thickness of the superlattice systems Ni/Co, Ni/Cu and Pd/Ag is studied. Experimentally an oscillatory dependence was found for the first two, while the latter exhibited a monotonous behavior. In our calculations we find that, in these superlattices, the current is carried by the *sp*–character electrons, which are quite insensitive to the interfaces. To interpret the experimentally observed resistivity oscillations we suggest a scattering mechanism of these carriers against *d*–character quantum well states that are present in only one of the superlattice materials, when the well state energy is close to E_F.

(Accepted for publication in Phys.Rev.B)
Manuscripts available from: weissman@cnea.edu.ar

Electronic properties of transition metal clusters: Consideration of the spill over in a bulk parametrization

Javier Guevara, Francisco Parisi, Ana Maria Llois and Mariana Weissmann
Departamento de Física, Comisión Nacional de Energía Atómica, 1429 Buenos Aires, Argentina

Abstract

We calculate the electronic structure of 3d-transition metal clusters with a model Hamiltonian which takes into account electron spill over at the cluster surface and uses bulk parameter values for the interactions. We perform calculations for fcc and bcc clusters of up to 177 atoms making use of symmetry properties. We obtain magnetic moments and ionization potentials for Ni, Co and Fe clusters, and compare with different experimental results obtaining that the essential features of the electronic and magnetic properties are reproduced, starting from an *spd*-bulk parametrization, if a realistic approach for electron spill over is considered.

(Accepted for publication in Phys.Rev.B)
Manuscripts available from: guevara@cnea.edu.ar

Optical evidence of $4f$-band formation in CeN

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†*European Commission, European Institute for*
Transuranium Elements, Postfach 2340, D-76125 Karlsruhe, Germany
‡*Theoretical Division,*
Los Alamos National Laboratory, Los Alamos, NM 87545

Abstract

We report *ab initio* calculations of the ground state and optical properties of CeN, which show that the $4f$ electrons in CeN are itinerant and that the intra-atomic $4f$-Coulomb interaction is largely screened. A coherent $4f$ band of width $\sim$2 eV is formed, from which an accurate description of the optical spectrum is obtained. The lattice parameter, linear specific heat coefficient, and magnetic susceptibility are also well reproduced. While CeN was previously classified to be a mixed valence compound, our results show that the more appropriate picture is that of a $4f$-band material.

(Accepted for publication in Phys. Rev. B)
Manuscript available from: anna.delin@fysik.uu.se

Magneto-Optical Properties of U $5f$ Electrons in U_3P_4

J. Köhler, L.M. Sandratskii and J. Kübler
Institut für Festkörperphysik, Technische Hochschule, D-64289 Darmstadt, Germany

Abstract

To investigate the nature of the $5f$ electrons in the noncollinear ferromagnet U_3P_4 the photon-frequency dependence of the normal-incidence reflectivity and the polar magneto-optical Kerr rotation are studied theoretically and compared with available experimental data. The calculations are carried out treating the U $5f$ electrons as itinerant and the results are found to be in good agreement with experimental data. We show that the U $5f$ states contribute substantially to the optical properties. We discuss the role played by the noncollinearity of the magnetic structure in determining the optical properties. We conclude that the magnetism of this compound can be described in terms of well-defined moments of the U atoms which are formed by itinerant U $5f$ electrons.

(submitted to Phys. Rev. B, Rapid Communication)
Latex version can be obtained from: jess@spy.fkp.physik.th-darmstadt.de

Optical conductivity in A_3C_{60} (A=K, Rb)

J. van den Brink[1,2], O. Gunnarsson[1] and V. Eyert[1,3]
[1] *Max-Planck-Institut für Festkörperforschung, D-70506 Stuttgart, Germany*
[2] *Laboratory of Solid State and Applied Physics, Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*
[3] *Hahn-Meitner-Institut, Glienicker Straße 100, D-14109 Berlin, Germany*

Abstract

We study the optical conductivity in A_3C_{60} (A =K, Rb). The effects of the electron-phonon interaction is included to lowest order in the coupling strength λ. It is shown that this leads to a narrowing of the Drude peak by a factor $1+\lambda$ and a transfer of weight to a mid-infrared peak at somewhat larger energies than the phonon energy. Although this goes in the right direction, it is not sufficient to describe experiment.

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

Optimized effective potential method with exact exchange and exact RPA correlation

Takao Kotani and Hisazumi Akai
Department of Physics, Osaka University, Toyonaka 560, Japan

Abstract

We present a new density-functional method of the self-consistent electronic-structure calculation which does not exploit any local density approximations (LDA). We use the exchange-correlation energy which consists of the exact exchange and the correlation energies in the random-phase approximation. The functional derivative of the correlation energy with respect to the density is obtained within a static approximation. For transition metals, it is shown that the correlation potential gives rise to a large contribution which has the opposite sign to the exchange potential. Resulting eigenvalue dispersions and the magnetic moments are very close to those of LDA's and the experiments.

(Submitted to Phys. Rev. Lett.)
Manuscripts available from: kotani@phys.wani.osaka-u.ac.jp

$p(2 \times 2)$ versus $c(2 \times 2)$ configurations for one Mn monolayer on Fe(001)

O. Elmouhssine, G. Moraïtis, C. Demangeat, and J. C. Parlebas
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Groupe d'Etude des Matériaux Métalliques,
23, rue du Loess, 67037 Strasbourg Cedex, France

Abstract

The spin polarization of a Mn monolayer on Fe(001) and the interfacial magnetic coupling have been investigated using the tight-binding linear muffin-tin orbital method. We have studied five spin configurations for the Mn monolayer and found that the two lowest in energy, namely $c(2 \times 2)$ and $p(2 \times 2) \uparrow$ (the up-arrow $\uparrow$ indicates that the magnetization of the Mn layer points in the same direction than the Fe substrate one), are nearly degenerate. These two configurations lead to different interfacial magnetic couplings and mean surface magnetizations. This result sheds some light onto recent contradictory experimental data.

(Physical Review B**55** (1997) R7410)
Available from: claude@Belenus.u-strasbg.fr

A Theoretical Treatment of Atomic Short Range Order and Magnetism in Iron-rich b.c.c. Alloys

J.B. Staunton*, M.F. Ling+ and D.D. Johnson°

* *Department of Physics, University of Warwick, Coventry, U.K.*

+ *Department of Physics, University of Monash, Australia*

° *Computational Materials Science Department, Sandia National Laboratories, Livermore, CA, U.S.A.*

Abstract

We use a 'first-principles' concentration-wave approach based on a finite-temperature, electronic density-functional, mean-field, grand potential of the random alloy to investigate the atomic short-range order (ASRO) in some $\underline{Fe}V$ and $\underline{Fe}Al$ solid solutions in both ferromagnetic and paramagnetic phases. Thermally-induced spin fluctuations are modelled in terms of local moments on the Fe sites. This picture produces satisfactory estimates of all the alloys' Curie temperatures, T_c. We compare our calculations with ASRO deduced from neutron and X-ray diffuse scattering measurements on single crystals carried out either in situ at or quenched from temperatures above and below T_c. Our calculations describe the measured ASRO well. Both alloy systems exhibit $B2$-type ordering correlations in their paramagnetic states which strengthen in the case of $\underline{Fe}V$ and weaken for $\underline{Fe}Al$ as the temperature is lowered into the ferromagnetic state. We extract electronic mechanisms for these effects. The ASROs of the ferromagnetic alloys also show intensity around (1/2,1/2,1/2) which is traced to a Fermi surface feature and may be a precursor to the DO_3 ordering in $\underline{Fe}Al$. Finally, suggestions for further polarised neutron, in-situ measurements are made.

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Magnetic anisotropy of close-packed (111) ultra-thin transition-metal films: Role of interlayer packing

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Abstract

The magnetic anisotropy of close-packed (111) ultra-thin transition-metal films is studied in the framework of a d-electron tight-binding Hamiltonian which includes hopping, exchange, and spin-orbit interactions on the same electronic level as well as the dipole-dipole energy contributions. The role of the interlayer packing on the magneto-anisotropic behavior is determined by considering fcc- and hcp-like films having up to 4 layers. Using parameters corresponding to Fe, Co and Ni we perform self-consistent calculations from which the magnetic anisotropy energy (MAE) is obtained in a nonperturbative fashion as difference between electronic energies. The role of the self-consistent determination of spin-polarized charge redistribution on the MAE is quantified by comparison with simpler constant-exchange-splitting calculations. The spin and orbital magnetic moments and the MAE are analyzed as a function of film thickness, d-band filling and d-electron exchange splitting giving emphasis to the differences between fcc- and hcp-like films. Finally, the main limitations of the model are pointed out together with some relevant extensions.

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A First-principles Theory of Magnetocrystalline Anisotropy of Disordered Alloys: Application to Cobalt-Platinum

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Abstract

We present a first-principles theory of magnetocrystalline anisotropy of disordered alloys within the framework of the spin-polarised fully relativistic Korringa-Kohn-Rostoker coherent-potential approximation in which relativistic effects such as spin-orbit coupling and magnetisation are treated on an equal footing. Unlike in some other methods, we calculate the magnetocrystalline anisotropy energy (MAE) of a material directly rather than obtaining it by substracting the total energies of the material for two magnetisation directions calculated separately. Since the total energy of a system is several orders of magnitude larger than its MAE ($\sim \mu eV$), this approach provides a robust method. Our predictions of the MAE and magnetic easy axis of elemental bcc-Fe, fcc-Co and fcc-Ni are in reasonable accord with previous calculations as well as with the experimental results. We calculate the MAE of disordered fcc-Co_xPt_{1-x} alloys for $x = 0.25$, 0.5, and 0.75 and find that, the magnetic easy axis for these alloys is along the [111] direction of the crystal, and that the magnitude of MAE is largest for the equiatomic composition. We also find that the magnitude of MAE decreases with temperature in these alloys, but the magnetic easy axis remains unchanged.

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Ab-Initio Total Energy Studies of the Static and Dynamical Properties of Ice Ih

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Abstract

We present a detailed study of the structural and dynamical properties of ice Ih. Methods used include the ab-initio pseudopotential and molecular orbital techniques. In order to simulate the proton disorder present in ice Ih super-cells are constructed with the orientation of water molecules determined in such a way that all possible nearest neighbour orientations are included while still obeying the Bernard-Fowler ice rules. For structures considered all structural parameters are relaxed. The dependence of bond length on the orientation of surrounding molecules in both the dimer and fully coordinated system is discussed. All local dimer orientations are accounted for in the supercell of ice Ih considered. The dynamical properties of a 16 molecule super-cell model of ice Ih are then investigated via direct determination of the zone centre dynamical matrix. Here the dynamical matrix is calculated directly from atomic forces obtained when each atom is shifted away from its equilibrium position. The vibrational modes are then calculated and the mode frequency as a function of microscopic deformation is discussed.

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Optical properties of Si_mGe_n superlattices : a CPA treatment of the interface diffusion

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Abstract

The use of the Coherent Potential Approximation (CPA) is proposed for the description of the interdiffusion across the Si-Ge interfaces of the Si_mGe_n superlattices (SLs). A generalization of the Kubo-Greenwood formula for the optical conductivity within the CPA, is used to describe quantitatively the effect of the interface diffusion on the optoelectronic properties of the SLs, the latter described within the tight-binding approximation using an orthogonal basis set including interactions up to third nearest neighbors. Our results being in very good agreement with other theoretical approaches and recent experimental measurements of the optical absorption coefficient and the optical transitions in the Si_4Ge_4, and Si_mGe_n , $m+n=10$, SLs, indicate that our approach is not only computationally efficient but accurate as well.

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On-site correlation in valence and core states of ferromagnetic nickel

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Abstract

We present a method which allows to include narrow-band correlation effects into the description of both valence and core states and we apply it to the prototypical case of nickel. The results of an ab-initio band calculation are used as input mean-field eigenstates for the calculation of self-energy corrections and spectral functions according to a three-body scattering solution of a multi-orbital Hubbard hamiltonian. The calculated quasi-particle spectra show a remarkable agreement with photoemission data in terms of band width, exchange splitting, satellite energy position of valence states, spin polarization of both the main line and the satellite of the *3p* core level.

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Ensemble Density-Functional Theory for ab-initio Molecular Dynamics of Metals and Finite-Temperature Insulators

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Abstract

A new method is presented for performing first-principles molecular-dynamics simulations of systems with variable occupancies. We adopt a matrix representation for the one-particle statistical operator $\hat{\Gamma}$, to introduce a "projected" free energy functional G that depends on the Kohn-Sham orbitals only and that is invariant under their unitary transformations. The Liouville equation $[\hat{\Gamma}, \hat{\mathrm{H}}] = 0$ is always satisfied, guaranteeing a very efficient and stable variational minimization algorithm that can be extended to non-conventional entropic formulations or fictitious thermal distributions.

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A theoretical description of spin-resolved Appearance Potential Spectroscopy

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Abstract

A theoretical description of spin-resolved Appearance Potential Spectroscopy (APS) is presented on the basis of a single-particle description of the underlying electronic structure. The final expression for the signal intensity turns out to be essentially a cross section-weighted self-convolution of the density of states above the Fermi energy – in close analogy to the result for core-valence-valence – Auger electron spectroscopy (CVV-AES). Application of the formalism presented to bcc-Fe and fcc-Ni leads to results in very satisfying agreement with corresponding experimental data. Because this is achieved only by treating the involved transition matrix elements in a proper way, their properties are discussed in some detail.

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Relativistic bandstructure of disordered magnetic alloys

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Abstract

The concept of the Bloch spectral function (BSF) has been extended to deal with disordered magnetic alloys with their electronic structure described using the spin polarized relativistic Korringa-Kohn-Rostoker Coherent Potential Approximation (SPR-KKR-CPA) formalism. Applications are presented for the alloy system fcc-Fe_xNi_{1-x} that shows a rather well defined dispersion relation and Fermi surface. Additional spin decomposition of the BSF clearly reveals the spin hybridisation due to spin-orbit coupling as well as its anisotropy in **k**-space.

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Density Functional Theory of Epitaxial Growth of Metals

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Abstract

This chapter starts with a summary of the atomistic processes that occur during epitaxy. We then introduce density functional theory (DFT) and describe its implementation into state-of-the-art computations of complex processes in condensed matter physics and materials science. In particular we discuss how DFT can be used to calculate parameters of microscopic processes such as adsorption and surface diffusion, and how they can be used to study the macroscopic time and length scales of realistic growth conditions. This meso- and macroscopic regime is described by the *ab initio* kinetic Monte Carlo approach. We discuss several specific theoretical studies that highlight the importance of the different diffusion mechanisms at step edges, the role of surfactants, and the influence of surface stress. The presented results are for specific materials (namely silver and aluminum), but they are explained in simple physical pictures suggesting that they also hold for other systems.

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Paper available from: http://www.fhi-berlin.mpg.de/th/paper.html
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Physical Origin of Exchange Diffusion on fcc (100) Metal Surfaces

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Abstract

For the (100) surfaces of Pt and Ir experiments revealed that self-diffusion proceeds by atomic exchange rather than hopping. Using density-functional theory we find that the physical origin of this phenomenon is different to that at Al, where it had been explained being activated by the formation of directional bonds at the transition state. We predict that exchange diffusion should also occur on Au(100) and show that the tensile surface stress plays a crucial role for the exchange diffusion. This explains why the exchange process is favorable for the late 5d, but not for 3d and 4d fcc (100) metal surfaces.

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Theory of Dichroism in the Electromagnetic Response of Superconductors

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Abstract

A microscopic theory of dichroism in the magneto-optical properties of superconductors is presented. Four distinct mechanisms for dichroism in superconductors are identified. Two are modifications of mechanisms known from the normal state, two are novel effects found in superconductors only. The theory is illustrated by numerical calculations for a simple model system. The interplay between relativistic symmetry breaking and superconducting coherence is found to give rise to a variety of new effects, not known from dichroism in the normal state.

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7 HIGHLIGHT OF THE MONTH

Variable cell-shape molecular dynamics

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Abstract

One problem frequently encountered in the simulation of real materials, like amorphous solids, liquids, complex surfaces or defects, is that the positions of the constituent atoms are not well known from experiment, and must be determined from the calculations. This can be done with Monte Carlo or molecular dynamics simulations based on the calculation of the total energy of the system. If the volume or cell shape of the material is not known, then variations in cell shape have to be included in the simulation. Here we review briefly variable cell-shape molecular dynamics methods, present a new approach, and give a few examples of variable cell-shape molecular dynamics and structural optimization for $MgSiO_3$, Si and ternary Ca nitrides using forces calculated from first principles.

7.1 INTRODUCTION

With the development of new simulation methods and the increase in available computational power, molecular dynamics has become an important tool in the simulation of matter in the condensed state [1, 2]. In its simplest applications, molecular dynamics is used to integrate Newton's equations of motion for the nuclei subject to empirical forces. For example, one would choose a Lennard-Jones potential to simulate liquid argon, or a Born-Mayer potential to simulate NaCl. Starting with the Car-Parrinelo method, [3] it has been possible to use in molecular dynamics simulations forces that are determined from first principles quantum-mechanical calculations of the electronic structure.

In the simplest molecular dynamics schemes, the shape of the simulation cell and number of particles are held constant, and the integration of Newton's equation of motion with forces derived from a potential conserves the energy (within the precision of the integration scheme), and one expects to be simulating a micro-canonical ensemble. However, in laboratory conditions,

one often controls the intensive variables temperature T and pressure p, instead of the extensive variables E and V. Therefore more subtle molecular dynamics schemes were developed to simulate systems at constant temperature or pressure [1, 2, 4, 5, 6, 7, 8]. In the case of constant pressure simulations, the size and shape of the simulation cell must be allowed to change. In order to do so, an "extended system" is constructed which includes degrees of freedom for the cell. A microscopic simulation of the structural, mechanical, and dynamical response of material systems to external stress of interest in tribology, material fatigue and wear, crack propagation, stress induced phase and structural transformations, lubrication and hidrodynamical phenomena, is more conveniently done with varying cell shapes. In this highlight we review briefly variable cell-shape molecular dynamics methods, present a new approach, and give a few examples of structural optimization from first principles.

7.2 VARIABLE CELL-SHAPE MOLECULAR DYNAMICS

Andersen [6] proposed to use the volume V of a cubic simulation cell as a dynamical variable in an extended hamiltonian, thus allowing for volume fluctuations (but not shape fluctuations) driven by the dynamical imbalance between the imposed external pressure, $p_{\rm ext}$, and the actual instantaneous internal pressure, $p_{\rm int}$ (given by the virial theorem). As the simulation cell is periodically repeated, the dynamics associated with the cell is not physical, but is a computational trick to allow a relaxation of the cell. In the extended lagrangian for the dynamics, Andersen included a fictitious kinetic energy term associated with the rate of change of volume,

$$K^{\rm A}_{\rm cell} = \frac{W^{\rm A}}{2}\dot{V}^2, \tag{1}$$

where $W^{\rm A}$ is a fictitious "mass" associated with the cell. He also added the term $U_{\rm cell} = p_{\rm ext}V$, which is the potential from which the constant external pressure acting on the cell is derived. During the simulations, the volume V fluctuates about an average value such that, in the limit of long simulation times, the time average of the calculated internal pressure is equal to the chosen external pressure, $\overline{p}_{\rm int} = p_{\rm ext}$. The equations of motion can be derived from the Lagrangian,

$$\mathcal{L}_A = K^{\rm A}_{\rm cell} + \frac{1}{2}\sum_k m(k)\dot{r}^2(k) - U_{\rm model} - p_{\rm ext}V \tag{2}$$

where $r(k)$ is the position of particle k, and $U_{\rm model}$ is our interatomic potential (Lennard-Jones, Kohn-Sham total energy etc...).

Andersen's method is best suited to study equilibrium properties of fluids, for which the shape of the cell is irrelevant. To study shear flow (viscosity) in fluids or to study solids it is not enough to change volume with constant shape. For example, a given cell shape may be compatible with the periodicity of one crystal structure and be incompatible with another solid phase, and so the fixed cell shape may artificially prevent the appearance of thermodynamically more stable phases. In order to study structural phase transitions, Parrinello and Rahman [7, 8] extended Andersen's method to allow for changes in both the volume and the shape of the cell. They used as dynamical variables the cartesian components

$$h_{ij} = \vec{e}_i \cdot \vec{a}_j$$

of the three vectors $\vec{a}_j$ defining the periodicity of the simulation cell. Here $\vec{e}_i$ are the three orthonormal vectors that define a cartesian coordinate system. To generate the dynamics, a fictitious kinetic energy of the cell

$$K_{\rm cell}^{\rm PR} = \frac{W^{\rm PR}}{2} \sum_{i=1}^{3} \sum_{j=1}^{3} (\dot{h}_{ij})^2, \tag{3}$$

is defined, where $W^{\rm PR}$ is again a fictitious mass. Several authors have pointed out some shortcomings of the original method of Parrinello and Rahman: it is not invariant under modular transformations (defined below), the consistency between the condition of mechanical equilibrium and the virial theorem is only verified in the large N limit, and it has spurious cell rotations [9, 10, 11, 12].

For a given periodic system, there are infinite equivalent choices of the basic simulation cell. If $\vec{a}_i$ are three vectors commensurate with the periodic system, then the transformation $\vec{a}'_j = \sum_k M_{kj}\vec{a}_k$, with M an integer matrix with $|\det M| = 1$, gives another set of vectors describing the periodicity. It is desirable that the dynamics should not depend on the particular choice that is made, i.e., the equations of motion should be formally invariant with respect to the interchange between equivalent cells (modular transformations) [9, 10]. This characteristic improves the physical content of the simulation, by eliminating symmetry breaking effects associated with the fictitious part of the dynamics [10]. Of course, in the thermodynamic limit ($N \to \infty$) these effects vanish, but they may be important in computer simulations, which may use only a small number of particles. That is often the case in first-principles molecular dynamics [3].

The orientation in space of the simulation cell is irrelevant for the structural and thermodynamical description of the system (principle of material-frame indifference [12]). However, it is included in the dynamics if one uses the components of the cell edges as dynamical variables, and spurious cell rotations have been obtained in actual simulations with the Parrinello-Rahman method, namely in the simulation of molecules, whose internal degrees of freedom sometimes cause the internal stress to be asymmetrical [13]. Methods to eliminate them have been proposed, such as constraining the matrix of the lattice vectors to be symmetrical [13] or upper triangular [14] (geometrical constraints), or by symmetrization of the infinitesimal strain at each time step (dynamical constraint) [12].

A Lagragian that is invariant with respect to modular transformations was proposed by Cleveland. [9] He used

$$K_{\rm cell}^{\rm Cl} = \frac{W^{\rm Cl}}{2} {\rm Tr}(\dot{h} A^T A \dot{h}^T), \tag{4}$$

as the cell kinetic energy, where the matrix A is defined by $A = \{\vec{a}_2 \times \vec{a}_3, \vec{a}_3 \times \vec{a}_1, \vec{a}_1 \times \vec{a}_2\}$, and is related to the reciprocal lattice vectors. The interpretation of the definition in equation 4 is not trivial. Wentzcovitch rederived similar expressions, [10] but she also suggested the use of other dynamical variables in the simulation, namely the *symmetric* stress tensor ϵ, and showed that from the cell kinetic energy

$$K_{\rm cell}^{\rm W} = \frac{W^{\rm W}}{2} {\rm Tr}(\dot{\epsilon}\dot{\epsilon}^T), \tag{5}$$

one obtained a Lagrangian that is invariant with respect to modular transformations. The stress tensor is defined with respect to a reference cell shape, $h = (1+\epsilon)h_0$. The initial cell shape is arbitrary, and the dependence of the dynamics on that choice can be removed by using what in

material science is called the true stress, $h = \exp(\epsilon)h_0$ instead of the engineering stress defined previously.

The symmetrical metric tensor,

$$g_{ij} \equiv \vec{a}_i \cdot \vec{a}_j = g_{ji},$$

defines all the geometric properties of the simulation cell. Using it as a variable for the dynamics, allows us to cast the problem in a metric language and simplifies the search for good cell kinetic energies because only scalar expressions are acceptable. [15] A simple non-negative scalar that is quadratic in the time derivatives of all the components of g is

$$K^{\mathrm{g}}_{\mathrm{cell}}\left(g_{ij}, \dot{g}_{ij}\right) = \frac{W^{\mathrm{g}}}{2}\left(\det g_{ij}\right)\dot{g}_{ji}\left(g^{ik}\dot{g}_{kl}g^{lj}\right), \tag{6}$$

where W^{g} is a fictitious cell "mass" with the dimensions of mass times length^{-4}.

The fictitious Lagrangian for the extended system in the presence of an applied external pressure in this case is

$$\begin{array}{c}\mathcal{L}_2\left(s^i(k), \dot{s}^i(k), g_{ij}, \dot{g}_{ij}\right) = \frac{1}{2}\sum_k m(k)\dot{s}^i(k)g_{ij}\dot{s}^j(k) - U\left(s^i(k), g_{ij}\right) + \\ \frac{W^g}{2}\left(\det g_{ij}\right)\dot{g}_{ji}g^{ik}\dot{g}_{kl}g^{lj} - p_{\mathrm{ext}}\sqrt{\det g_{ij}},\end{array} \tag{7}$$

where the $s^j(k)$ are the atomic lattice coordinates defined by $\vec{r}(k) = s^j(k)\vec{a}_j$.

7.3 ANISOTROPIC EXTERNAL STRESS

A constant applied anisotropic stress is in general non-conservative, and thus there is no conserved extended hamiltonian in a constant anisotropic stress simulation [9, 16]. Of course some experimental situations are essentially non-conservative, and therefore best simulated by an appropriate non-conservative dynamics [9, 16].

Molecular dynamics simulations with an applied anisotropic stress were first proposed by Parrinello and Rahman [8]. Ray and Rahman [17] later showed that the original formulation was valid only in the limit of small deformations, and they proposed an extension valid for finite deformations, in which it is the thermodynamic tension [17, 18]

$$\tau = \frac{V}{V_0}h_0 h^{-1}\sigma^{\mathrm{cart}}_{\mathrm{ext}}\left(h^T\right)^{-1}h_0^T, \tag{8}$$

where h_0 and V_0 are the reference lattice and its volume, and $\sigma^{\mathrm{cart}}_{\mathrm{ext}}$ is the external stress in cartesian coordinates. The physical interpretation of the thermodynamic tension is not trivial.

The thermodynamic variable conjugate to the metric is $\sigma^{ij}_{\mathrm{ext}}$, the external stress in contravariant lattice coordinates. [15] Keeping it constant when the cell deforms leads to a conservative external stress, if one uses the potential

$$U_{\mathrm{cell}}\left(g\right) = \frac{1}{2}\sigma^{ji}_{\mathrm{ext}}g_{ij}, \tag{9}$$

The metric notation is quite compact when compared with the definition of τ in Eq. 8.

7.4 STRUCTURAL OPTIMIZATION

A problem encountered in the simulation of materials is the determination of the equilibrium structure of a crystal at a given pressure (or anisotropic stress) predicted by a given model $U\left(s^i(k), g_{ij}\right)$ of its total energy. This can, in principle, be achieved by the minimization (under the appropriate constraint) of U, which is quite difficult because it is a multivalleyed function of many variables. A practical strategy is to use a simulated annealing to bring the configuration to a deep valley, followed by a search of a minimum in that valley. The annealing step can be carried out by the variable cell shape molecular dynamics described previously coupled to a thermostat, brownian dynamics forces, or a periodic rescaling of the velocities. The local minimization can be done efficiently if one has the gradient of the function to be minimized.

If we want to obtain the crystal structure at zero temperature and for an applied pressure of $p_{\rm ext}$, we must minimize its enthalpy,

$$H\left(s^i(k), g_{ij}\right) = U\left(s^i(k), g_{ij}\right) + p_{\rm ext}\sqrt{\det g_{ij}}.$$

The gradient of the enthalpy with respect to atomic positions is

$$\frac{\partial H}{\partial s^i(k)} = \frac{\partial U}{\partial s^i(k)} = -F_i(k),$$

which is minus the covariant components of the force on that atom. Notice that in molecular dynamics derived from the Lagrangian of Eq. 7, it is the contravariant components, $F^i(k) = g^{ij}F_j(k)$ that appear in the equation of motion. The gradient of the enthalpy with respect to the metric is

$$\frac{\partial H}{\partial g_{ij}} = \frac{\partial U}{\partial g_{ij}} + \frac{1}{2}p_{\rm ext}g^{ij}\sqrt{\det g_{ij}}.$$

These gradients can be fed into any gradient based minimization algorithm to optimize the crystal structure for a chosen external pressure $p_{\rm ext}$.

7.5 APPLICATIONS

Table I shows a comparison of calculated and experimental structural constants for $MgSiO_3$, a mineral with a distorted perovskite of geological importance. The calculations were done using the strain tensor as the dynamical variable, and a damped dynamics minimization scheme. [19] The structure is orthorhombic with lattice constants, a, b, and c, the other lines in the table give the atomic coordinates. The last column gives what the values would be for an undistorted perovskite structure. It is clear from the table that one can optimize quite complicated structures, and that LDA is successful in the prediction of ground state properties of complex silicates.

Figure 1 shows the results of a first principles simulation of Si under pressure using the metric as variable. A similar simulation using the Parrinello-Rahman Lagrangian was done previously. [20]

It is well-known that silicon undergoes several phase transformations with increasing pressure, and its pressure-volume phase diagram has been extensively studied [21]. Starting from a diamond lattice, the structure changes at ~11 GPa into β-Sn, and between 13 and 16 GPa transforms into simple hexagonal. Other densely packed phases appear at around 38 GPa. In the first

	Calc.(Pbnm)	Exp.(Pbnm)	Undistorted
a	4.711	4.777	4.909
b	4.880	4.927	4.909
c	6.851	6.898	6.942
Mg_x	0.5174	0.5131	0.500
Mg_y	0.5614	0.5563	0.500
O_x^1	0.1128	0.1031	0.000
O_y^1	0.4608	0.4654	0.500
O_x^2	0.1928	0.1953	0.250
O_y^2	0.1995	0.2010	0.250
O_z^2	0.5582	0.5510	0.500

Table 1: Experimental and theoretical parameters of the zero pressure *Pbnm* phase of $MgSiO_3$. This phase (four $MgSiO_3$ units) has Si atoms located at $(1/2, 0, 0)$, $(1/2, 0, 1/2)$, $(0, 1/2, 0)$, and $(0, 1/2, 1/2)$, Mg's at $\pm(Mg_x, Mg_y, 1/4), \pm(1/2 - Mg_x, Mg_y + 1/2, 1/4)$, and two sets of inequivalent O's at $\pm(O_x^1, O_y^1, 1/4), \pm(1/2 - O_x^1, O_y^1 + 1/2, 1/4)$ and $\pm(O_x^2, O_y^2, O_z^2), \pm(1/2 - O_x^2, O_y^2 + 1/2, 1/2 - O_z^2), \pm(O_x^2, O_y^2, O_y^2 + 1/2), \pm(1/2 + O_x^2, 1/2 - O_y^2, O_z^2)$.

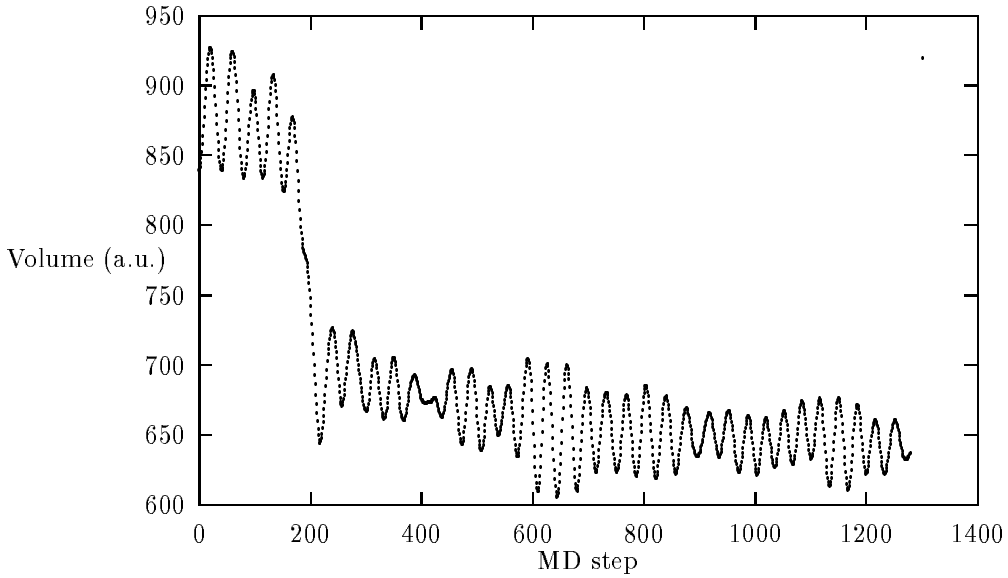

Figure 1: The volume (in atomic units) of an eight-atom Si cell is shown as a function of the molecular dynamics step in a first-principles simulation with an applied pressure of 25 GPa. The volume starts by oscillating around the volume of the initial diamond phase, but after 200 steps shows a rapid decrease to values near the equilibrium value at 25 GPa.

$\sim$ 0.7 ps (200 steps) of the simulation, we observed (Fig. 1) that the volume of the simulation cell was fluctuating around a value that corresponds to the volume of the metastable diamond structure of Si at 25 GPa ($V \sim 885$ a.u. for the 8 atoms of the conventional cubic unit cell). There was then a rapid drop in the volume, accompanied by a rapid rise in the ionic temperature to around 3500K (well above the melting point). The simulation was interrupted after 1000 steps, well before equilibrium with the thermal bath was reached. After the transition, the volume of the cell oscillated around 650 a.u., slightly below the volume of the stable simple hexagonal

	Experimental	Theoretical	Experimental	Theoretical
compound	$AsNCa_3$	$AsNCa_3$	$PNCa_3$	$PNCa_3$
a (Å)	6.716	6.720	6.709	6.707
b (Å)	6.711	6.715	6.658	6.659
c (Å)	9.520	9.526	9.452	9.451
Δ_1	0.0329	0.0400	—	0.0464
Δ_2	0.0321	0.0400	—	0.0459
δ	0.0209	0.0265	—	0.0396
γ_1	0.0399	0.0510	—	0.0747
γ_2	0.0048	0.0100	—	0.0220
λ_1	0.0000	0.0032	—	0.0084
λ_2	0.0170	0.0263	—	0.0449

Table 2: Experimental and numerical results for the lattice and distortion parameters of $AsNCa_3$ and $PNCa_3$.

structure at that pressure, but above the density of the close-packed structures. Remembering that at atmospheric pressure Si contracts upon melting, and considering the high temperatures of the simulation, our results indicate that at high pressures, the liquid phase may still be denser than the solid phase.

Table II shows the results of an optimization of the structure of ternary calcium nitrides using the metric as variable, [22] compared to the experimental results. [23] The material is an anti-perovskite, and again the distortions from the ideal crystal (small parameters in the table) is correctly predicted by the calculations. This last results are from a Lisbon-Antwerp collaboration that received psik support.

7.6 CONCLUSIONS

Variational cell-shape molecular dynamics can be used in structural optimization, or the simulation of phase transitions. It is only recently that it started being applied to real materials with forces and stresses derived from first principles total energy calculations. As the dynamics of the cell is fictitious, the choice of the kinetic energy associated with the cell motion is not unique. In fact even a choice of the dynamical variables associated with the cell motion has to be made. The original choice for the cell variables were the cartesian components of the cell vectors, but choosing the strain tensor or the metric tensor has some advantages. We expect that first-principles variational cell-shape molecular dynamics will become a very useful tool in the study of equilibrium structures in crystals at a fixed pressure.

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